UNIVERSITAT ROVIRA I VIRGILI

NEW BASIC CATALYSTS FOR FINE CHEMICALS SYNTHESIS

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DOCTORAL THESIS

NEW BASIC CATALYSTS FOR FINE CHEMICALS SYNTHESIS

Presented by:

Iuliana Maria Cota

Department d'Enginyeria Quimica

UNIVERSITAT ROVIRA I VIRGILI

Tarragona

2010

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NEW BASIC CATALYSTS FOR FINE CHEMICALS SYNTHESIS

DOCTORAL THESIS

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Universitat Rovira i Virgili
Departament d'Enginyería Química
Escola Técnica Superior d'Enginyería Química

NEW BASIC CATALYSTS FOR FINE CHEMICALS SYNTHESIS

Presented by:

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I, Francisco Medina Cabello, professor in the Department d'Enginyeria Química, Universitat Rovira I Virgili,

CERTIFY:

That the present study, entitled "New basic catalysts for fine chemicals synthesis" presented by Iuliana Maria Cota for the award of the degree of Doctor, has been carried out under my supervision at the department of Chemical Engineering of this university, and that it fulfils all the requirements to be eligible for the European Doctorate Label.

Tarragona, 23 April 2010

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CERTIFY:

That the present study, entitled “New basic catalysts for fine chemicals synthesis” presented by Iuliana Maria Cota for the award of the degree of Doctor, has been carried out under my supervision at the department of Chemical Engineering of this University, and that it fulfils all the requirements to be eligible for the European Doctorate Label.

Montpellier, 23 April 2010

To my beloved parents, Maria and Ilie

to my brothers, Cristi and Cosmin

for their continuous support.

"El fin muy cerca está, lo afrontaré serenamente,
ya ves, yo he sido así, te lo diré sinceramente
Viví la intensidad y no encontré jamás fronteras
jugué sin descansar a mi manera.
Jamás viví un amor que para mí fuera importante
tomé solo la flor y lo mejor de cada instante
Viajé y disfruté, no se si más que otro cualquiera
si bien, todo ello fue a mi manera.
Tal vez lloré, tal vez reí,
tal vez gané, tal vez perdí
ahora sé que fui feliz, que si lloré también amé
y todo fue, puedo decir, i did it my way.
Quizás también dudé cuando mejor me divertía
quizás yo desprecié aquello que no comprendía
hoy sé que firme fui y que afronté ser como era
y así logré seguir, a mi manera.
Porque ya sabrás que el hombre al fin
conocerás por su vivir
no hay porque hablar, ni que decir,
ni recordar, ni hay que fingir
puedo llegar hasta el final, A MI MANERA!!"

Il Divo-My Way (A mi Manera)

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Now that I start a new era of my life I will take with me the memories that bound me to all these special people and I will treasure them forever.

Abstract

In the last years, there is an increasing interest in substituting old technologies by cleaner catalytic alternatives to afford more environmental friendly processes in the chemical industry. In this way, it is a continuous challenge to find new base catalysts able to perform, with high activity and selectivity, reactions for the synthesis of pharmaceutical and fine chemicals. These reactions are indeed known to be catalyzed by basic sites and industrially are carried out in the homogeneous phase with KOH or NaOH. The use of these kinds of bases has numerous disadvantages such as waste production, corrosion and no catalyst recovery. Thus, research of new catalytic materials and new reaction designs which allow to increase the efficiency of these industrials processes while reducing the waste generation is the key to achieve a sustainable development.

Recently, Heterogeneous Catalysis have been more applied in basic catalysis and numerous efforts have been made to prepare new catalytic materials with controlled basic and superbasic properties, such as layered double hydroxides (LDH) and ionic liquids, in order to increase the efficiency of these kind of processes.

The research described in this thesis has focused on the study of new synthesis protocols for base catalysts. The basic properties have been characterized by several techniques and by illustrative test reactions such as the liquid-phase aldol condensation between aldehydes and ketones, double bond migration of olefins and synthesis of unsymmetrical organic carbonates.

In the first chapter of this thesis we applied DBU (diazabicyclo[5.4.0]undec-7-ene) and TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene), two strong N-bases, as catalysts for several aldol condensation reactions with interest for fine chemistry. We demonstrated that DBU which possesses Lewis basic properties is inactive for aldol condensation reactions; however when it reacts with equimolar amounts of water a complex possessing Brønsted basic properties is formed. The obtained DBU-H_2O complex and TBD efficiently catalyzed several aldol condensation reactions yielding the corresponding products with high conversion and selectivity thus representing a convenient and green alternative for the traditional homogeneous catalysts.

In the second chapter, highly basic catalysts were obtained by intercalation of guest negatively charged M^{n+}-based colloids ($M^{n+} = Ca^{2+}$, Sr^{2+}, Ba^{2+}, La^{3+}) into the host Mg/Al LDHs, preparation route takes advantage of the anionic exchange capacity and the ability to expand the interlayer space of the LDH. The nature of the intercalated cations allows to finely control the basicity of the obtained materials in order to perform reactions requiring different basic strength. The mixed oxides obtained by thermal activation of these precursors were successfully applied as catalysts for highly demanding basic reactions with interest for fine chemistry, namely: double bond migration of olefins and synthesis of unsymmetrical organic carbonates. Also, a new one-step synthesis route for hydrocalumite-type materials was developed, material which showed high activity for condensation of benzaldehyde and acetone.

In the third chapter a new synthesis protocol for short aliphatic chain ionic liquids and an extensive study of their physico-chemical properties is presented. The catalytic potential of this new ILs was tested for several aldol condensations; good results in terms of conversion and selectivity were obtained. Moreover an efficient recovery process was developed, the catalysts being recycled and reused for three consecutive cycles without significant loss of activity. In addition, the most active ionic liquids belonging to this family were immobilized on alanine and tested in the citral-acetone and benzaldyde-acetone condensations. The catalysts can be recycled and reused for three consecutive cycles without significant loss of activity.

The work done in this thesis can be regarded as a progress in the design of new catalytic systems, more active and efficient for use in fine chemical processes.

Resumen

En los últimos años, existe un creciente interés en la sustitución de viejas tecnologías por alternativas catalíticas más limpias para el desarrollo de procesos respetuosos con el medio ambiente para la industria química. De esta manera, es un desafío continuo encontrar nuevos catalizadores básicos capaces de realizar, con alta actividad y selectividad, las reacciones para la síntesis de productos de alto valor añadido tanto químicos como farmacéuticos. Estas reacciones son catalizadas por sitios básicos y a nivel industrial se llevan a cabo en la fase homogénea empleando KOH o NaOH como catalizadores. El uso de este tipo de bases tiene muchas desventajas, tales como la producción de residuos, la corrosión y la imposibilidad de recuperación del catalizador. En este sentido, la investigación de nuevos materiales catalíticos y nuevos diseños de reacción que permiten aumentar la eficacia de estos procesos industriales y reducir la generación de residuos es la clave para lograr un desarrollo sostenible.

Recientemente, el empleo de catalizadores heterogéneos con propiedades básicas y superbásicas controladas, tales como hidróxidos dobles laminares (LDH) y líquidos iónicos, con el fin de aumentar la eficacia de este tipo de procesos, es de gran interés.

La investigación descrita en esta tesis se ha centrado en el estudio de nuevos protocolos de síntesis para catalizadores básicos. Las propiedades básicas se han caracterizado por diversas técnicas y así como mediante el empleo de reacciones modelo como la condensación aldólica en fase líquida entre aldehídos y cetonas, la isomerización de olefinas y la síntesis de carbonatos orgánicos asimétricos.

En el primer capítulo de esta tesis se ha estudiado la aplicación de DBU (diazabicyclo[5.4.0]undec-7-ene) y TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene), dos bases nitrogenadas fuertes, como catalizadores en varios reacciones de condensación aldólica de interés para la química fina. Se ha demostrado que DBU que posee propiedades básicas de Lewis es inactiva para reacciones de condensación aldólica,

pero cuando reacciona con cantidades equimolares de agua se forma un complejo que posee propiedades básicas de Brønsted. El complejo DBU-H_2O y el TBD catalizan eficazmente varias reacciones de condensación aldólica obteniéndose los productos correspondientes con alta conversión y selectividad por lo que representan una alternativa conveniente y verde para los catalizadores homogéneos tradicionales.

En el segundo capítulo de la tesis, se han obtenido catalizadores altamente básicos por intercalación de complejos con carga negativa que contienen cationes M^{n+} (M^{n+} = Ca^{2+}, Sr^{2+}, Ba^{2+}, La^{3+}) en la estructura de tipo Mg / Al LDHs; la ruta de preparación aplicada aprovecha la capacidad de intercambio aniónico y la capacidad de ampliar el espacio interlaminar de la estructura LDH. La naturaleza de los cationes intercalados permite controlar la basicidad de los materiales obtenidos con el fin de realizar reacciones que requieren distinta fuerza básica. Los óxidos mixtos obtenidos por activación térmica de estos precursores se han aplicado con éxito como catalizadores para reacciones de alta exigencia básica de interés para la química fina, como por ejemplo: la migración del doble enlace de las olefinas y la síntesis de carbonatos orgánicos asimétricos. Además, se ha desarrollado un nuevo protocolo síntesis en una sola etapa para materiales de tipo hidrocalumita; el material sintetizado mostró alta actividad para la condensación de benzaldehído con acetona.

En el tercer capítulo de la tesis se ha desarrollado un nuevo protocolo de síntesis para líquidos iónicos alifáticos de cadena corta. Además, se presenta un amplio estudio de las propiedades físico-químicas de los líquidos iónicos sintetizados. Las propiedades catalíticas de los líquidos iónicos se han probado empleado varias reacciones de condensación aldólicas obteniéndose buenos resultados en términos de conversión y selectividad. Por otra parte un eficiente proceso de recuperación se ha desarrollado; los catalizadores se pueden reciclar y reutilizar durante tres ciclos consecutivos sin una pérdida significativa de la actividad. Además, los líquidos iónicos más activos pertenecientes a esta familia se han inmovilizado en alanina y se han probado en las reacciones de condensación del citral con acetona y benzaldehído con acetona. Los catalizadores pueden ser reciclados y reutilizados durante tres ciclos consecutivos sin una pérdida significativa de la actividad. Por consiguiente, el trabajo realizado en esta Tesis permite avanzar en el diseño de nuevos sistemas catalíticos más activos y eficientes para su utilización en procesos de química fina.

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Chapter I: Application of strong N-bases as organocatalyst for aldol condensation reactions

Chapter II: LDHs family as precursors for basic catalysts applied in fine chemistry

Chapter III: New short aliphatic chain ionic liquids: synthesis thermodynamics and catalytic activity in aldol condensations

General introduction

Solid acid–base catalysts play an important economical and ecological role in chemical and petrochemical industry as well as refinery technology. In a study done by K. Tanabe and W.F. Hölderich [1] it was shown that for different industrial processes such as alkylation, isomerization, amination, cracking, etherification, esterification, condensation reactions, etc., solid acid–base catalysts such as zeolites, oxides, complex oxides, phosphates, ion-exchange resins are employed. Among them the acid catalysts represented the largest group.

Most of the reactions of great interest for pharmaceutical and fragrance industries, such as esterifications, Michael additions, Knoevenagel and Claisen-Schmidt condensations or cross-condensations of aldehydes and ketones, are carried out in basic medium frequently using traditional homogeneous catalysts with basic properties like NaOH and KOH [2, 3]. However, with this kind of catalysts numerous disadvantages arise: loss of catalyst due to the separation difficulties at the end of the reaction, corrosion problems in the equipment used as well as generation of large amounts of residual effluents which must be subsequently treated to minimize their environmental impact. Consequently, new technological solutions have to be developed in order to overcome the referred disadvantages and to generate new and more sustainable processes in the field of the so-called “Green Chemistry” [4]. Thus, research of new catalytic materials and new reaction designs which allow to increase the efficiency of these industrials processes while reducing the waste generation is the key to achieve a sustainable development.

In contrast to extensive studies of solid acid catalysts, fewer efforts have been given to the study of solid base catalysts. The studies of solid base catalysts were started by Pines et al. [5]; they showed that sodium metal deposited on alumina acted as an effective catalyst for double bond migration of alkenes. Later in 1970s, studies of solid base catalysts became more popular [6]. Certain metal oxides with a single component were found to act as solid base catalysts in the absence of such alkali metals as Na and K. In recent years, non-oxide type catalysts have been recognized as heterogeneous basic catalysts.

The catalysts act as base toward the reactants either by abstraction of a proton from the reactants (Brønsted base) or by donation of an electron pair to the reactants (Lewis base) to form anionic intermediates which undergo catalytic cycle. The types of solid base catalysts are described in Table 1.

Table 1 *Types of heterogeneous basic catalysts [7]*

- Supported alkali metal ions
  - Alkali metal ions on alumina
  - Alkali metal ions on silica
  - Alkali metal on alkaline earth oxide
  - Alkali metals and alkali metal hydroxides on alumina
- Clay minerals
  - Hydrotalcites
  - Chrysotile
  - Sepiolite
- Non-oxide
  - KF supported on alumina
  - Lanthanide imide and nitride on zeolite
- Superbases [8]
  - $Cs_xO/\gamma\text{-}Al_2O_3$
  - $Na/NaOH/\gamma\text{-}Al_2O_3$
  - Na/NaOH/MgO
  - Eu_2O_3/Al_2O_3[9]
  - KNO_3/ZrO_2 [10]
  - Li, Na, K/ MaO, CaO, SrO, BaO [11]
  - Li, Na, K/ mesoporous silicon nitride [12]

In his study Hattori [7] proposed four fundamental parameters to recognize a material as heterogeneous base catalyst:

- the existence of the basic sites on the surface of the material evidenced by characterizations methods such as color change of the acid–base indicators, adsorption of acidic molecules and spectroscopies (UV, IR, XPS, ESR, etc.);
- the existence of a correlation between the catalytic activity and the amount or strength of the basic sites;
- the materials should exhibit similar activities to those of homogeneous basic catalysts and the reaction mechanisms occurring on the surfaces to be the same as those in homogeneous basic solutions;
- the indication that anionic intermediates are involved in the reactions mechanism proved by the product distributions, spectroscopic observations and mechanistic studies.

In the recent years, heterogeneous base catalysts have been applied to numerous organic syntheses [13]:

- Isomerization of alkenes and alkynes: since p*K*a values of alkenes are high, strongly basic catalysts are required for the isomerization. Among them, alkali amides supported on Al_2O_3 and alkaline earth metal oxides show very high activity for isomerization.
- C-C bond formation: aldol condensation, Claisen-Schmit and Knovenagel condensation, nitroaldol reactions, Michael addition, conjugate addition of alcohols, etc. These type of reactions can be catalyze by alkaline earth oxides, hydrotalcites, mixed oxides derived from hydrotalcites, AIPON, CsNaX, KF/Al_2O_3, KOH/ Al_2O_3.
- Nucleofilic ring opening of epoxides: MgO and MCM-41 grafted with amine functions proved to be the most efficient catalysts for these reactions.
- Oxidation reactions: are catalyzed by hydrotalcites and KF/Al_2O_3.
- Si-C bond formation: takes place in the presence of MgO, KF/Al_2O_3, KNH_2/Al_2O_3.
- Pudovik reactions (P-C- bond formation): KOH/Al_2O_3 was reported as very efficient catalyst [14].

- Synthesis of heterocycles: is catalyzed with high performance by Cs-loaded ZMS-5 zeolite, Zn-Al mixed oxides prepared from hydrotalcites like materials.

In the last years, basic materials ranging from alkaline or alkaline-earth exchanged X zeolites with medium strength, to highly basic Na/NaOH/Al_2O_3 covering a large range of strength have been synthesized [15-17]. The continue pursuit to design highly basic catalysts, has allowed the development of the superbasicity concept, for those materials that posses basic sites stronger than $H\_=26$ (with $H\_$ corresponding to the pK_a values of the colored indicator) [18].

Preparation and study of the solid superbase catalysts is a developing area attracting more and more attentions, because the solid superbase catalysts possess a high activity for the various reactions under mild conditions and can substitute the homogeneous base catalyst to minimize the production of pollutants [19]. Various kinds of inorganic solid superbases (Na–NaOH/Al_2O_3, Na/MgO, NaOH/MgO, KF/ZrO_2, etc.) [20, 21] and organic solid superbases (LICKOR, KCH_3, $RbNH_2$, etc.) [22, 23] were prepared in recent years and found application in numerous reactions.

One reason for the limited use of the heterogeneous basic catalysts arises from the rapid deactivation due to CO_2 and H_2O while being handled under normal atmosphere; the catalysts should be pretreated at high temperatures and handled in the absence of air prior to use for the reaction.

Nowadays, an increasing number of heterogeneous base catalysts with a variety of base strength are available and they are being tested in base-catalyzed reactions. Though it is said that solid-base catalysts can replace the homogeneous base in the reactions which are currently carried out with the latter, there are still problems to solve. Although a variety of methods have been applied, there is no definitive of unified way of characterizing solid bases, especially base strength. There are a number of examples of heterogeneous base-catalyzed reactions which cannot be understood in terms of number and strength of the basic sites [7]. Also, the catalytic actions of heterogeneous base catalysts are not always simple copies of those of homogeneous basic catalysts.

Applications of solid base catalysts to new reactions are important. There should be many reactions which solid base catalysts can effectively promote, but have not been examined yet. A deep study into the surface reaction mechanisms and functions required for the reactions together with the accumulation of the data will enable to design heterogeneous base catalysts active for desired reactions.

General objectives

In the last years, there is an increasing interest in substituting old technologies by cleaner catalytic alternatives to afford more environmental friendly processes in the chemical industry. In this way, it is a continuous challenge to find new base catalysts able to perform, with high activity and selectivity, reactions for the synthesis of pharmaceutical and fine chemicals. These reactions are indeed known to be catalyzed by basic sites and industrially are carried out in the homogeneous phase with KOH or NaOH. The use of these kinds of bases has numerous disadvantages such as waste production, corrosion and no catalyst recovery.

Recently, heterogeneous catalysts have been more and more applied in basic catalysis and numerous efforts have been made to prepare new catalytic materials with controlled basic and superbasic properties, such as layered double hydroxides (LDH) and ionic liquids, in order to increase the efficiency of these kinds of processes.

The aim of this project is to study new synthesis protocols for base catalysts and test their catalytic potential for reactions with interest for fine chemistry.

One first aspect developed in this project is to study the catalytic properties of two strong N-bases, DBU (diazabicyclo[5.4.0]undec-7- ene) and TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene), as catalysts for several aldol condensation reactions with interest for fine chemistry. These two organic bases are cheap, commercially available and can be easily separated from the reaction media.

In the second chapter, the main objective is to obtain highly basic catalysts from hydrotalcites precursors, able to perform highly demanding basic reaction. For this purpose hybrid materials are synthesized by anionic exchange of host Mg/Al LDH with guest entities previously formed by complexation of Ca^{2+}, Sr^{2+},Ba^{2+} or La^{3+} with Edta or citrate. The basic properties of the mixed oxides obtained by thermal activation of these intercalated LDH are investigated by several characterization techniques and their catalytic activity is tested in the isomerization reaction of 2,3-dimethyl-1-butene (DB-1) and transesterification reaction of 1-phenylethanol with diethylcarbonate.

Another aspect studied in this chapter is the development of a new, one step synthesis protocol for hydrocalumite. Hydrocalumites belong to the LDH family, like hydrotalcites. In the last years hydrotalcites have been widely studied due to their high potential as basic catalysts, while the application of hydrocalumites has been less investigated. Thus we found studies about the structure of hydrocalumites, since they are formed during the hydration of cement compounds but we found only scarce references about their application as basic catalysts although they must have basic properties similar to hydrotalcites.

The catalytic properties of the resulting solids are tested in the aldolisation reaction of benzaldehyde and acetone, so far studied using meixnerite and then chosen for sake of comparison. Furthermore, physical and chemical properties of the synthesized materials are determined using different characterization techniques.

The main objective of the third chapter is to develop and study the applications of a new family of ionic liquids based on substituted amine cations of the form R_XNH (X is the number of alkyl substitutions) combined with organic anions of the form $R'COO^-$ (being of different nature R and R'). An extensive study of the physico-chemical properties of these new ionic liquids will be carried out. Moreover, their catalytic activity in several condensation reactions of carbonyl compounds will be studied. The products obtained from these reactions are applied in pharmacological and flavor and fragrance industry.

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Chapter one

Application of strong N-bases as organocatalysts for aldol condensation reactions

1.1. Introduction

It is widely acknowledged that there is an increasing interest for more environmental friendly processes in the chemical industry. The key to the development of environmentally sustainable processes is the substitution of old technologies by cleaner catalytic alternatives. In this way, it is a continuous challenge to find new basic catalysts able to perform, with high activity and selectivity, condensation reactions for the synthesis of pharmaceutical and fine chemicals. Industrially, these reactions are carried out in the homogeneous phase with KOH or NaOH as catalysts [1, 2]. However, the use of these catalysts presents numerous drawbacks: loss of catalyst due to the separation difficulties, corrosion problems in the equipment as well as generation of large amounts of residual effluents which must be subsequently treated to minimize their environmental impact.

In our continuing effort to develop environmentally benign catalysts we decided to investigate the use of two N-bases, DBU (diazabicyclo[5.4.0]undec-7-ene) and TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene) as catalysts for several aldol condensation reactions with interest for fine chemistry. These two organic bases are commercially available and can be easily separated from the reaction media.

1.2. DBU (diazabicyclo[5.4.0]undec-7-ene)

Diazabicyclo[5.4.0]undec-7-ene (DBU) is known as non-nucleophilic, strong tertiary amine base. It is widely used in organic synthesis, especially as solvent in dehydrohalogenation [3].

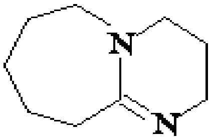

***Figure 1**. DBU structure.*

DBU (Figure 1) has been used as organocatalyst for a wide range of reactions: Baylis-Hillman reactions [4], synthesis of 2,4-dihydroxyquinazolines from 2-

aminobenzonitriles and carbon dioxide [5], Nef reactions [6], reactions of salicylic aldehydes with allenic ketones and esters [7], deconjugation of 7-substituted 3,4-Didehydro-2-oxepanones [8], Mukaiyama reactions [9], benzylation of N-, O-, and S-atoms with dibenzyl carbonate [10], etc.

In what is referred to aldol condensation reactions, DBU was applied as catalyst for several types of condensations. It was demonstrated that the condensation of acyldiazomethanes with aldehydes and imines can be promoted using catalytic amounts of DBU [11]. The reaction products (β-hydroxi α-diazo carbonyl compounds or β-amino α-diazo carbonil compounds) were obtained in high yields (64-95%).

Hary condensations of partially protected and non-protected pyranoses with nitromethane in various solvents for the synthesis of *C*-glycopyranosides in the presence of DBU/molecular sieve catalyst were described by Phiasivongsa et al. [12].

In a recent study [13], a DBU-mediated aldol condensation-dehydration sequence has been used to prepare a series of synthetically important substituted 2- and 3-azachalcones; moreover Michael products that typically accompany this sequence with inorganic bases were not observed in this protocol of high practical value [13].

Xiao et al. [14] described the DBU-catalyzed condensation of ethyl diazoacetate with aldehydes in pure water affording the corresponding β-hydroxy α-diazo carbonyl compounds with good yields (up to 84%). Since water is a cheap and environmental-friendly solvent, this procedure represents a convenient and green method to prepare β-hydroxy α-diazo carbonyl compounds.

1.3. TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene)

Bicyclic guanidines have been widely applied as organocatalysts due to their high basicity. The major advantages over ionic bases, includes ease of handling and mildness of reaction conditions.

TBD (Figure 2) is a strong guanidine base (pK_a=24.97) [15] widely utilized as an acid scavenger and base catalyst in numerous reactions [16].

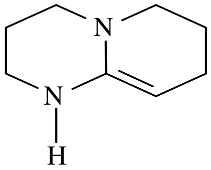

Figure 2. *TBD structure.*

Simoni et al. [17] shown that TBD is active in the nitroaldol (Henry) reactions. The use of TBD as catalyst in Michael addition or Michael-type conjugate reaction was proved to be successful for a wide variety of Michael donors and acceptors [18]. The direct addition of P(O)-H bonds to activated alkenes has been shown to be catalyzed by TBD [19]. During this study a one-pot, three component reaction involving diphenyl-phospine, malonitrile and an aldehyde was catalyzed effectively by TBD, affording the corresponding tri-substituted phosphine oxide in high yields. Further work involving phosphorous reagents has shown that TBD promotes the Witting reaction, providing a practical alternative to ionic base-promoted procedures [20].

TBD was shown to be a suitable base-catalyst for the synthesis of symmetric *N,N'*-substituted ureas under solvent-free conditions [21] and is also an active catalyst for the aminolysis of esters in presence of various amines [22]. A recent report has demonstrated that TBD is an active catalyst for the synthesis of propylene carbonate from propylene glycol and carbon dioxide [23].

The incorporation of catalytically active species on inert supports offers significant advantages over their homogeneous counterparts. It was shown that polystyryl-supported TBD was an efficient promoter for the addition of nucleophiles to unsaturated substrates [24], including the synthesis of a library of substituted benzofuranes [25]. It can be also used under solvent-free conditions for a number of organic transformations including 1, 2-epoxide ring-opening, aldol-type condensations and Michael additions [26]. In fact, it was noted that solvent-free conditions greatly increased the efficiency of this catalyst for the nucleophilic ring-opening of oxiranes by thioles [27]. Following these reports, micelle-templated silicas functionalized by TBD were produced and their application in transesterification catalysis was studied [29].

Inorganic-organic hybrid catalysts functionalized with TBD were synthesized, using as support the silica mesoporous material MCM-41 and an organic linker group derived from 3-trimethylsilyl propoxy methylene oxirane [29]. A range of catalytic transformations have been investigated using this material, including Michael additions [29], Knoevenagel condensations [30], preparation of carbamates form diethyl carbonate [31] and the synthesis of thioureas from carbon disulfide and primary amines [32].

Silica supported TBD was shown to catalyze the chemical coupling of CO_2 with propylene carbonate [33]. In a novel biocatalytic application, polystyryl-supported TBD has been used in tandem with *Candida rugosa* lipase immobilized on polypropylene powders for the production of (S)-naproxen from (R,S)-naproxen 2,2,2-trifluoroethyl ester [34].

Further examples of the applications of bicyclic guanidines and their supported counterparts have been recently reported, demonstrating that this area continues to be of great interest.

Objectives of chapter one

The main objective of this first chapter is to study the catalytic properties of DBU and TBD, two strong N-bases widely used in organic synthesis.

In the first part (art. 1) we study the reaction between DBU, which has Lewis basic properties, and water leading to the formation of a complex which presents Brønsted basic properties. The obtained complex is applied as catalyst for several aldol condensation reactions.

In the second part of this chapter (art.2) the catalytic properties of TBD for the aldol condensation reactions between several ketones and aldehydes to obtain valuable products in fine chemistry is studied.

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Scientific article (Art 1)

DBU-H_2O complex as a new catalyst for aldol condensation reactions

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The DBU-H_2O complex as a new catalyst for aldol condensation reactions

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Abstract

Finding new Brønsted-type basic catalysts that can perform condensation reactions of interest to fine chemistry with good activities and selectivity is a constant challenge. In this communication we report the activity of the DBU-H_2O system as a basic catalyst for aldol condensation reactions. Diazabicyclo[5.4.0] undec-7-ene (DBU) is a non nucleophilic, strong tertiary amine base that is widely used in organic synthesis. We demonstrate that DBU, which has Lewis basic properties, is inactive for aldol condensation reactions. However when it reacts with equimolar amounts of water it transforms towards a second resonance structure with Brønsted basic properties and therefore, high activity for these reactions. Besides, the DBU-H_2O complex is found to be very efficient, with reusability for several times.

Keywords: DBU, base catalysts, aldol condensation.

1. Introduction

Finding new Brønsted-type basic catalysts that can perform condensation reactions to synthesize pharmaceutical and fine chemicals with good activities and selectivity is a constant challenge [1]. In commercial production processes NaOH and KOH are used as homogenous catalysts [2]. However they have numerous disadvantages; the catalyst is lost due to separation difficulties, the equipment has problems of corrosion and large amounts of residues are generated. Recently, because of the industrial importance of the process many studies have focused on developing C–C bond formation reactions that do not use alkaline catalysts.

1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) is a non-nucleophilic, strong tertiary amine base, which has been widely used in organic synthesis, especially as solvent in dehydrohalogenation [3]. Its basic properties suggest that it can be used as an effective catalyst in aldol condensation reactions. In this work, we have demonstrated that despite its Lewis basic properties, it is inactive for aldol condensation reactions. However, when it reacts with equimolar amounts of water, it transforms into a complex that has Brønsted basic properties and which is therefore highly active for this kind of reactions.

2. Reaction of DBU with water

Nagata et al. [4] accidentally found that complexation of fullerenes with DBU was considerably faster in the presence of a small amount of water. The complex formed in their system had a zwitterion structure and they believed that the complexation process was accelerated by the highly polar nature of water, which stabilized the polar transition state of the zwitterionic complex. Xiao et al. [5] showed that DBU catalyzes the condensation of ethyl diazoacetate with aldehydes in water. They concluded that the reaction can proceed effectively with 30% DBU in water but they did not explain why the water is necessary. It was assumed that it acted as a solvent. However, it is well known that the addition of water in basic catalysts obtained from hydrotalcites-like materials plays an important role in the activity for several condensations reactions [1, 6–8]. The higher activity of the rehydrated hydrotalcite- like samples suggests that this type of reactions in the heterogeneous phase is specifically catalyzed by hydroxide ions [6].

In this communication we have studied the DBU-H_2O system as catalyst for several aldol condensation reactions. The role of the addition of water has been studied using NMR tests which demonstrated that water reacts with DBU and changes the DBU structure to a second resonance structure (Figure 1). This second resonance structure of DBU, that contains hydroxide ions, is responsible for the catalytic activity in aldol condensation reactions.

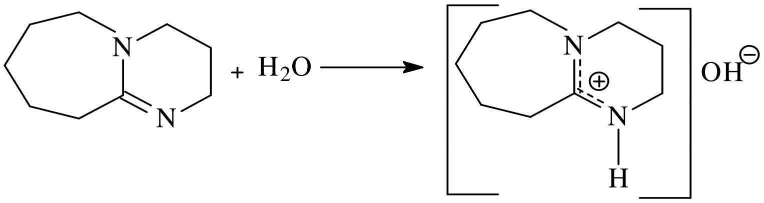


Figure 1. *Reaction of DBU with H_2O.*

3. NMR results

In order to determine the carbon spectrums of the DBU-H_2O complexes an NMR Varian Spectrometer Gemini 300 model was used. The homogeneity of the magnetic field was adjusted with 0.7 ml D_2O. Samples with different DBU-H_2O molar ratios were prepared and ^{13}C spectra were acquired at different times using 0.7 ml of the samples with no lock signal. Each of the spectrum series was made with 64 scans of 45^0 ^{13}C pulses using a ^{13}C inversed gated 1H-decoupling sequence, with a waiting time between the pulses of 10 s. In order to assign the DBU structures (Figure 2) we used: ^{13}C, ^{1}H, HSQC, HMBC, and COSY methods in a Varian Mercury-VX 400 Spectrometer.

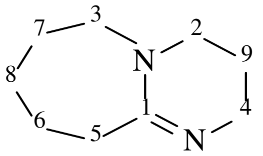


Figure 2. *DBU structure assigned by NMR methods.*

The spectra obtained for DBU-H_2O complexes showed that the carbons 3, 2 and 4 were shielded with 3.3; 3.5 and 5.2 ppm and that carbon 1 was de-shielded with 14.6 ppm. These results are in agreement with the literature, which sustains that the protonation of amines leads to a shielding of the C atoms directly bounded to the N atom. This chemical shift is around -2 ppm for the C atom in α position, between -3 and -4 ppm for the β position and between -0.5 and 1.0 ppm for the γ position. Tertiary and quaternary carbons situated in α position, however, undergo a deshielding (+0.5 to +9 ppm) due to the protonation of the N atom [9].

Our RMN results indicate that the DBU structure undergoes protonation at the N atoms and that the positive charge is delocalized due to interaction with the π-electrons of the double bonds and the n-electrons of the second N atom [10] (see Figure 1).

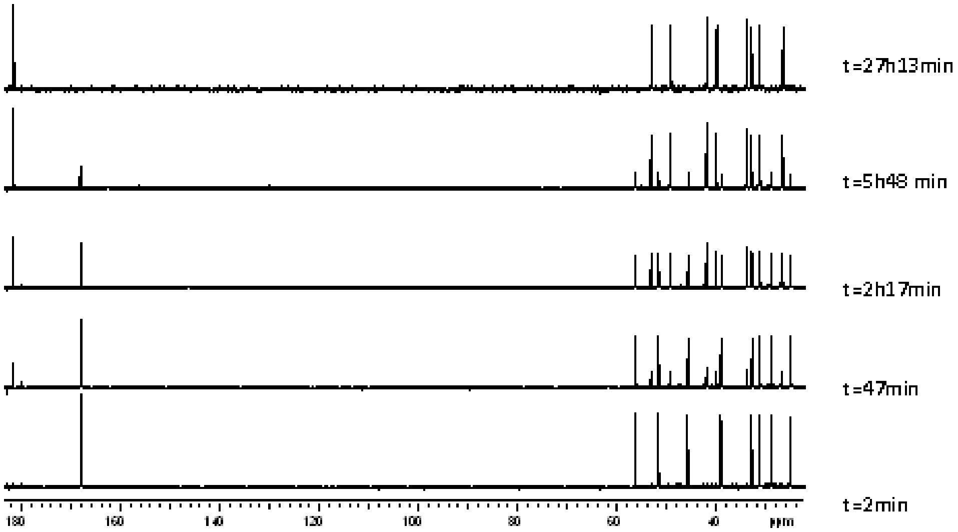


Figure 3. *Evolution in time of DBU-H_2O complex molar ratio 1:10.*

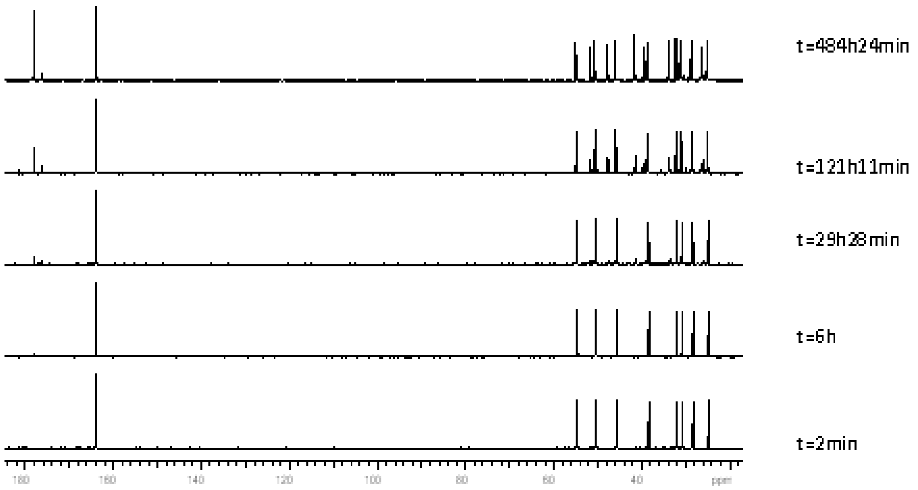


Figure 4. *Evolution in time of DBU-H_2O complex: molar ratio 1-1.*

In our experiments we tested different amounts of water to determine the optimum quantity required to obtain the protonated DBU. We noticed that the formation of the protonated structure at room temperature depends on the DBU-H_2O molar ratio and also on time (see Figs. 3 and 4).

For the DBU-H_2O molar ratios between 1 and 2 conversion was minor. For the molar ratios between 3 and 6, the profile of the curves is similar but does not reach 100% conversion. The DBU-H_2O molar ratio that we used to determine the catalytic activity was 1/25, because in this case the complete switch from one resonance structure to the other took 2 h (see Figure 5).

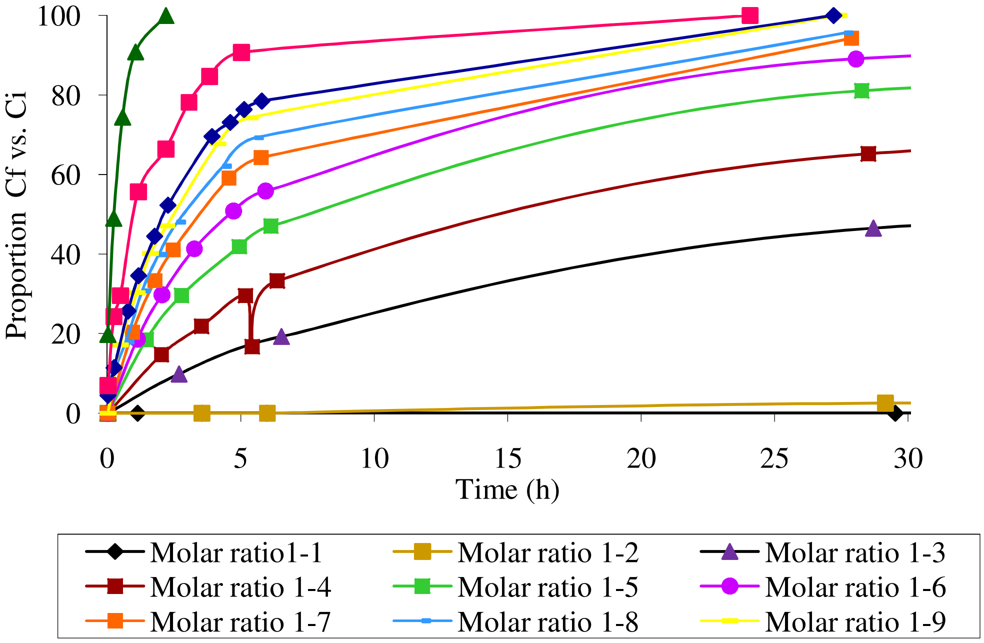


Figure 5. *NMR results for different DBU-H_2O molar ratios. The measurements refer to the same carbon peak: C_i represents the high of the first resonance structure carbon peak and C_f refers to the high of the second structure.*

4. IR results

Infrared spectra were recorded on a Bruker-Equinox-55 FTIR spectrometer. The spectra were acquired by accumulating 64 scans at 4 cm^{-1} resolution in the range 400–4000 cm^{-1}.

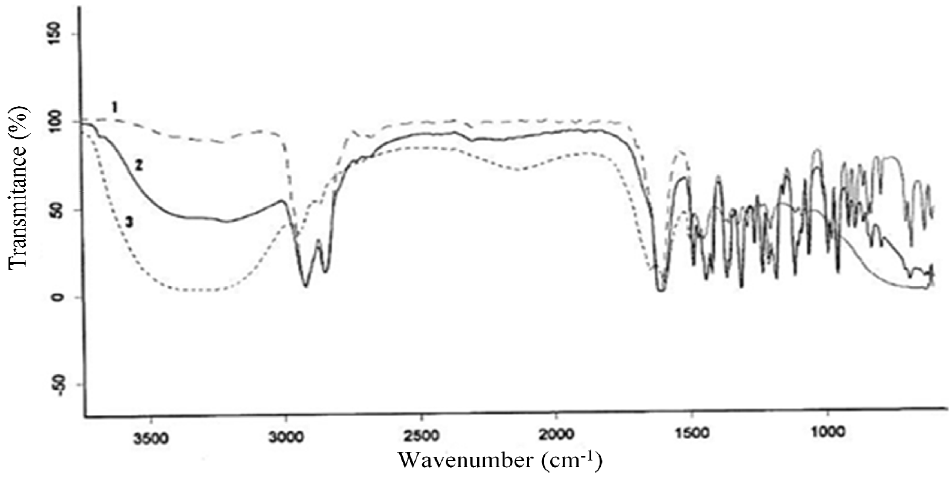


Figure 6. *IR spectra of DBU (1), 1:1 mixture of DBU-H_2O complex (2) and 1:25 mixture of DBU-H_2O complex (3).*

Figure 6 shows the IR spectrum for DBU, a 1:1 mixture of DBU-H_2O complex and a 1:25 mixture of DBU-H_2O complex. For purposes of comparison, the spectra of protonated DBU and free DBU are given. Proof that the DBU-H_2O complex was formed is given by the ν(C=N) vibrations (see Figure 7).

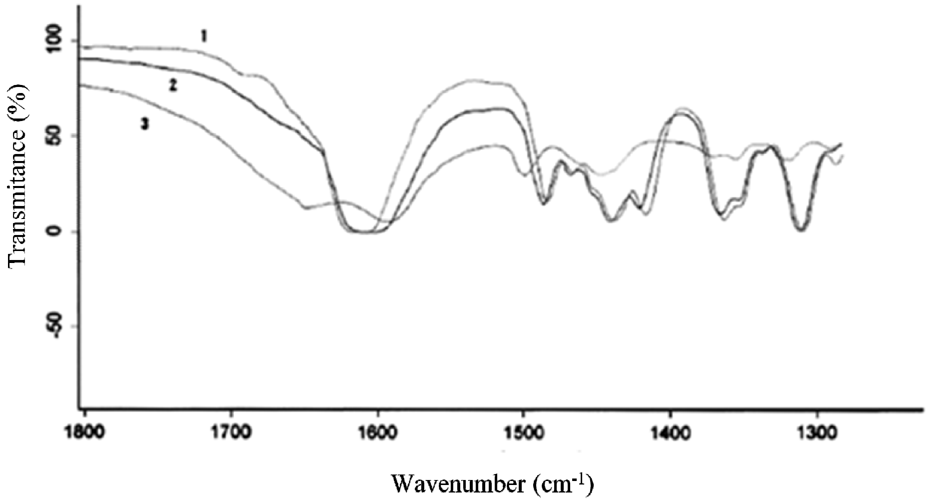


Figure 7. *IR spectra in the region 1300-1800 of DBU (1), 1:1 mixture of DBU-H_2O complex (2) and 1:25 mixture of DBU-H_2O complex (3).*

In the free DBU spectra, we observe a band around 1606 cm^{-1} which can be assigned to $\nu_{(C=N)}$. In the case of DBU-H_2O (1:1) the same band is observed but with a slightly different intensity, while in the case of the DBU-H_2O (1:25) spectrum, this band disappears completely. DBU-H_2O (1:25) spectrum shows a broad signal extending from 3000–3600 cm^{-1}, which is not characteristic for DBU spectrum. The band can be assigned to a strong $(N)_{DBU}$. . .$(OH)_{water}$ hydrogen bond. Since this broad band is usually observed in the case of acid-base interactions, it seems that DBU behaves as a strong hydrogen bond acceptor [9]. This broad band may be the result of the $\nu_{(N^+–H)}$ band superimposing on the free OH^- resulting from the deprotonation of the water molecules. A weak N–H bending absorption can be observed at around 1586 cm^{-1}.

5. Catalytic activity in aldol condensation reactions

The reactions were performed in a 100 ml batch reactor equipped with a condenser system, under argon atmosphere, in order to avoid CO_2. To a stirred solution of substrate and ketone a mixture of DBU and H_2O was added, and the flask was maintained at 333 K. Samples were taken at regular time periods and analyzed by gas chromatography (GC) using a FID detector and a AG Ultra 2 column (15 m x 0.32 mm x 0.25 µm). Tetradecane was used as internal standard. In the absence of water no catalytic activity was detected after 24 h of reaction. This indicates that Lewis basic sites of DBU are not active for these reactions. This result is in agreement with the low activity for aldol condensations obtained using amines grafted on MCM catalysts compared to rehydrated hydrotalcite-like ones [11]. In order to determine the optimum DBU-H_2O molar ratio, we prepared several DBU-H_2O proportions and then tested them in the aldol condensation reaction between citral and acetone (see Figure 8).

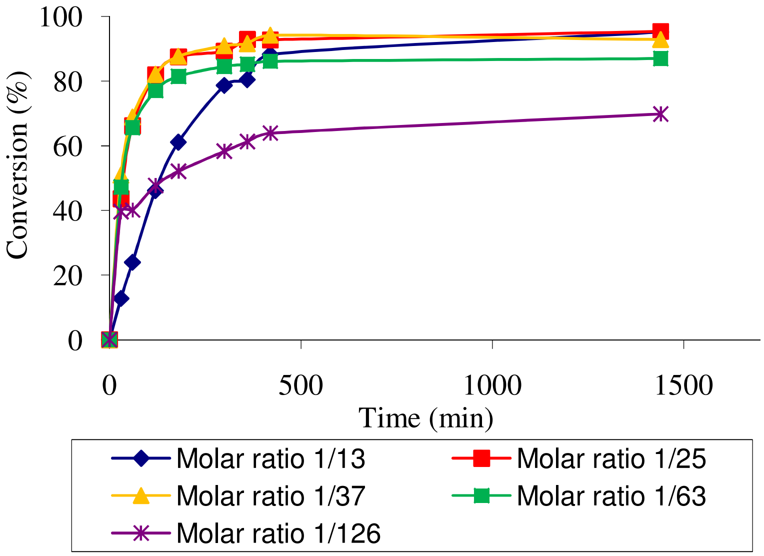
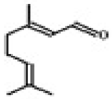
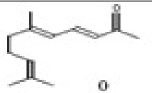
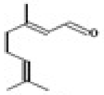
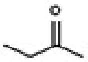
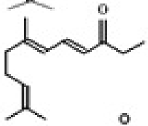
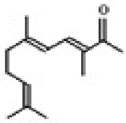
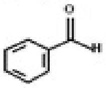
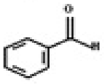
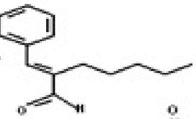
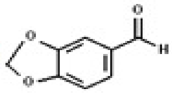


Figure 8. *Conversions of citral in citral-acetone condensation with different DBU-H_2O molar ratios.*

As we can see in Figure 8, the highest conversion was obtained for 1/25 DBU-H_2O molar ratio. For molar ratios higher than 1/25 the conversion obtained after 24 h decreases proportionately with the increase in water content. This behavior can be explained by the fact that increasing the water content leads to a decrease in DBU concentration in the reaction system. In order to determine the catalytic activity of the DBU-H_2O system, several condensation reactions of different carbonyl compounds were carried out. The products obtained from these reactions are interesting for the pharmacological, flavor and fragrance industries. The results are summarized in Table 1.

Table 1 *Condensation reactions catalyzed by DBU-H_2O complex*[a]

Entry	Substrate	Ketone	Product	Time (h)	Conversion (%)	Selectivity (%)
1				6	88.17	89.61
2			 	6	11.64	88.54
3				2	99.9	93.97
4				6	71.04	30.53
5[b]				6	22.22	84.55

[a] *Reaction conditions: ratio ketone / substrate = 4.4; T = 333 K; DBU = 0,66ml (4.4mmol), H_2O = 2ml (111.11mmol)*
[b] *Ratio ketone / substrate (propanal / piperonal) = 2.*

The condensation reaction between citral and acetone leads to the formation of pseudoionones which is an intermediate in the commercial production of vitamin A. Citral consists of two isomers, neral and geranial, caused by the cis–trans isomerism at the C=C bond near the aldehyde group [2]. The two isomers of citral (entry 1) can be converted into the corresponding pseudoionones (89.17%) in 6 h with good selectivity.

When 2-butanone is used instead of acetone, the based-catalyzed formation of two different carbonions results in n-methyl and isomethyl pseudoionones [2]. At 6 h of reaction, citral is coupled with 2-butanone (entry 2) with a conversion of 11.64% and good selectivity (88.54%).

In 2 h of reaction a conversion of 100% and a selectivity of 93.97% are obtained in the production of benzylidenacetone (entry 3) from the condensation between acetone and benzaldehyde.

In the synthesis of jasminaldehyde (entry 4) a conversion of 71.04% and a selectivity of 30.53% were obtained in 6 h of reaction. The undesired product came from the self condensation of heptanal to 2-n-pentyl-2-nonenal. This secondary reaction can be inhibited to some extent by the slow addition of heptanal.

In the condensation reaction between piperonal (heliotropine) and propionaldehyde (entry 5) a conversion of 22.22% was achieved in 6 h. A by-product involving the self-condensation of propanal was also present. The formation of this by-product can be avoided by the step addition of propanal.

We have studied the reusability of the catalyst in the synthesis of jasminaldehyde (entry 4). The reaction mixture is formed by two phases: an organic phase containing the reagents and an aqueous phase that contains the DBU-H_2O complex. After the first run, the organic phase containing the product (jasminaldehyde) was removed from the aqueous phase. Then a new organic phase was added for a new run. The activity of the catalyst was similar for three runs. This indicates that DBU-H_2O complex is an efficient and reusable catalyst for aldol condensation reactions.

6. Conclusions

We have demonstrated that DBU, which has Lewis basic properties, is inactive for aldol condensation reactions. However when it reacts with equimolar amounts of water it undergoes protonation at the N atom and transforms into a second resonance structure. This second resonance structure has Brønsted basic properties and is therefore highly active for aldol condensation reactions that are of interest in fine chemistry. Moreover, the DBU-H_2O complex is found to be very efficient with reusability for several times. This fact indicates an advantage compared with that of the traditional used catalyst (NaOH or KOH) that are not reusable.

Acknowledgments

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Scientific article (Art 2)

1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) an efficient catalyst for aldol condensation reactions

I. Cota, F. Medina, J. E. Sueiras, D. Tichit

(in preparation)

1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) an efficient catalyst for aldol condensation reactions

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Abstract

In the last years, there is an increasing interest in substituting old technologies by cleaner catalytic alternatives to afford more environmental friendly processes in the chemical industry. In this way, it is an exciting challenge to find new basic catalysts able to perform, with high activity and selectivity, condensation reactions for the synthesis of pharmaceutical and fine chemicals. TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene) is a strong bicyclic guanidine base which has been shown to promote various reactions. In this work, the catalytic properties of TBD for the aldol condensation reactions between several ketones and aldehydes were studied. It was found that TBD, a cheap and commercially available guanidine base, efficiently catalyzes aldol condensation reactions yielding products interesting for the pharmacological and fragrance industries. This methodology works under solvent free conditions and affords in very good yields the corresponding products. Moreover, a simple and effective separation protocol was developed.

Keywords: TBD, aldol condensations, base catalysis, guanidine bases, citral.

1. Introduction

It is widely acknowledged that there is an increasing interest for more environmental friendly processes in the chemical industry. The key to the development of environmentally sustainable processes is the substitution of old technologies by cleaner catalytic alternatives. In this way, it is an exciting challenge to find new basic catalysts able to perform, with high activity and selectivity, condensation reactions for the synthesis of pharmaceutical and fine chemicals. Industrially, these reactions are carried out in the homogeneous phase with KOH or NaOH as catalysts [1, 2]. However, with this kind of catalysts numerous disadvantages arise: loss of catalyst due to the separation difficulties at the end of the reaction, corrosion problems in the equipment used as well as generation of large amounts of residual effluents which must be subsequently treated to minimize their environmental impact. Consequently, new technological solutions have to be developed in order to overcome the referred disadvantages and to generate new and more sustainable processes.

On the other hand, TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene) is a strong bicyclic guanidine base with a $pK_a = 24.97$ [3]. It has been shown to promote various reactions including the Witting and Horner-Wadsworth-Emmons reactions [4], nitroaldol (Henry) reaction [5], secondary amine alkylation [6], carboxylation of propylene glycol with CO_2 [7], Michael reactions [8, 9], synthesis of symmetrically N,N'-substituted ureas [10], 5- and 6-enolexo aldolisation of acyclic ketoaldehydes [11], etc.

The objective of this study is to test the catalytic properties of TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene) for the aldol condensation reactions between several ketones and aldehydes to obtain valuable products in fine chemistry.

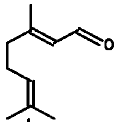
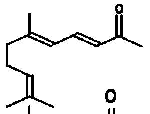
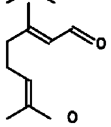
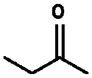
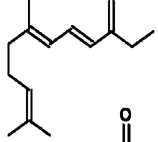
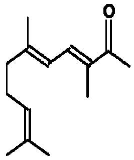
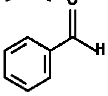
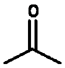
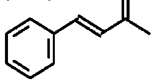
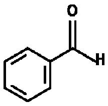
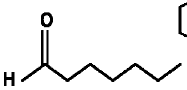
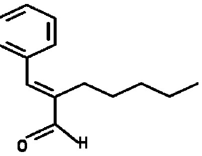
2. Experimental

The reactions were performed in liquid phase using a 100 ml batch reactor equipped with a magnetic stirrer and a condenser system under argon atmosphere in order to avoid contamination with CO_2. To a stirred solution of substrate and ketone (ratio ketone/substrate = 4.4) was added the catalyst and the flask was maintained at 333 K using a water bath. Samples were taken at regular time periods and analysed by gas chromatography (GC) using a FID detector and an AG Ultra 2 column (15 m x 0.32 mm x 0.25 μm). Tetradecane was used as internal standard. Reagents and TBD were purchase from Sigma Aldrich and used without further purification.

3. Results and discussions

TBD is a strong guanidine base (pK_a = 24.97) [3] widely utilized as an acid scavenger and base catalyst [10]. In order to determine the catalytic properties of TBD we used aldol condensation between several aldehydes and ketones as model reactions, yielding interesting products for the pharmacological and fragrance industries. The results are summarized in Table 1.

***Table 1** Condensation reactions catalyzed by TBD*[a]

Entry	Substrate	Ketone	Product	Time (h)	Conversion (%)	Selectivity (%)
1				2	99	76
2			 	6	99	90
3				0.5	99	78
4				6	97	84

[a] *Reaction conditions: ratio ketone/substrate 4.4 ; T = 333 K; TBD = 0.5 g (3.4 mmol)*

An important precursor for the synthesis of vitamin A is the pseudoionone, which is synthesized by condensation reaction between citral and acetone. Commercial citral is a mixture of two isomers due to the cis-trans isomerism at the C=C bond close to the aldehyde group [12]. The two isomers of citral (entry 1) are converted into the corresponding pseudoionones in only 2 h with a conversion of 99% and selectivity of 76%. No traces of diacetone alcohol derived from the self-condensation of acetone were found but other secondary products coming from the self condensation of citral and oligomers derived from citral are detected is small quantities in the reaction mixture.

When MEK (methyl ethyl ketone) is used instead of acetone, a mixture of cis-trans isomers of *n*-methyl and isomethyl pseudoionones are obtained as reaction products [13]. After 6 h citral is coupled with MEK (entry 2) with a conversion of 99% and a selectivity of 90%. No *β*-hydroxyl ketones were detected under the reaction conditions, however traces of other condensation products coming from the self-condensation of the reagents and oligomers derived from citral were detected.

In the condensation reaction of benzaldehyde and acetone the first step is the deprotonation of an acetone molecule to give the enolate anion whose nucleophilic attack on the C=O group of benzaldehyde leads to the β-aldol. This latter is easily dehydrated on weak acid sites and benzylidenacetone is obtained. In 0.5 h a conversion of 99% is achieved with a selectivity of 78% toward benzylidenacetone (entry 3), due to the formation of dibenzylidenacetone as secondary product.

The condensation between benzaldehyde and 1-heptanal leads to the formation of jasminaldehyde a product widely used in perfumery. In the synthesis of jasminaldhyde (entry 4) a conversion of 97% obtained in 6 h, with selectivity around 84%. The undesired product comes from the self condensation of heptanal to 2-n-pentyl-2-nonenal, secondary reaction which can be inhibited to some extent by a slow addition of heptanal during the reaction.

The main disadvantage of using TBD as catalyst is it's solubility in the reaction mixture. In a previous study [14] the fixation of carbon dioxide by guanidines was reported. The main product formed in the reaction of TBD with CO_2 in the presence of small amounts of catalytic water is the bicarbonate structure [14].

Since in our reaction system water is formed we considered applying the CO_2 fixation as separating method. In a typical experiment, at the end of the reaction CO_2 was bubbled in the reaction mixture. Within a few minutes a white precipitate was form, which was easily separated from the reaction mixture by filtration.

4. Conclusions

In conclusion, it was found that TBD, a cheap and commercially available guanidine base, efficiently catalyzes aldol condensation reactions yielding products interesting for the pharmacological and fragrance industries. This methodology works under solvent free conditions and affords in very good yields the corresponding products. Moreover, the separation protocol is simple and effective.

Acknowledgments

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Conclusions of chapter one

We demonstrated that DBU, a non-nucleophilic strong tertiary amine base possessing Lewis basic properties, is inactive for aldol condensation reactions. However when it reacts with equimolar amounts of water a complex possessing Brønsted basic properties is formed. The obtained DBU-H_2O complex is highly active for aldol condensation reactions with interest for fine chemistry. Moreover, it can be easily recovered and used for several consecutive runs.

For the same aldol condensation reactions, TBD a cheap and commercially available strong guanidine base widely applied as organocatalyst, efficiently catalyzes aldol condensation reactions yielding products interesting for the pharmacological and fragrance industries. This methodology works under solvent-free conditions and affords with very good yields the corresponding products. Moreover, a simple and effective protocol for the separation of the catalyst from the reaction medium was developed which emphasizes that theses catalysts are environmentally benign.

The DBU-H_2O complex and TBD efficiently catalyzed several aldol condensation reactions yielding the corresponding products with high conversion and selectivity thus representing a convenient and green alternative for the traditional homogeneous catalysts.

Chapter two

LDHs family as precursors for basic catalysts applied in fine chemistry

2.1. Introduction

Layered double hydroxides (LDHs) also called anionic clays or hydrotalcite-like compounds, have a general formula $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}[A_{x/m}]^{m-} \cdot nH_2O$, where M^{2+} and M^{3+} are di- and trivalent metal cations, respectively, A^{m-} represents the *m*-valent anion (typically carbonate), which is needed to compensate the net positive charge of the layers, and *n* is the number of water molecules in the interlayer space [1].

Pure LDHs phases exist for $0.2 \leq x \leq 0.3$, values outside of the specified *x* range will form:

- boehmite (α-AlOOH) for $x > 0.337$,
- hydromagnesite ($4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$) for $0.105 < x < 0.201$,
- a mixture of hydromagnesite and $Mg(OH)_2$ for $x < 0.105$ [2-5].

LDHs are available as naturally occurring minerals and as synthetic materials. They were first prepared in the laboratory in 1942 when Feitknecht [6, 7] reacted dilute aqueous metal salt solutions with base, although the first detailed structural analyses of LDHs were not carried out until the late 1960s by Allmann [8, 9] and Taylor [10, 11]. Later on, in 1971 the first patent describing the LDH obtained by precipitation as precursor for catalysts applied in hydrogenation was published [12].

Hydrotalcites may be the starting point for a wide range of basic or acid-basic catalysts:

- They can be used, as such, in their lamellar form. In this case, their reactivity is mainly governed by the nature of the intercalated anion and by the amount of remaining water [13].
- Highly homogeneous mixed oxides obtained from their thermal decomposition can catalyze a wide range of reactions. In this case, creation of M^{2+}-O^{2-} and M^{3+}-O^{2-} acid–base pairs sites mainly accounts for the catalytic properties. The basicity is indeed governed by the nature and the ratio of M^{2+} and M^{3+} cations, and the calcination temperature [14, 16].

- Reconstructed lamellar materials can be obtained from rehydration of the previous mixed oxides, which allows introducing almost any kind of compensating anions or anionic complexes that can be of use in the catalytic process.

In all cases, the composition will have to be obviously adapted to the target reaction. Indeed, any base-catalyzed reaction occurs with a maximum of activity when the basic character of the catalyst corresponds to the base strength required to activate the particular reactant molecule [17, 18].

The mixed oxides obtained from LDH exhibit high specific surface areas and their basic strength is generally found moderate. On the other hand, it is well known that alkaline-earth (AE) or rare earth cations (RE) oxides, particularly CaO, SrO, BaO, La_2O_3, Y_2O_3, exhibit high strength. Therefore, an interesting route in obtaining highly basic catalysts would be to incorporate AE or RE cations into LDH structures in order to enhance the basic properties and the catalytic activity of the mixed oxides obtained by thermal decomposition of these precursors. However, due to their large ionic radius, most of the alkaline, AE or RE cations cannot be accommodated, or only scarcely, in the brucite-like sheets of LDHs. Nanocomposites obtained by intercalation of guest negatively charged M^{n+}-based colloids (M^{n+} = AE or RE metal cation) into the host Mg/Al LDHs by means of anion exchange can be regarded as an alternative route for the preparation of AE or RE cations doped Mg(Al)O mixed oxides. This preparation route takes advantage of the anionic exchange capacity (AEC) and of the ability to expand the interlayer space of the LDHs.

For several base-catalyzed reactions that are important for the pharmaceutical and fragrance industry, a particular sort of LDH that contains OH^- as compensating anions in the interlayer space, which corresponds to the natural mineral meixnerite, is increasingly regarded as good alternative to the traditional homogeneous base catalysts such as NaOH and KOH, because it exhibits outstanding properties of Brønsted-type catalyst [19-21].

A main drawback of meixnerite is that it is not easy to prepare by classical co-precipitation or anionic exchange procedures due to the difficulty of having OH^- as sole compensating anion. Therefore, meixnerite is likely prepared by reconstruction using the memory effect, a specific property of the Mg(Al)O mixed oxide [21]. The memory effect represents the ability to restore the lamellar structure with OH^- groups in the interlayer space when Mg(Al)O is contacted with decarbonated water.

LDHs with other compositions are potentially able to give highly basic Brønsted-type catalysts. It is particularly the case of hydrocalumite, a Ca/Al LDH which belongs to the AFm phases, a group of hydrated compounds found in cement pastes. It is the only LDH structure which contains an AE cation, i.e. Ca^{2+}, into the layers. Besides its interest as hydration product of cements, which has induced extensive investigations [22-24], hydrocalumite has been also recently studied as host structures for the intercalation of guest monomers and polymers [25]. In contrast, studies dealing with the use of hydrocalumite as catalyst or catalyst precursors are very scarce, in spite of the close composition of this calcined material with CaO known as being highly basic. This emphasizes that it will be interesting to investigate the basic properties of hydrocalumite intercalated with OH^- species in order to establish if it is able to provide basic Brønsted-type solid more basic than the meixnerite referring to the higher basicity of MgO than CaO.

Hydrocalumites described in literature contain Cl^- [26-29] or NO_3^- [29-31] as compensation anions. The preparation of OH^--containing hydrocalumite remains a challenge for several reasons. As for the other LDHs the anionic exchange is difficult to achieve. Moreover, the reconstruction method, advantageously used in the case of Mg/Al LDH to prepare meixnerite, largely failed in the case of hydrocalumite. Vieille et al. [26] studied the reconstruction of hydrocalumites and they concluded that it is possible only for samples calcined below 673 K. Nevertheless, the XRD pattern of the reconstructed sample reveals the presence of hydrocalumite along with a residual amorphous phase, indicating that the restoration of the lamellar structure is not complete.

Therefore, the preparation of OH^--containing hydrocalumite can only be contemplated by a synthesis method. For this purpose we decided to perform a controlled hydrolysis of Ca^{2+} and Al^{3+} alkoxides. Such one step synthesis protocol of OH^--containing hydrocalumite has been investigated in this work.

2.2. Hydrotalcite-like materials

2.2.1. Structure

Hydrotalcites (HTs) consist of layers of metal cations (M^{2+} and M^{3+}) of similar radii, in an octahedral environment forming brucite-like structures $M(OH)_2$ [32]. In brucite structure, Mg^{2+} ions are sixfold coordinated to OH^- to form octahedra that share edges with their neighbours to constitute infinite two-dimensional sheets [34]. Substitution of divalent for trivalent cations (with similar radius) gives rise to positively charged layers whose charge density is proportional to the molar fraction of trivalent cation ($x = M^{3+}/(M^{2+}+M^{3+})$) [36]; x can vary in the range of 0.1-0.5 [37] or 0.2-0.5 [38]. However, Vaccari et al. state that the range for pure phases is restricted to 0.2-0.34, since for higher or lower values of x, segregation of $Al(OH)_3$ or $Mg(OH)_2$ occurs [37].

The whole HT structure is constituted by the stacking of such layers intercalating charge-balancing anionic species and water molecules as shown in Figure 1.

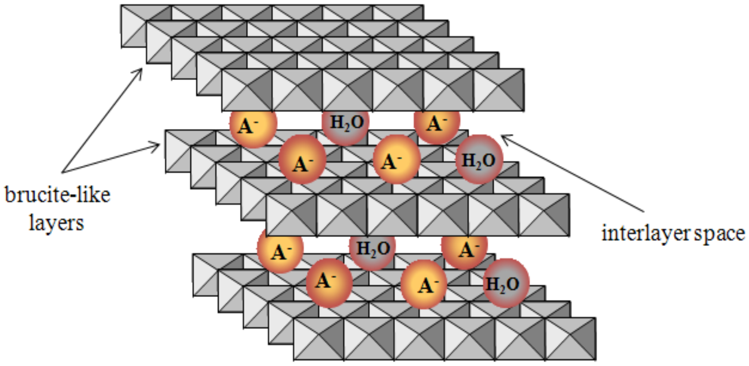

***Figure 1**. Schematic representation of LDH structure.*

The interlayer interactions of HTs are mediated by coulombic forces between the positively charged layers and the anions in the interlayer, and hydrogen bonding between hydroxyl groups of the layer with the anions and the water molecules in the interlayer [36]. Water molecules are connected through extensive hydrogen bonding to the hydroxyl ions of the metal hydroxide layers and the interlayer anions [39-41].

2.2.1.1. Nature of cations in the layers

In general, M^{2+} and M^{3+} ions that have an ionic radius not too different from that of Mg^{2+} (0.65 Å) can be accommodated in the brucite-like layers to form HTs. They belong mainly to the third and fourth periods of the periodic classification of the elements. The most commonly found are:

- divalent cations: Mg, Mn, Fe, Co, Ni, Cu, Cd, Zn,
- trivalent cations: Al, Mn, Fe, Co, Ni, Cr, Ga.

The ionic radii are in the range 0.65-0.80 Å for divalent cations and 0.62-0.69 Å for trivalent ones (with the main exception of Al = 0.50 Å) [36]. Ions such as Be^{2+} are too small for the octahedral coordination in the layers and ions of comparable size to Ba^{2+} are in contrast too large [7, 42].

All divalent ions from Mg^{2+} to Mn^{2+}, except Cu^{2+}, form hydrotacites; Cu^{2+} only forms hydrotalcites in the presence of other divalent cations owing to the Jahn-Teller effect [43]. The Jahn-Teller effect leads to the formation of the more energetically favorable distorted octahedral when ratio of Cu^{2+} to the other divalent cation is greater than 1 [44, 45].

A particular case of HT is $[LiAl_2(OH)_6]^+A^- \cdot mH_2O$, which consists of sheets of aluminum octahedra with vacancies filled by lithium atoms [46-49].

2.2.1.2. Nature of anions in the interlayer space

The electrostatic interactions between the positively charged hydroxide layers and the anions become stronger when their respective charges increase making the structure more stable [32]. This means that the formation of HT is for instance more favourable with divalent than monovalent anions [50-52].

In naturally occurring HTs the most common anion is carbonate; however a large variety of anionic species can be positioned between the hydroxide layers, including:

- halides [43, 44, 53, 54]
- oxy-anions: carbonate, nitrate, sulphate, bromate [43, 44, 53, 54]
- silicates [55-57]
- polyoxo-metalate anions: chromate, dichromate, $(Mo_7O_{24})^{6-}$, $(V_{10}O_{28})^{6-}$, $(PW_{11}O_{39})^{7-}$, $(H_2W_{12}O_{40})^{6-}$ [43, 44, 58-64]
- complex anions: ferro and ferricyanide [65-67]
- organic anions: aliphatic and aromatic carboxylates [68], alkyl chain compounds [69, 70], sulfonates and phosphonates [71, 72], porphyrin and phthalocyanine derivatives [1, 73] etc.

Recently, considerable attention has been paid to the intercalation of biomolecules or pharmaceutical agents into HTs. The intercalation of amino-acids [74, 75], nucleoside monophosphates and deoxyribonucleic acid [76], c-antisense oligonucleotides (As-myc) [77], nucleoside monophosphates and deoxyribonucleic acid (DNA) and vitamin (A,C,E) into HTs have been reported [77, 78]. The biomolecule intercalated HTs hybrids have potential usage as novel reservoirs and carriers.

2.2.2. Properties

Post synthesis treatments can modify the as prepared HTs to obtain materials with higher basicity and therefore better catalytic properties. The fine-tuning of the HTs basicity can be achieved by introducing a suitable anion in the interlayer space, by a controlled thermal activation or by doping with various elements.

2.2.2.1. Anionic exchange

The field of intercalation chemistry has been for long time of interest for scientists owing to the possibility to improve the electrical, optical and magnetic properties of the host materials with only minimal change of the structure. In addition, intercalation reactions can be used as a low temperature method to prepare novel materials which may not be accessible by other techniques [43].

The HTs have rich intercalation chemistry and a great number of reviews have been published to account for the diversity of these reactions [2, 52, 73, 79].

Several mechanisms of anionic exchange involving HTs have been proposed in the literature. The general assumption is a topotactic mechanism [50, 51], however other mechanisms have been proposed, including:

- a two-step process involving the dissolution of the HT phase followed by the re-precipitation of the new HT with the desired anion (D-R mechanism) [80],
- first order kinetics [81],
- a two step mechanism involving the adsorption of the incoming anion followed by the desorption of the initial anion [82, 83].

Considering that the only structural change brought about by anion exchange is a variation in the interlayer distance (which is dependent on the size of the incoming anion), it is generally thought that the anionic exchange takes place topotactically, since a close structural relationship between parent and product phases exists [32].

However, observations have been noted in recent studies which suggest that the anion exchange reaction follows the D–R mechanism. The observations included a mass loss of the HT during anion exchange reactions, which can be attributed to bulk dissolution [84-86], and unitary salts formed as impurity phases during anion exchange reactions [87]. According to the topotactic mechanism [88], the lamellar structure of HTs allows the diffusion of anionic species of higher affinity in the interlayer regions, as shown in Eq. (1):

$$[M^{2+} - M^{3+} - X] + Y^{-} \longrightarrow [M^{2+} - M^{3+} - Y] + X^{-} \qquad (1)$$

where M^{2+} - M^{3+} are the positively charged hydroxide layers, X represents the initial anionic species in the interlayer space, Y represents an anionic species with a higher affinity for the interlayer region which will replace X. According to Eq. (1), the outgoing X anion is exchanged for the incoming Y anion in a single step, where the host hydroxide layer essentially remains unperturbed.

A two-step topochemical reaction has also been proposed [82], where the initial step is the separation of the HT lattice into its corresponding positively charged hydroxide layers and free anions, Eq. (2), followed by the restacking of the highly reactive layers to form the HT with the new anionic species incorporated into the interlayer region, Eq. (3).

$$[M^{2+} - M^{3+} - X] \longrightarrow [M^{2+} - M^{3+}]^{+} + X^{-} \quad (2)$$

$$[M^{2+} - M^{3+}]^{+} + Y^{-} \longrightarrow [M^{2+} - M^{3+} - Y] \quad (3)$$

It was supposed that under certain conditions of temperature, pH, and anion concentration, the precursor HT could dissolve and the dissolved cations would re-precipitate with the incoming anions.

Intercalation of the new anionic species is based on two factors:

- its higher affinity than the original anionic species,
- the new HT has a greater thermodynamic stability than the original one, reflected by a lower solubility product [33].

Radha et al. [33], proposed the D–R mechanism, based on the fact that no reliable estimates of the strengths of these interactions and the strength of interlayer bonding have been reported in literature.

Identifying which of these mechanisms is involved in the anion exchange reactions is difficult due to:

- the high rate of anion exchange reactions, making kinetic studies difficult,
- intermediate phases are highly unstable,
- in the D–R mechanism, the dissolution of HT takes place at the solid–liquid interface [33].

Studies done by Miyata et al. [5, 41, 53] established a ranking of anion affinity for intercalation. It is greatest for anions of high charge density [53, 66]. The affinity of the anions was determined to be:

- monovalent anions: $OH^{-} > F^{-} > Cl^{-} > Br^{-} > NO_3^{-} > I^{-}$
- divalent anions: $CO_3^{2-} > SO_4^{2-}$

The carbonate anion has proven to be the preferred anion for intercalation, and once intercalated proves very difficult to exchange with other anions. The high affinity of carbonate in Mg/Al HT prevents its use as an anion-exchange material, unless precautionary steps (nitrogen atmosphere and carbonate free solutions) are used to minimize the carbonate content in the hydrotalcite matrix [32].

HTs containing nitrate anions are the most suitable precursors for anion exchange reactions due to their easy displacement from the interlayer. In general, the anion-exchange reaction is carried out by simply dispersing the precursor HT in aqueous solution containing an excess of the anion to incorporate.

For anions of different sizes the exchange reaction is particularly revealed by the variations of the interlayer distance of the LDH. As an example the compound $Zn_2Cr(OH)_6X\cdot 2H_2O$ displays a basal spacing d = 7.51 Å for $X^- = F^-$ and d = 32.6 Å for $X^- = n\text{-}C_{18}H_{37}SO_4^-$ [89].

In the last years, a large variety of anions, such as organic molecules, metallo-organic complexes, polymers and biomolecules or pharmaceutical and cosmetic agents have been intercalated into HTs interlayer space. Some of the resulting materials are extensively studied in the fields of catalysis, matrices for the controlled release of drugs, plastic additives, adsorbents, flame retardants, ion exchangers, batteries and (bio) sensors [90-97].

2.2.2.2. Hydrotalcites as precursors of mixed oxides

Thermal decomposition (calcination) of HTs precursors at temperature below 873 K gives rise to mixed oxides of industrial interest for catalytic or other practical applications (Figure 2) [1, 98].

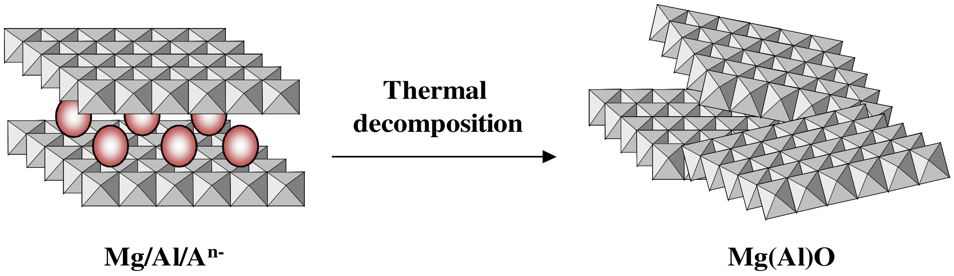

Figure 2. *Schematic representation of thermal decomposition of LDH structure.*

The thermal decomposition is generally characterized by two endothermic transitions in the TG/DSC analysis. The first transition below 523 K corresponds to the loss of interlayer water, while the second taking place at higher temperatures (370-570 K), is due to the loss of hydroxyl groups from the brucite-like layers and of the compensating anions from the interlayer space [1, 35]. These transitions depend qualitatively and quantitatively on many factors such as the nature and relative amounts of cations, the type of anions, the crystallinity and heating atmosphere [37].

The most interesting properties of the obtained mixed oxides are:

- high surface area (100-300 $m^2 \cdot g^{-1}$),
- formation of very small and stable metal crystallites with dispersion which cannot be achieved by impregnation procedures [99],
- synergetic effects between the elements, due to their intimate interdispersion,
- memory effect which allows reconstruction under mild conditions of the original structure by contacting with water [37].

A relevant feature regarding catalytic applications is that the mixed oxides posses acid and basic sites whose nature, strength and relative amounts depend on the nature and molar ratio of cations, and of the calcination temperature. The most widely investigated until now is Mg(Al)O.

The acid character is due to the presence of Mg^{2+} and Al^{3+} cations which generates acid sites of medium-high strength [100].

Besides, three types of basic sites are found in this mixed oxide:

- strong Lewis basic sites linked to isolated O^{2-} ions,
- medium basic sites belonging to M^{n+}- O^{2-} pairs,
- weak Brønsted basic OH^- sites.

The strength of the basic sites strongly depends on the calcination temperature; an increase in the calcination temperature (673-823 K) generally provokes the appearance of stronger basic sites and an increase in the total basicity of the material. When the calcination temperature is further raised up to 923 K the proportion of strong O^{2-} sites decreases at the expense of M^{n+}- O^2 pairs and basic OH^- disappear [34]. An excessive temperature provokes the appearance of spinel phases (e.g., $MgAl_2O_4$), which usually should be avoided in order to preserve the platelet morphology [15].

The basicity of Lewis sites associated to framework oxygen depends on their coordination. Lower coordination is related to higher basicity. Therefore sites located at corners are more basic than sites located at the edges, which in turn are more basic than sites located on faces [13, 17].

The mixed oxides obtained by thermal decomposition exhibit much higher basic properties than the fresh HTs [37, 101]. Mixed oxides can thus show basic sites with pKa's up to 16.5 [102-104], acting as weak Lewis acid/strong base catalysts.

They find applications in a large variety of reactions: aldol reactions, Claisen-Schmit and Knoevenagel condensations, transesterification, alkylation of phenol by alcohols, oxidation of thiols, Baeyer-Villiger oxidation of ketones, polymerization of lactones, methanol synthesis, epoxidation of activated olefins with H_2O_2, and reduction of aldehydes and ketones by hydrogen transfer from alcohols [38, 90].

2.3. Hydrocalumites materials

Hydrocalumite belongs to the AFm phases, a group of hydrated compounds found in cement pastes and composed of positively charged main layers $[Ca_2M^{3+}(OH)_6]^+$ and a negatively charged interlayer $[X \cdot nH_2O]^-$ where X^- is a mineral anion [105]. The structure (Figure 3) is based on corrugated brucite-like main layers with an ordered arrangement of Ca^{2+} and M^{3+} ions, seven-and six-coordinated, respectively, in a fixed ratio of 2:1; the seventh apex of the Ca-polyhedron is a water molecule from the interlayer [27]. The composition of the hydroxide layer of this structure type is limited; the divalent and trivalent cations are typically Ca^{2+} and Al^{3+}. The replacement of Al^{3+} by Fe^{3+}, Cr^{3+}, Ga^{3+}, and of Ca^{2+} by Cd^{2+} have been reported but only few data are available on these phases [106-108]. In spite of this lack of information, it is widely assumed that the difference in size between Ca^{2+} and M^{3+} ions is responsible for their ordered arrangement in a fixed M^{2+}: M^{3+} ratio of 2: 1 [27].

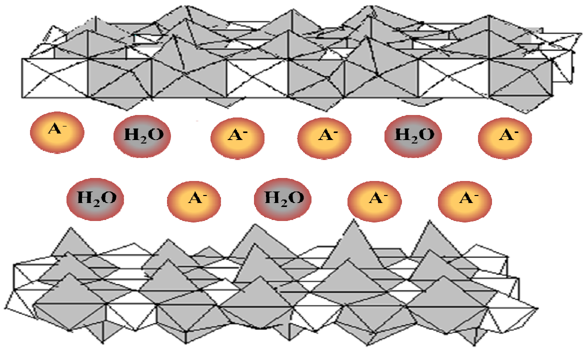

Figure 3. *Schematic representation of hydrocalumite structure.*

In the existing literature, hydrocalumites are prepared using the coprecipitation of metallic salts at controlled pH method; the hydrocalumites obtained using this method contain as compensation anion Cl^- [26-29] or NO_3^- [29-31].

The X-ray diffraction patterns of the hydrocalumites (Figure 4) are characteristic of well crystallized products. The interlayer distance for hydrocalumite materials is in the range of 0.778-0.783 nm for Friedel's salt (Ca_2Al-Cl), 0.818 nm for Br^-- containing AFm phases ($Ca_2Al(OH)_6Br\cdot 2H_2O$) and 0.857 nm for NO_3^--containing AFm phases ($Ca_2Al(OH)_6NO_3\cdot 4H_2O$), respectively [27, 105].

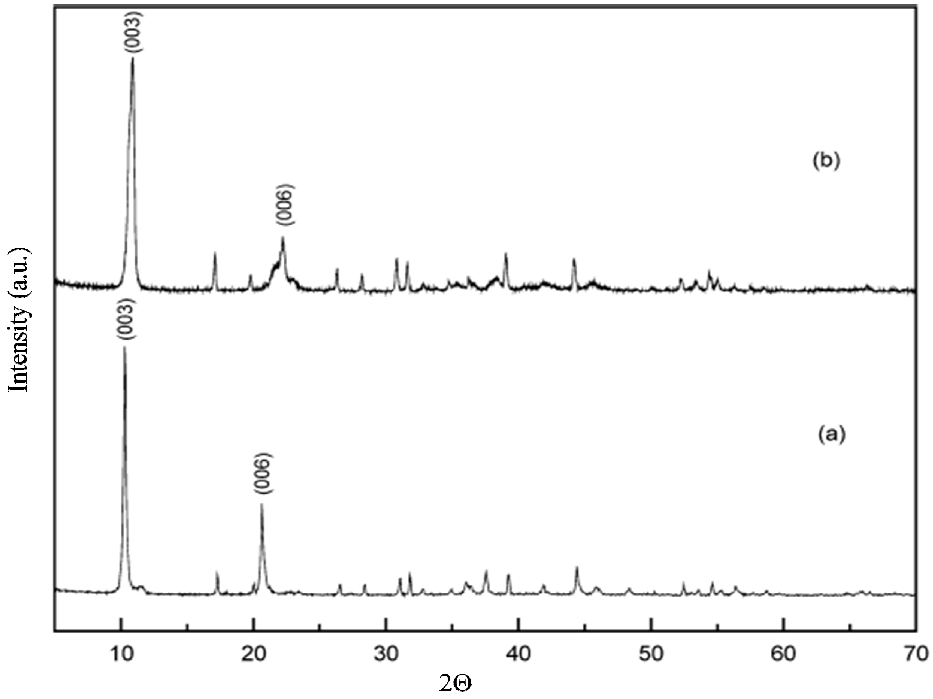

Figure 4. *XRD pattern of the Ca-Al-NO_3^- (a) and Ca-Al-Cl^- (b) [31].*

The electrostatic interactions between the positively charged hydroxide layer and the anion become stronger as the charge on the anion increases and the interlayer becomes more stable. This facilitates the exchange of NO_3^- by anions such as CO_3^{2-} and PO_4^{3-}. Due to the high charge density (0.286 nm^2/e^-) of the hydrocalumites, the anions are literally packed between the sheets, which makes the exfoliation process practically impossible [111].

The thermogravimetric analysis (TGA) of the hydrocalumite materials reveals three main weigh losses over the temperature ranges $298 \leq T \leq 523$ K, $523 \leq T \leq 673$ K and $673 \leq T \leq 1273$ K [25] as shown for example in Figure 5 for the Cl^-- containing hydrocalumite.

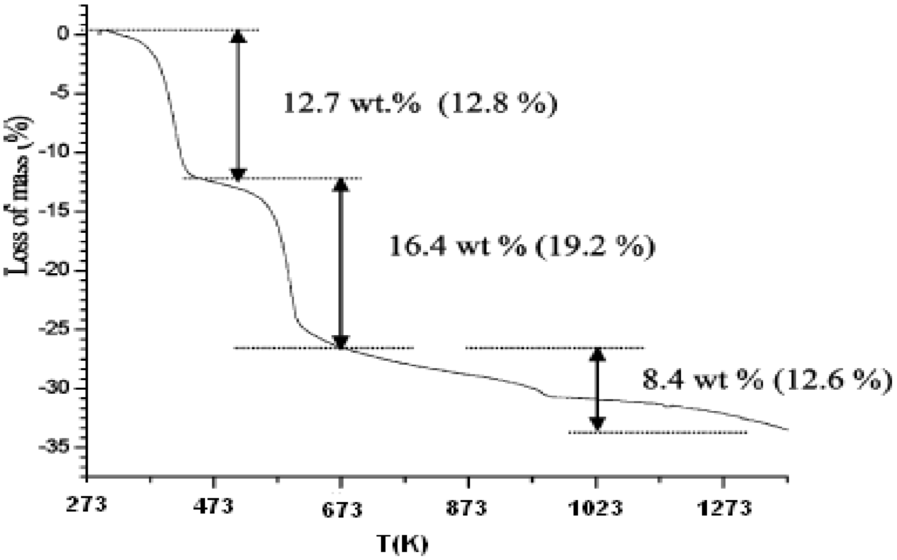

Figure 5. *TGA curves of the Ca/Al-Cl⁻ hydrocalumite [25].*

These mass losses are respectively assigned to dehydration, decomposition of the anions with also dehydroxylation of the layers, and finally concurrent release of water formed by recombination of hydroxyls and decomposition of remaining anions

In the case of NO_3^--containing hydrocalumite differences between the weight losses and the temperature range for the decomposition and removal of the anions appear due to the different polarizability of Cl^- and NO_3^-. The decomposition of nitrates is greatly delayed due to their intermediate reduction into nitrites, process which enhances the third mass loss [112].

The reconstruction method, advantageously used in the case of Mg/Al LDH to prepare the meixnerite-like phases was studied by Vieille et al. in the case of the hydrocalumite [25]. The samples heat-treated up to 553 K rapidly recover their original structure on cooling upon exposure to the ambient atmosphere. After calcinations above 533 K, both the hydrated and dehydrated phases are present on cooling and reversibility is completely lost at 553 K. At 673 K, Friedel's salt is converted to an amorphous phase; while a calcination temperature of ca. 773 K leads to the formation of crystalline calcite $CaCO_3$, which starts transforming to CaO above 973 K. Finally, raising the temperature up to 1223 K results in the formation of mayenite $Ca_{12}Al_{14}O_{33}$ and in the sharpening of CaO reflections [25]. Nevertheless, the XRD pattern of the reconstructed sample reveals the presence of the initial hydrocalumite and of a residual amorphous phase, indicating that the restoration of the lamellar structure is not complete.

Besides their interest as hydration product of cements, they have been also studied as host structures for the intercalation of guest monomers and polymers [25] while studies dealing with their use as catalysts are very scarce, in spite of the high potentialities.

Objectives of chapter two

The main objective of this chapter is to synthesize catalysts with increased basicity able to perform highly demanding basic reaction. With this purpose, nanocomposites obtained by intercalation of guest negatively charged M^{n+}-based colloids ($M^{n+} = Ca^{2+}$, Sr^{2+}, Ba^{2+}, La^{3+}) into the host Mg/Al LDHs by means of anion exchange are synthesized. Then, the nanocomposites are calcined in order to obtain mixed oxides containing highly dispersed M^{n+} microdomains. This method can be regarded as an alternative route for the preparation of alkaline-earth or rare-earth cations doped Mg(Al)O mixed oxides.

A secondary objective is to obtain OH^- exchanged hydrocalumites by direct synthesis with the aim of giving rise to highly basic Brønsted-type catalysts.

In the first part of this chapter (art. 3) hybrid materials are synthesized by anionic exchange of host Mg/Al LDH with guest entities previously formed by complexation of Ca^{2+}, Sr^{2+} or Ba^{2+} with Edta. The basic properties of the mixed oxides obtained by thermal activation of these intercalated LDH is investigated by means of the disproportionation reaction of 2-methyl-3-butyn-2-ol (MBOH) and by FTIR spectroscopy of adsorbed $CDCl_3$ as probe. The catalytic activities of the samples in the isomerization reaction of 2,3-dimethyl-1-butene (DB-1) is being correlated with their basic properties.

In the second part (art. 4) highly basic catalysts are obtained by intercalation of preformed negatively charged guest La hydroxy citrate colloids into host Mg/Al LDHs to give nanocomposites precursors of La/Mg(Al)O mixed oxides. The La loading is being controlled by the colloids exchange rate in order to achieve a better dispersion of the cations and improve the basic properties of the new materials. The transesterification reaction of 1-phenylethanol with diethylcarbonate (DEC), known as catalyzed by strong basic sites, is used to evaluate the performance of the La-containing catalysts.

In the third part (art. 5) a comparison between several protocols of synthesis for La-containing LDHs is made. The basicity of the obtained catalysts is determined by microcalorimetry. Their catalytic performance is tested for the double bond migration of olefins, a highly demanding basic reaction.

In the last part of this chapter (art.6) one step synthesis protocol of OH^--containing hydrocalumite is investigated. The catalytic properties of the resulting solids are tested in the aldolisation reaction of benzaldehyde and acetone, so far studied using meixnerite and then chosen for sake of comparison. Furthermore, physical and chemical properties of the synthesized materials are determined using different characterization techniques.

References of chapter two

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Scientific article (Art 3)

Alkaline-earth-doped mixed oxides obtained from LDH nanocomposites as highly basic catalysts

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Alkaline-earth-doped mixed oxides obtained from LDH nanocomposites as highly basic catalysts

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Abstract

The anionic exchange of the nitrate compensating anions in host Mg/Al LDH by negatively charged $[M(Edta)]^{2-}$ (M = Ca^{2+}, Sr^{2+}, Ba^{2+}) guest entities has been performed. The increase from 0.83 nm to 1.5 nm of the d_{003} interlayer distance shows that intercalation has taken place leading to well ordered lamellar materials with 3–9 wt % of alkaline-earth (AE) cations loading. The basic properties of the M/Mg(Al)O mixed oxides catalysts obtained by thermal decomposition of the [M(Edta)]–Mg/Al LDH precursors have been investigated by TPD of CO_2, FTIR spectroscopy of adsorbed $CDCl_3$ and catalytic test reaction of 2-methyl-3-butyn-2-ol (MBOH). The AE-containing mixed oxides exhibit higher basicity than Mg(Al)O with, particularly, a large increase of the densities of sites of medium and high strength. Remarkably, the nature of the AE cations allows to finely tune the basicity. All the AE-containing mixed oxides are able to perform the isomerization reaction of 2,3-dimethyl-1-butene (DB-1) into 2,3- dimethyl-2-butene (DB-2), the Ca-containing sample being the most active according to its larger content of strong basic sites.

Keywords: Layered double hydroxides, basicity, catalysts, alkaline-earth cations, 2,3-dimethyl-1-butene.

1. Introduction

In recent years layered double hydroxides (LDH) have attracted considerable attention as precursors of environmentally benign basic catalysts able to perform many reactions of interest in fine chemical synthesis [1–4]. A main advantage of the catalysts obtained from LDH is their high specific surface area and their versatile character which allows adjusting the nature and number of sites. Besides, their basic strength is generally found moderate. In other respects, AE metal oxides are known for their high basic strength and their low specific surface areas. An interesting route would be then to incorporate AE metal ions into LDH structures in order to enhance the basic properties and the catalytic activity of the mixed oxides obtained by thermal decomposition of the AE containing LDH precursors. However, this cannot be achieved by direct incorporation of the AE cations in the brucite-like layers, due to their too large ionic size. Therefore, an alternative procedure must be found, which can be the intercalation of negatively charged complexes containing the required AE cations. This preparation route takes advantage of the anionic exchange capacity (AEC) and the ability to expand the interlayer space of the LDH. With this aim, hybrid materials have been synthesized by anionic exchange of host Mg/Al LDH with guest entities previously formed by complexation of Ca^{2+}, Sr^{2+} or Ba^{2+} with Edta. The basic properties of the mixed oxides obtained by thermal activation of these intercalated LDH have been investigated by means of the disproportionation reaction of 2-methyl-3-butyn-2-ol (MBOH) [5] and by FTIR spectroscopy of adsorbed $CDCl_3$ as probe [6]. The catalytic activities of the samples in the isomerization reaction of 2,3-dimethyl-1-butene (DB-1) have been correlated to their basic properties.

2. Experimental

2.1. Materials

The host Mg/Al LDH ($Mg^{2+}/Al^{3+} = 2$) was synthesized by coprecipitation of a first aqueous solution of $Mg(NO_3)_2 \cdot 6H_2O$ (1.2 M) and $Al(NO_3)_3 \cdot 9H_2O$ (0.6 M) delivered by a chromatography-type pump (2 ml·min^{-1}) into a beaker containing 100 ml of water and a second solution of NaOH (2 M) added using a pH-Stat apparatus (718 Stat Titrino, Metrohm) in order to keep the pH at a constant value of 10 ± 0.2. The suspension was aged overnight at 333 K under vigorous stirring. Finally, the precipitate was filtered and washed with distilled water. The NO_3–Mg/Al LDH host thus obtained was dried overnight in an oven at 373 K. The guest $[M(Edta)]^{2-}$ (M = Ca^{2+}, Sr^{2+}, Ba^{2+}) entities were obtained by complexation of the M cations with Edta in aqueous solution. For this purpose, $SrCO_3$ or $BaCO_3$ was added to the Edta disodium salt solution (0.08 M) at a molar ratio [M]/[Edta] = 1 and heated at 363 K. In the case of Ca^{2+}, the commercially available product, Edta calcium disodium salt (Aldrich, 98%), dissolved in water was likely used. The intercalated materials were synthesized by dispersion of the host Mg/Al–NO_3 LDH (1 g) into the amount of the freshly prepared aqueous suspension of the guest entity corresponding to 2 times the theoretical AEC of the LDH (~ 3.8 meq·g^{-1}). The suspension was then hydrothermally treated in a batch reactor at 393 K under 5 MPa nitrogen pressure for 4 h. The solid was then recovered by centrifugation, washed with deionized water and dried overnight at 353 K. The samples thus obtained were hereafter labelled as M(Edta)–Mg/Al (M = Ca^{2+}, Sr^{2+}, Ba^{2+}). The M/Mg(Al)O (M = Ca^{2+}, Sr^{2+}, Ba^{2+}) catalysts were obtained by thermal decomposition of the M(Edta)–Mg/Al LDHs in air flow at 923 K for 8 h.

2.2. Characterization

Powder X-ray diffraction patterns (XRD) of the samples were collected in a Siemens D5000 diffractometer using (40 kV, 20 mA) using monochromatized Cu Ka radiation (l = 1.541Å) and a scan rate of 1 K·min^{-1}. N_2 adsorption and desorption isotherms at 77 K were measured using a Micromeritics ASAP 2000 surface analyzer on samples previously calcined at 923 K under argon for 5 h and degassed in vacuum at 523 K (10^{-4} Pa). Specific surface areas were calculated using the BET method. Chemical composition of the samples was determined by ICP-OES at the Central Analysis Service of the CNRS (Solaize, France). The basic properties of the solids were characterized by means of DRIFT spectroscopy with adsorbed $CDCl_3$ as probe molecule. DRIFT spectra were recorded using a Bruker-Equinox-55 FTIR spectrometer in the region of 400 – 4000 cm^{-1} at the resolution of 4 cm^{-1}; the number of scans was equal to 64. The sample, previously calcined at 923 K, was pressed into the DRIFT cell and pretreated in a helium stream (10 cm^3 STP min^{-1}) at 873 K for 1 h. The sample cooled at 303 K was then treated in a helium stream saturated with $CDCl_3$ for 20 min. Spectra were measured each 5 min until achieving sample saturation. The basic sites densities of the samples calcined at 923 K were determined by TPD of CO_2 in a Thermo Finnigan TPD/R/O 1100 equipped with a programmable temperature furnace and a TCD detector. Typically, ~ 200 mg of the solid were placed between quartz wool in a quartz reactor. After adsorption of CO_2 (3 vol % CO_2 in He; 20 cm^3 STP min^{-1}) for 10 min, the catalyst was treated in He (20 cm^3 STP min^{-1}) at 373 K to remove the physically adsorbed CO_2. The CO_2 uptake was measured by treating the sample from room temperature up to 1223 K at a heating rate of 10 $K \cdot min^{-1}$. The basic sites number was calculated from the CO_2 peaks deconvolution using the software of the equipment, assuming that one molecule of CO_2 adsorbs on each basic site.

2.3. *Catalyst test reactions*

Decomposition of 2-methyl-3-butyn-2-ol (MBOH) and isomerization of 2,3-dimethyl-1-butene (DB-1) were chosen as model reactions. MBOH conversion was performed under atmospheric pressure in a microflow fixed-bed reactor using 120 mg of catalyst previously calcined at 923 K for 18 h. MBOH was fed by bubbling N_2 (0.05 $l \cdot min^{-1}$) through a saturator at 298 K (P_{MBOH} = 2.5 kPa). The MBOH vapor stream was then introduced in the reactor containing the catalyst at 388 K in order to have moderate conversions and the effluent stream was sampled every 5 min for analyzing on line with a gas chromatograph (Hewlet Packard Model 5890) equipped with a Megabor capillary column(30 m x 0.546 mm) and FID detection. All connecting lines were heated. The DB-1 isomerization reaction was carried out into a quartz glass fixed-bed reactor where the catalyst (200 mg) was previously calcined at

923 K for 18 h in order to avoid its exposure to air after activation. The DB-1, without further purification, was fed by bubbling He (0.005 $l \cdot min^{-1}$) through a saturator at 175 K (P_{DB-1} = 0.002 kPa). This stream was then introduced in the reactor heated at 343 K and the reaction products were analyzed on line by gas chromatography using a 30 m HP-5 column.

3. Results and discussion

3.1. Composition and structure

The XRD patterns of NO_3–Mg/Al and of the M(Edta)–Mg/Al samples are depicted in Figure 1.

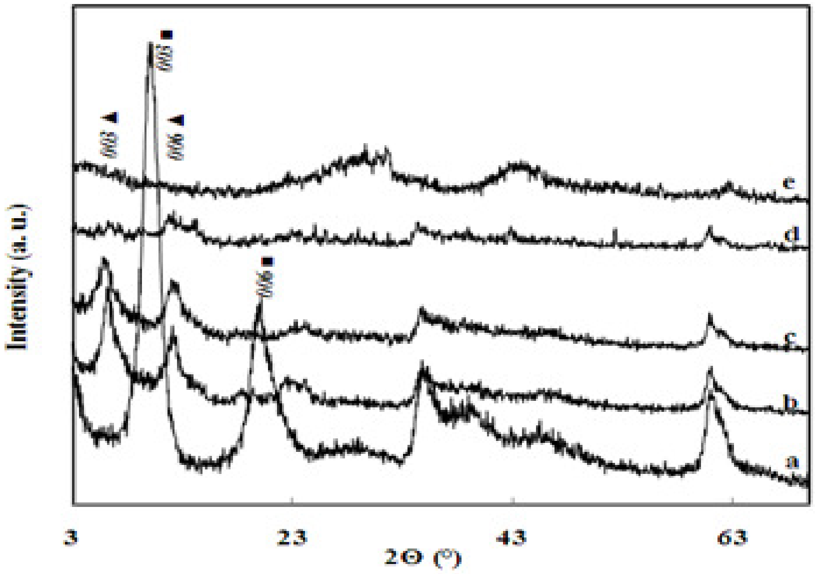

Figure 1. *XRD patterns of (a) NO_3–Mg/Al, (b) Ca(Edta)–Mg/Al, (c) Sr(Edta)–Mg/Al, (d) Ba(Edta)–Mg/Al and (e) M/Mg(Al)O calcined at 923 K samples; (■) corresponds to the basal reflections of NO_3–Mg/Al and (▲) corresponds to the basal reflections of M(Edta)-Mg/Al.*

That of NO_3–Mg/Al is typical of a LDH phase. Sharp and symmetric reflections ascribed to the basal (003), (006) and (009) planes, and broad and asymmetric reflections ascribed to the non-basal (012), (015) and (110) planes in the space group R-3m are clearly distinguished. The interlayer spacing d_{003} = 0.83 nm is consistent with the presence of NO_3^- as charge compensating anions. Comparatively to NO_3–

Mg/Al, the d_{003} interlayer distance increases to 1.50 nm in the M(Edta)–Mg/Al samples. This value is close to that previously reported for a [Eu(Edta)]–Mg/Al LDH [7] and shows that the intercalation of the $[M(Edta)]^{2-}$ complexes has taken place. The presence in the intercalated LDHs of several intense basal (00l) reflections account for well ordered layered structures probably resulting from the hydrothermal conditions of the anionic exchange. Comparatively to NO_3–Mg/Al, an inversion of intensity between the two first (00l) peaks is observed. This can account for the high electron density induced by the presence of the metal complexes in the interlayer space as previously reported [7, 8].

The same value of the cell a parameter (a = 0.303 nm), calculated from the position of the (110) diffraction peak ($a = 2 \times d_{110}$), is found in NO_3–Mg/Al LDH and in the M(Edta)–Mg/Al samples showing the stability of the host structure during the anionic exchange. This value corresponds to an Mg/Al molar ratio close to 2 in the brucite-like layers.

Table 1 *Elemental analysis, proposed formula and BET specific surface area of the nanocomposites*

Sample	**Chemical composition (wt %)**						**S_{BET}[a] ($m^2 \cdot g^{-1}$)**
	Mg	**Al**	**M^{2+}**	**C**	**N**	**Suggested formula**	
NO_3-Mg/Al	16.7	9.06		0.30	5.04	$[Mg_{0.66}Al_{0.34}(OH)_2][(NO_3)_{0.35}(CO_3)_{0.02}] \cdot 0.72\ H_2O$	137
Ca(Edta)-Mg/Al	13.14	7.49	3.37	11.86	3.22	$[Mg_{0.66}Al_{0.34}(OH)_2][(Ca(Edta))_{0.1}(Edta)_{0.02}(NO_3)_{0.039}] \cdot 1.14\ H_2O$	100
Sr(Edta)-Mg/Al	13.71	8.12	6.46	10.32	2.32	$[Mg_{0.66}Al_{0.34}(OH)_2][Sr(Edta))_{0.084}(Edta)_{0.015}] \cdot 1.06\ H_2O$	153
Ba(Edta)-Mg/Al	14.02	7.37	8.44	11.03	2.42	$[Mg_{0.68}Al_{0.32}(OH)_2][Ba(Edta))_{0.072}(Edta)_{0.035}] \cdot 0.94\ H_2O$	111

[a] *BET surface area determined on samples calcined at 923 K and outgassed at 523 K.*

Table 2 *ν_{CD} frequencies of $CDCl_3$ adsorbed on the M/Mg(Al)O catalysts and the number of the surface basic sites*

Sample	**Basic sites**						
	Total Nb[a] ($\mu mol \cdot m^{-2}$)	**W**		**M**		**S**	
		ν_{CD} (cm^{-1})	**Nb[b] ($\mu mol \cdot m^{-2}$)**	**ν_{CD} (cm^{-1})**	**Nb[b] ($\mu mol \cdot m^{-2}$)**	**ν_{CD} (cm^{-1})**	**Nb[b] ($\mu mol \cdot m^{-2}$)**
Mg(Al)O	0.75	2254	0.70	2230	0.07	2181	0.04
Ca/Mg(Al)O	1.06	2243	0.74	2213	0.07	2191	0.24
Sr/Mg(Al)O	0.67	2251	0.29	2228	0.26	2187	0.12
Ba/Mg(Al)O	0.77	2248	0.10	2225	0.60	2183	0.07

[a] *Determined by TPD of CO_2 of samples calcined at 923 K.*

[b] *Estimated by deconvolution of $CDCl_3$ DRIFT spectra of samples calcined at 923 K.*

The elemental analysis of the samples allows proposing the structural formula reported in Table 1. The Mg/Al molar ratio in the nanocomposites is close to that of the host NO_3–Mg/Al LDH. Excepted for Ca(Edta)–Mg/Al, the initial NO_3^- anions of the host NO_3^-Mg/Al LDH are totally displaced by both $[M(Edta)]^{2-}$ complexes and free $[Edta]^{4-}$ during the exchange. Molecular dynamic studies of the AE cations complexes of Edta in aqueous solution have already shown that in the endo complex type, the AE cation is coordinated by four monodentate carboxylate groups and two nitrogen atoms of Edta. An exo complex is also obtained in the case of Ca^{2+} coordinated by two bidentate carboxylate groups. Moreover, the relative stabilities of the complexes with $[Edta]^{4-}$ ranges from Ca^{2+} to Sr^{2+} and Ba^{2+} [9]. This order of stability is in agreement with the exchange rate of the host LDH by the $[M(Edta)]^{2-}$ complexes and then with the AE cations content of the M(Edta)–Mg/Al samples.

The M/Mg(Al)O mixed oxides catalysts obtained after thermal decomposition of the M(Edta)–Mg/Al LDHs at 923 K exhibit XRD patterns characteristics of the periclase-like structure. These XRD patterns are also similar to that of the Mg(Al)O mixed oxide obtained by calcination of NO_3–Mg/Al at 923 K and depicted in Figure 1e. The specific surface areas of the mesoporous M/Mg(Al)O mixed oxides ranges from 100 to 153 $m^2 \cdot g^{-1}$. They are similar to that of Mg(Al)O at 137 $m^2 \cdot g^{-1}$. These results show that the introduction of the AE cations into the Mg(Al)O mixed oxides does not significantly modifies its structural and textural properties.

3.2. Basic properties

TPD of CO_2 allows to determine the total density of surface basic sites of the different mixed oxides which varies as follows: Sr/Mg(Al)O < Mg(Al)O ~ Ba/Mg(Al)O < Ca/Mg(Al)O (Table 2). There is a clear tendency towards an increase of the basic sites density when alkaline-earth cations are introduced. The lower sites density observed for Sr/Mg(Al)O than for Mg(Al)O accounts for the high specific surface area of the former mixed oxide almost 50% higher than the other M/Mg(Al)O mixed oxides.

The adsorption of the acidic $CDCl_3$ probe molecule has been also successfully used to characterize the number and strength of the different basic sites of LDHs and of binary oxides [4, 10]. The ν_{CD} frequency value of the H-bonded complexes of $CDCl_3$ adsorbed on the different basic sites decreases as their strength increases. The DRIFT spectra in the ν_{CD} region (2300–2120 cm^{-1}) of $CDCl_3$ adsorbed at 303 K on the M/Mg(Al)O catalysts and, for the sake of comparison, on Mg(Al)O are reported in Figure 2.

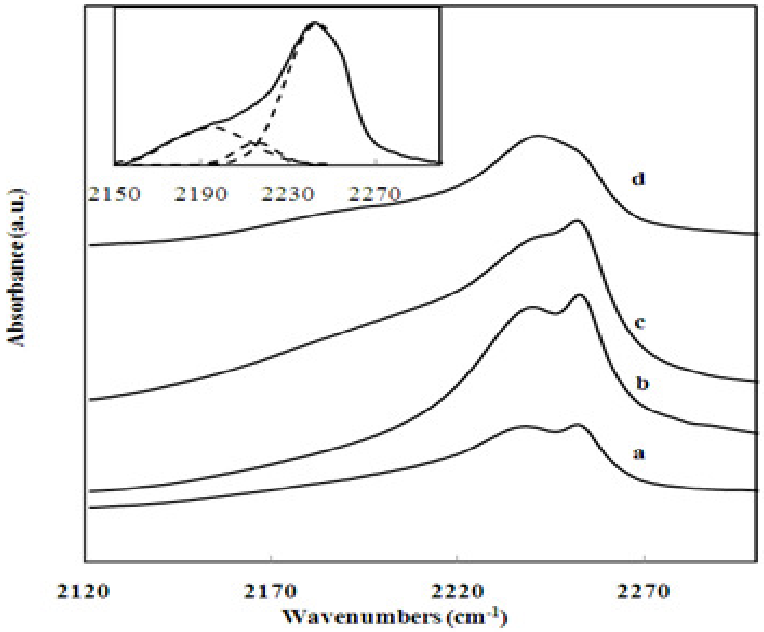

***Figure 2.** DRIFT spectra (ν_{CD} region) of $CDCl_3$ adsorbed at 303 K on (a) Ba/Mg(Al)O, (b) Mg(Al)O, (c) Sr/Mg(Al)O and (d) Ca/Mg(Al)O. For sake of clarity the spectra have been shifted vertically. Insert shows the deconvolution of the 2190–2300 cm^{-1} region of Ca/Mg(Al)O.*

In all cases broad bands are observed which account for the formation of several H bonded complexes. A shoulder towards lower frequencies, absent in Mg(Al)O, is noted in the M/Mg(Al)O mixed oxides, particularly in the Ca- and Sr-containing ones. Deconvolution of the bands using the scientific graphing and data analysis software package Origin fits well considering three components at 2251–2243, 2228–2213 and 2191–2183 cm^{-1} characteristic of the H-complexes of $CDCl_3$ with weak (W), medium (M) and strong (S) basic sites, respectively. The ν_{CD} frequencies and the contents of the W, M and S sites on the different catalysts are reported in Table 2. Mg(Al)O is found as weakly basic. W basic sites indeed represent about 95% of the total number with the highest value of the ν_{CD} frequency. Relatively to Mg(Al)O, the introduction of AE cations modifies significantly the basic properties as shown by: (i) the shift of the ν_{CD} frequencies by 2–17 cm^{-1} to lower values for W and M sites, and in contrast by 2–10 cm^{-1} to higher ν_{CD} frequencies for S sites; (ii) an increase of M and S sites densities at the expense of the W sites density.

These evolutions account for a general increase of the average basic strength after introduction of the AE cations in the Mg(Al)O mixed oxides. Moreover, the nature of the AE cations influences the relative densities of M and S sites which behave in opposite way, the former being in larger amount for Ba and the latter for Ca. It is noteworthy, regarding on one hand the density and on the other hand the strength of S sites evaluated by the ν_{CD} frequency shift of the $CDCl_3$ peak, that they vary in opposite way. So, Ba/Mg(Al)O actually contains a small number of basic sites, but of very high strength.

The conversion of MBOH is increasingly used to characterize the acido-basicity of oxides, likely those with basic character, as recently reviewed [11]. Indeed, dehydration of MBOH into 3-methylbut-3-en-1-yne occurs on acid sites, while disproportionation into acetone and acetylene occurs on basic sites, allowing clear identification of the predominant acidic or basic nature of the catalytic sites of the materials. However, this test reaction is not able to infer on the Brønsted or Lewis nature of the different sites. All the mixed oxides of the study, i.e. Mg(Al)O and M/Mg(Al)O, behave as basic catalysts yielding only acetylene and acetone in stoichiometric amounts as reaction products. It is worthy to note that: (i) the M/Mg(Al)O mixed oxides whose MBOH conversion ranges from 17.3 to 24.8% after 1 h reaction time are more active than Mg(Al)O (conversion = 2.8%) and that among the AE-containing mixed oxides the order of reactivity is: Ba/Mg(Al)O > Sr/ Mg(Al)O > Ca/Mg(Al)O. This behavior, when it is compared to the previous results obtained by FTIR of $CDCl_3$, shows that the conversion of MBOH follows the increase in the sum of M and S sites density in the catalysts (Figure 3).

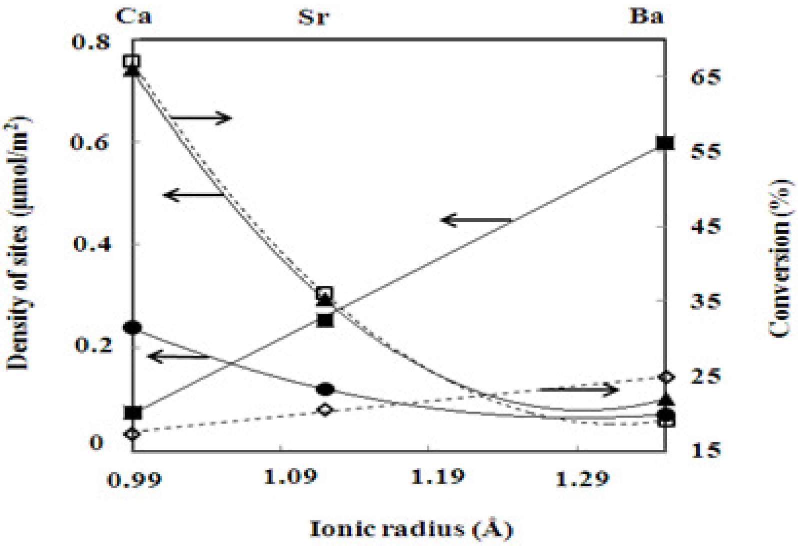

Figure 3. *Density of (▲) weak, (■) medium and (●) strong basic sites and catalytic activity in the (◊) MBOH conversion and (□) DB-1 isomerization in function of the ionic size of the alkaline-earth cations.*

In summary, characterization of the basicity of the M/Mg(Al)O catalysts by means of TPD of CO_2, FTIR spectroscopy of $CDCl_3$ and catalytic test reaction of MBOH reveals that the introduction of AE cations into Mg(Al)O allows to increase the density of basic sites, particularly those of medium and high strength. Moreover, the content of M and S sites behave in opposite way in function of the nature of the AE cations.

3.3. Catalytic activity

The double bond migration of DB-1 to the more thermodynamically stable DB-2 is known to proceed only on strong basic catalysts [12]. Accordingly M/Mg(Al)O catalysts give rise to conversions ranging from 19 to 67% which follow the same trend, i.e. Ba/Mg(Al)O < Sr/Mg(Al)O < Ca/Mg(Al)O (Figure 3), as their relative content in both W and S sites determined by FTIR spectroscopy of $CDCl_3$ (Table 2). As Mg(Al)O, which posses the higher number of W sites, has been reported almost inactive for this reaction [13], the previous results confirm that the strong basic sites created by introduction of the AE cations into the M/Mg(Al)O catalysts are responsible for their catalytic activity in the isomerization of DB-1. Remarkably, the catalytic activity of Ca/Mg(Al)O (67%) is in the range of that reached using a Ca(Al)O mixed oxide (89%) obtained from the decomposition of a Ca/Al-LDH precursor [13].

4. Conclusions

New basic mixed oxides catalysts were obtained when AE cations complexed with Edta and intercalated into Mg/Al LDH were used as precursors. The introduction of the AE cations does not significantly modifies the structural and textural properties of the Mg(Al)O mixed oxide but increases its content in basic sites of medium and high strength. An important feature is that the nature of the AE cations allows to finely control the basicity in order to perform reactions requiring different basic strength. Ba-containing mixed oxides with the largest content of sites of medium and high strength are consequently the most active for MBOH conversion. Due to their larger content of strong basic sites, the AE-containing mixed oxides are able to perform the highly demanding isomerization reaction of DB-1. The most active catalyst is in this case Ca/Mg(Al)O which posses the larger number of strong basic sites.

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Scientific article (Art 4)

Highly basic catalysts obtained by intercalation of La-containing anionic complexes in layered double hydroxides

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Highly basic catalysts obtained by intercalation of La-containing anionic complexes in layered double hydroxides

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Abstract

Nanocomposites have been obtained by intercalation of preformed negatively charged guest La hydroxy citrate colloids into host Mg/Al layered double hydroxides (LDH). These compounds have been used as precursors for La/Mg(Al)O mixed oxides catalysts. The La loading has been controlled by the colloids exchange rate in order to achieve a better dispersion of the lanthanum cations and thus improve the basic properties of the new catalysts. The increase of the d_{003} interlayer distance from 0.830 nm in the host LDH to 1.196 nm in the nanocomposites shows that the intercalation has taken place leading to 1.82-11.16 wt% of lanthanum cation loadings. The basic properties of the La/Mg(Al)O(x) mixed oxides were evaluated qualitatively using Hammett indicators and quantitatively by TPD of CO_2. Both techniques indicated the presence of strong basic sites. The transesterification of 1-phenylethanol with diethylcarbonate (DEC), which is known to involve strong basic sites, was used to evaluate the catalytic activity of the La/Mg(Al)O(x) mixed oxides. Yields into carbonate product increase with the density of strong basic sites of the catalyst.

Keywords: Layered double hydroxides, basic catalysts, lanthanum, nanocomposites, unsymmetrical organic carbonates.

1. Introduction

Layered double hydroxides (LDHs) are mainly used until now in the plastic industry [1, 2], or as antacid or drug carriers [3, 4]. Besides, they have been also largely investigated as catalysts or catalyst precursors due to their ability to give mixed oxides with a large variety of compositions, high-surface areas and tuneable acid-basic or redox properties. Indeed LDHs, also called anionic clays or hydrotalcite-like compounds, have a general formula $[M_n^{2+}M_m^{3+}(OH)_{2(n+m)}]^{m+}[A^{x-}]_{m/x}\cdot yH_2O$, where M^{2+} and M^{3+} are di- and trivalent metal cations, respectively, A^{x-} represents the x-valent anion (typically carbonate), which is needed to compensate the net positive charge of the layers exhibiting a brucite-like structure, and y is the number of water molecules in the interlayer space [5]. Basic Mg(Al)O mixed oxides obtained by thermal decomposition of Mg/Al-LDHs have been the most widely used as catalysts in C-C bond formation reactions, e.g. self-condensation and cross-aldol condensations of aldehydes and ketones, Knoevenagel and Claisen-Schmidt condensations, Michael additions [6-15]. All these reactions are very relevant in pharmaceutical and fragrance industries, where catalysts obtained from LDHs are increasingly replacing classical homogeneous catalysts (NaOH and KOH) [16, 17], due to their easy separation from the reaction mixture and their regeneration ability. The basic properties of the Mg(Al)O mixed oxides can be tailored through the Mg/Al ratio, the activation temperature, as well as by performing rehydration treatments [18, 19].

Among the most commonly used basic oxides catalysts, it is well known that those of alkaline-earth or rare earth cations, particularly CaO, SrO, BaO, La_2O_3, Y_2O_3, possesses sites of high strength. Accordingly, Mg/La mixed oxides obtained by thermal decomposition of coprecipitated Mg/La hydroxycarbonates [20 – 22], and Mg(Al)O mixed oxides doped with alkaline, alkaline-earth or rare-earth cations [23, 24] showed, comparatively to Mg(Al)O, an improved catalytic activity in base-catalysed reactions. However, due to their large ionic radius, most of the alkaline, alkaline-earth or rare-earth cations cannot be accommodated, or only scarcely, in the brucite-like sheets of LDHs [25, 26]. This is a main drawback to obtain highly active samples by thermal decomposition of such precursors. Nanocomposites obtained by intercalation of guest negatively charged M^{n+}-based colloids (M^{n+} = metal cation) in host Mg/Al LDHs by means of anion exchange [27, 28] can be regarded as an alternative route for the preparation of alkaline-earth or rare-earth cations doped Mg(Al)O mixed oxides.

In this work, highly basic catalysts have been obtained by intercalation of preformed negatively charged guest La hydroxy citrate colloids into host Mg/Al LDHs to give nanocomposites precursors of La/Mg(Al)O mixed oxides. The La loading has been controlled by the colloids exchange rate in order to achieve a better dispersion of the cations and improve the basic properties of the new materials. The transesterification reaction of 1-phenylethanol with diethylcarbonate (DEC), known as catalyzed by strong basic sites, was used to evaluate the performance of the La-containing catalysts.

2. Experimental

2.1. Preparation of LDH host structure

The NO_3-Mg/Al was synthesized by a conventional coprecipitation method under ambient atmosphere. In a typical synthetic run, 200 ml aqueous solution of $Mg(NO_3)_2 \cdot 6H_2O$ (0.41 M) (Panreac 98%) and $Al(NO_3)_3 \cdot 9H_2O$ (0.21 M) (Fluka ≥ 98%) in deionized water was added dropwise at a rate of 2 $ml \cdot min^{-1}$ and room temperature into a beaker. Simultaneously, appropriate volume of NaOH (2M) (Panreac 98%) was added at a controlled rate to maintain the pH close to 10 using a pH-STAT Titrino (Metrohm, France) apparatus. After complete precipitation, the gel obtained was refluxed at 353 K for 24 h. It was then repeatedly washed with distilled water at 298K (~6 l), and finally dried overnight at 353 K. This solid was named NO_3-Mg/Al.

2.2. Preparation of La-complex intercalated LDH

The La hydroxy citrate complexes were prepared by dissolution in 20 ml of water of the required amounts of $LaCl_3 \cdot 7H_2O$ (0.12 M) (Sigma Aldrich 99%) and $Na_3C_6H_5O_7$ (0.12 M) (Fluka ≥ 98%) salts (complexation degree $[C_6H_5O_7]/[La] = 1$) at room temperature followed by hydrolysis performed by addition of the appropriate amount of NaOH (0.12 M) (hydrolysis degree $[OH]/[La] = 1$) at room temperature under vigorous stirring for 0.5 h, leading in all cases to clear solutions.

The La-intercalated LDHs with 3 different La^{3+} loadings were obtained by anionic exchange of the NO_3^- anions of the host Mg/Al-NO_3 by the La hydroxy citrate complexes in competition with citrate anions under ambient atmosphere. For this purpose, Mg/Al-NO_3 (3g) was dispersed in 50 ml of an aqueous solution containing 22.4 10^{-3} mol of La hydroxy citrate complexes corresponding to 2 times the anionic exchange capacity of Mg/Al-NO_3 (3.74 $meq \cdot g^{-1}$) and increasing amounts of $Na_3C_6H_5O_7$ such as the $[La^{3+}]/\Sigma[(C_6H_5O_7)^{3-}]$ molar ratios were 1, 0.33 and 0.25, respectively. The negative charge provided by the La hydroxy citrate complexes in the exchange solutions correspond to 1, 0.14 and 0.10 times of the total negative charge present.

The mixture was hydrothermally treated in an autoclave reactor at 423 K for 4 h and 50 bars of argon. After the hydrothermal treatment, the HTLa(x) solid ($x= [La^{3+}]/\Sigma[(C_6H_5O_7)^{3-}] = 1$, 0.33 and 0.25) was recovered by filtration, washed with deionized water (1.5 l) and dried at 373 K for 2 h.

The La/Mg(Al)O(x) catalysts were obtained by thermal decomposition of the HTLa(x) precursors (200 mg) at 923 K in an air flow (100 $ml \cdot min^{-1}$) for 18 h. The obtained mixed oxides were cooled down to room temperature in argon flow (100 $ml \cdot min^{-1}$).

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2.3. Characterization techniques

Chemical analyses of the samples were carried out by inductively coupled plasma atomic emission spectroscopy (ICP-AES) at the Central Analysis Service of the CNRS (Solaize, France).

Powder X-ray diffraction patterns (XRD) were recorded on a Siemens D5000 diffractometer with Bragg-Brentano geometry with nickel-filtered $Cu_{K\alpha}$ radiation (λ=0.1541 nm). Data were collected in the 2Θ range of 4 to 70^0 with an angular step of 0.05^0 at 3 s per step, resulting in a scan rate of $1^0 \cdot min^{-1}$.

N_2 adsorption experiments at 77 K were carried out on samples previously calcined at 923 K for 5 h and outgassed at 523 K (10^{-4} Pa) with a Micromeritics ASAP 2000 instrument. Specific surface area was calculated using the BET method.

^1H NMR spectrum was recorded at 400.14 MHz with a Varian Mercury 400 spectrometer. The chemical shifts were referenced relative to external $CDCl_3$.

Thermal analysis was performed in a Labsys/Setaram TG DTA/DSC thermobalance, equipped with a programmable temperature furnace. The sample (150 mg) was heated from room temperature to 1173 K in air (80 cm^3 STP$\cdot min^{-1}$) at 5 $K \cdot min^{-1}$.

A qualitative measurement of the basic properties of La/Mg(Al)O(x) mixed oxides was performed using indicators with different pK_a. The strength of basic sites on the prepared catalyst was determined using following indicators: 4-chloro-2-nitroaniline (pKa = 17.2), 4-nitroaniline (pKa = 18.4), 4-chloroaniline (pKa = 26.5) and diphenyl methane (pKa = 35). The color change was visually observed after addition of 0.1 g of the sample previously calcined at 923 K, to a solution containing 5 mg of indicator dissolved in 5 ml of toluene.

The number and the strength of the basic sites of the samples calcined at 923 K were determined by TPD of CO_2 in a Thermo Finnigan TPD/R/O 1100 equipped with a programmable temperature furnace and a TCD detector. Typically, 200 mg of the solid were placed between quartz wool in a quartz reactor. The adsorption of CO_2 (3 vol. % CO_2 in He; 20 cm^3 STP·min^{-1}) was performed at room temperature for 10 min. After adsorption the sample was treated in He flow (20 cm^3 STP·min^{-1}) at 373 K for 10 min to remove the physically adsorbed CO_2. The CO_2 uptake was measured by heating the sample from room temperature up to 1173 K at a rate of 20 K·min^{-1}.

2.4. Catalytic test reaction

For a typical experimental procedure, an excess of DEC (33 mmol) (Sigma Aldrich 98%) and 1-phenylethanol (2 mmol) (Sigma Aldrich 98%) were placed in a three-necked round-bottomed flask equipped with a condenser and magnetic stirring. Freshly activated catalyst (0.1 g), kept under argon atmosphere after activation in the reactor, was rapidly moved into the three-necked round-bottomed flask in order to avoid contact with air. The reaction was performed at 403 K under nitrogen atmosphere and continuous magnetic stirring (500 rpm). Dodecane (0.05 ml) (Fluka ≥ 98%) was added as internal standard giving a homogeneous phase. Samples were analyzed by gas chromatography using an AG Ultra 2 column (25 m x 0.2 mm x 0.33 μm). The conversion was determined from the variation in the concentration of alcohol. The main reaction products are the unsymmetrical alkyl carbonate and ethanol. After completion of the reaction, the mixture was filtered to separate the catalyst and the filtrate was distilled at 403 K. The alkyl carbonate was analyzed by ^1H NMR, data: δ_H 1.2-1.35 (t, 3H), 1.4-1.5 (d, 3H), 4.1-4.35 (q, 2H), 5.65-5.85 (q, 1H), 7.25-7.5 (m, 5H).

3. Results and discussion

3.1. Composition and structure

The XRD patterns of the host Mg/Al-NO_3 and of the intercalated samples HTLa(x) are reported in Figure1. The pattern of Mg/Al-NO_3 is typical of a LDH phase with sharp and symmetric (00*l*) reflections (JCPDS 22-700) below 30° 2Θ and broad and asymmetric (0*kl*) reflections at higher 2Θ values. The interlayer spacing d_{003} = 0.830 nm is consistent with the presence of NO_3^- as charge compensating anions. The intercalation of the citrate and the La hydroxy citrate complexes is in conformity with the shift toward lower 2Θ angles of the (00*l*) reflections corresponding to a significant enlargement from 0.830 nm to 1.196 nm of the basal distance d_{003} relatively to the host Mg/Al-NO_3 in agreement with the spacing previously reported for citrate anion [29].

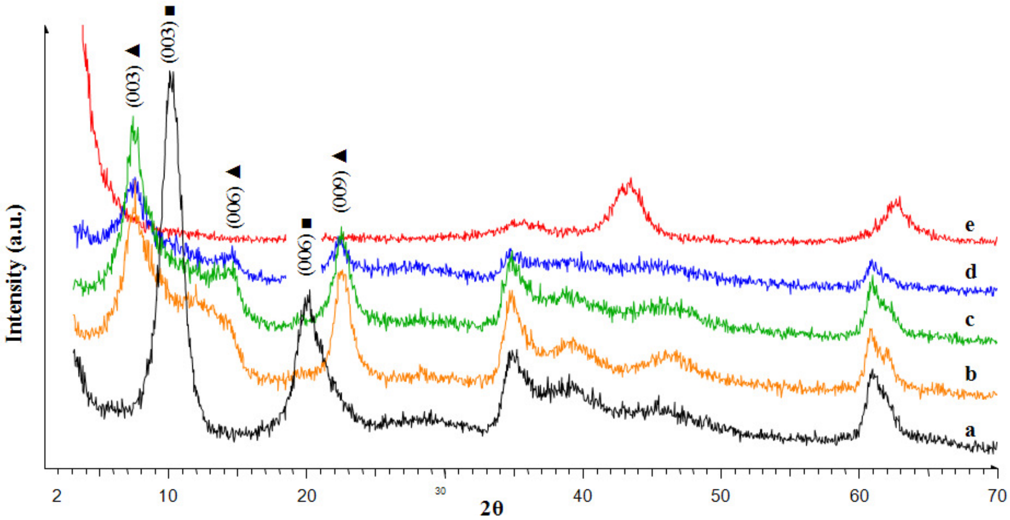


Figure 1. *XRD patterns of: (a) MgAl-NO_3, (b) HTLa(0.25), (c) HTLa(0.33), (d) HTLa(1), (e) La/Mg(Al)O(1) ((00l) reflections on (■) MgAl-NO_3 and (▲) HTLa(x)).*

The width increases while, in contrast, the intensity decreases for all diffraction peaks in the nanocomposites comparatively to the host LDH and as the La loading increases. This suggests higher stacking and turbostratic disorders rather than smaller crystal sizes in the nanocomposites than in the host structure. The broadening of the (00*l*) peaks is often observed when anionic complexes of large size are intercalated due to layers stacking faults [30, 31]. It must be pointed out that three (00*l*) harmonics are observed at 7.38, 14.80 and 22.28° 2Θ, corresponding to the (003), (006) and (009) peaks, in relation to the large size of the intercalated species. It can be noted that the (006) peak at 14.80° 2Θ becomes more defined and intense, relatively to the (003) and (009) peaks, as the $[La^{3+}]/\Sigma[(C_6H_5O_7)^{3-}]$ molar ratio increases in the intercalation solution. Such inversion of intensity of the first (00*l*) diffraction lines has been already reported after intercalation of negatively charged rare earth- or noble metal-containing complexes [31, 32]. It is attributed to the increase of the electron density in the interlayer space due to the presence of the metal. In the present case, the increase of the relative intensity of the (006) peak follows that of the $[La^{3+}]/\Sigma[(C_6H_5O_7)^{3-}]$ molar ratio and then the La^{3+} loading. Besides, the broadening observed in the 11-14° 2Θ range probably accounts for the presence of slight amount of intercalated CO_3^{2-} anions.

Chemical compositions of the HTLa(x) samples (Table 1) reveal closer Mg/Al molar ratios of 2 similar to that of the host Mg/Al LDH. The nitrogen contents of the samples show that, except for HTLa(1), nitrates of the host LDH are almost totally exchanged in the HTLa(x) samples. It is noteworthy that the La content decreases of almost one order of magnitude, when concurrently the C content decreases only from about 9.6 to 7.5 wt% between HTLa(1) and HTLa(0.25). These features could account for the intercalation of La-containing complexes with increasing complexation degree $[C_6O_7H_3]/[La]$ of 1.7, 6.2 and 7.7 for HTLa(1), HTLa(0.33) and HTLa(0.25), respectively, if one consider that they are the only anionic species present. However, the large discrepancy with the nominal complexation degree $[C_6H_5O_7]/[La] = 1$ used in solution (§ 2.2), on one hand and the similar interlayer distance ($d_{003} = 1.196$ nm) observed in all samples, on the other hand, lead us to rule out this possibility. We actually suggest that there is co-intercalation of free $(C_6O_7H_3)^{3-}$ anions and La hydroxy citrate complexes $[La(C_6H_5O_7)(OH)]^-$ with a complexation degree of 1. The carbon contents which allow to determine the relative amounts of the intercalated species lead to $[La^{3+}]/\Sigma[(C_6H_5O_7)^{3-}]$ molar ratios of 1, 0.16 and 0.13 for HTLa(1), HTLa(0.33) and HTLa(0.25), respectively. They are lower for the two latter samples than the molar ratios in solution, i.e. 1, 0.33 and 0.25, respectively, confirming that free $(C_6O_7H_3)^{3-}$ anions are also intercalated. Moreover, as previously suggested from the careful examination of the XRD patterns, presence of minor amounts of CO_3^{2-} species must not be ruled out as intercalation experiments were performed under ambient atmosphere.

In summary, anionic exchange of Mg/Al-NO_3 LDH with aqueous solutions containing at the same time pre-formed La hydroxy citrate species

($[La(C_6H_5O_7)(OH)]^-$) and citrate anions in different amounts leads to the intercalation of both species and to hybrid materials with controlled La loadings.

The La/Mg(Al)O(x) catalysts obtained by calcination in air at 923 K of the HTLa(x) samples show similar XRD patterns with broad peaks at ~ 42 and 62° 2Θ typical of the Mg(Al)O mixed oxide with the periclase-like structure (JCPDS 87-0653) as exemplified for La/Mg(Al)O(1) in Figure 1. No peaks assignable to La-containing phases are identified, suggesting that they exist as highly dispersed lanthanum oxide microdomains.

The La/Mg(Al)O(x) mixed oxides exhibit a type IV adsorption isotherm characteristic of mesoporous materials. Compared to Mg(Al)O, the mesopore volume increases in the La/Mg(Al)O(x) mixed oxides, which gives rise to an increase of the specific surface areas from 137 $m^2 \cdot g^{-1}$ in Mg(Al)O, up to 231 $m^2 \cdot g^{-1}$ in La/Mg(Al)O(0.25) (Table 1).

This increase of mesoporous volume can be assigned to the release of carbon dioxide due to citrate decomposition as already shown by Reichle et al. [33] in the case of carbonated LDHs.

Table 1 *Elemental analyses, specific surface areas, total pore volume and number of strong basic sites (Nb) of the samples.*

Sample	Mg (%)	Al (%)	La (%)	C (%)	N (%)	S.S. ($m^2 \cdot g^{-1}$)	Total pore volume ($ml \cdot g^{-1}$)	Nb[a] ($\mu mol \cdot g^{-1}$)	Nb[a] ($\mu mol \cdot m^{-2}$)	CO_2/La[b]
MgAl-NO_3	16.71	9.06	-	< 0.30	5.04	137	0.18			
HTLa(1)	12.75	7.06	11.16	9.61	0.11	144	0.21	39	0.23	0.05
HTLa(0.33)	16.40	8.86	2.51	8.03	< 0.10	228	0.31	20	0.14	0.11
HTLa(0.25)	16.65	9.00	1.82	7.49	< 0.10	231	0.29	16	0.06	0.12

3.2. Termogravimetric analysis

Figure 2 shows the termogravimetric analysis of the HTLa(x) samples. The decomposition profiles are in good agreement with those generally reported in the literature for the hydrotalcite-like compounds [34]. The three samples present a similar behavior with two distinct weight-loss processes and a total weight loss of ca. 40 % for HTLa(1) increasing to ca. 50 % for HTLa(0.33) and HTLa(0.25). The increase in the relative weight loss observed between HTLa(0.33) and HTLa(0.25) with respect to HTLa(1) can be attributed to the lower La^{3+} content in the former samples. The first weight loss of about 20% below 523 K, corresponds to the release of physisorbed and interlayer water molecules, while the second weight loss (523-923 K) originates from the dehydroxylation of the brucite-like layers and the decomposition of the intercalated La hydroxy citrate complexes and citrate anions, as well as the nitrates in the case of HTLa(1). There is no weight loss above 923 K and this is in agreement with the XRD patterns showing that the samples exhibit the Mg(Al)O mixed oxide structure.

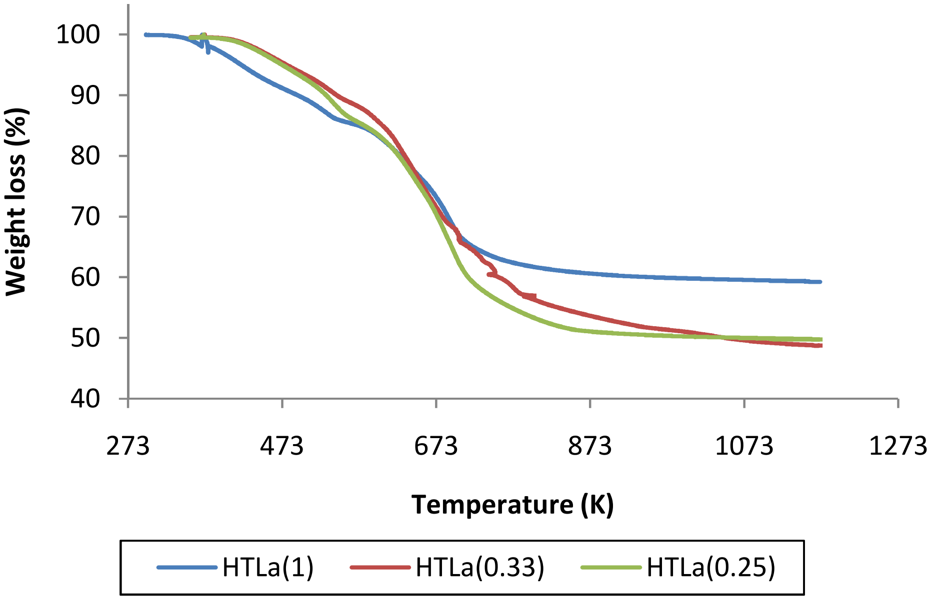


Figure 2. *TG profiles for: HTLa(0.25), HTLa(0.33) and HTLa(1).*

3.3. Basic properties

The basicity of the La-containing mixed oxides has been qualitatively evaluated with Hammett indicators. Basic sites with $26.5 < pK_a \leq 35$ were detected in these samples. They are much stronger than those present in the Mg(Al)O mixed oxide with $4.5 < pK_a < 9.3$ detected by color change of the indicators [35] or $10.7 < pK_a < 13.3$ determined by carrying out the condensation reaction of benzaldehyde with different activated methylenic groups [36].

Extensive information regarding basic properties is given by TPD of CO_2. All samples exhibit almost the same TPD profile up to 973 K. In contrast, the profiles differ significantly above this temperature (Figure 3). This accounts for modifications of number and strength of the strong basic sites due to the La content of the samples. The number of strong sites calculated as the amount of CO_2 desorbed between 973 and 1173 K is reported in Table 1. It increases with the La content of the samples. Moreover, the CO_2 desorption peak is slightly shifted toward higher temperatures when the amount of La in the sample decreases, indicating that stronger basic sites are formed. Besides, quantification reported in Table 1, shows that the CO_2 adsorption with respect to the La content concurrently increases. These features suggest that the creation of strong basic sites in the La-containing mixed oxides is assignable to the formation highly dispersed lanthanum oxide domains.

The generation of strong basic sites revealed by TPD of CO_2 is in agreement with the qualitative results obtained using the Hammett indicators.

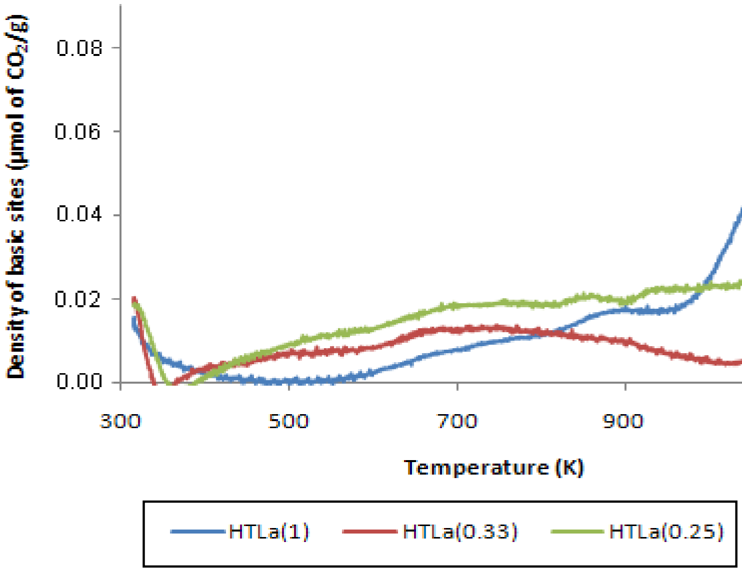
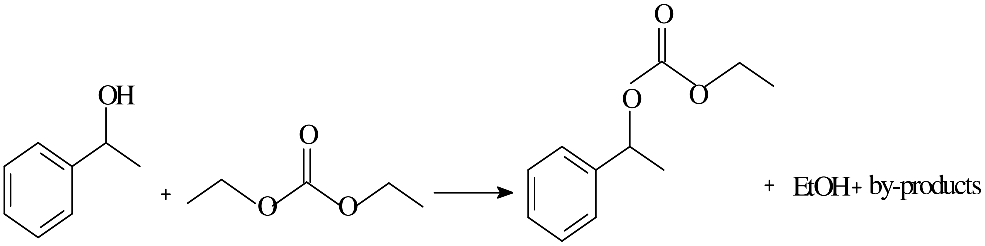


Figure 3. *TPD of CO_2 desorption profiles for: HTLa(0.25), HTLa(0.33) and HTLa(1).*

3.4. Catalytic activity

In order to determine the catalytic activity of the La-containing mixed oxides transesterification reaction of 1-phenylethanol and diethylcarbonate (DEC) was performed in a solvent free system (Scheme 1).



Scheme1 *Transesterification reaction between 1-phenylethanol and DEC for the synthesis of unsymmetrical organic carbonates.*

The synthesis of unsymmetrical organic carbonates via direct condensation of DEC with different alcohols is known to be catalyzed by strong basic catalysts. Carloni et al. [37] performed the reaction of several alcohols with DEC using MCM-41-TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene anchored on mesoporous MCM-41 silica) as catalyst. TBD is a strongly basic bicyclic guanidine with a $pK_a = 24.97$ [38]. In this reaction system conversions reach 93-96% after 24 h. Veldhurthy et al. [22]

performing the reaction with solids of different basic strength established that the catalytic activity is correlated with the number of strong basic sites adsorbing CO_2 with an enthalpy higher than 120 kJ mol^{-1} which are able to abstract a proton from 1-phenylethanol. Recent reports describe Mg/La mixed oxides [39] and CsF/α-Al_2O_3 [40] as new solid basic catalysts for the synthesis of organic carbonates.

The time required to reach the maximum conversion of 1-phenylethanol and the corresponding unsymmetrical carbonate yields obtained with the three La/Mg(Al)O(x) and the parent Mg(Al)O mixed oxides are reported in Table 2. The unsymmetrical alkyl carbonate is the main product of reaction; ethanol being eliminated by distillation due to its low boiling point and secondary products also present (8-15%) are hardly identified. It is noteworthy that La/Mg(Al)O(0.33) and La/Mg(Al)O(0.25) are the most active catalysts affording alkyl carbonate in a yield higher than 80% in 15 min, while La/Mg(Al)O(1) and Mg(Al)O require reaction time higher than 30 min. The La-free mixed oxide (Mg(Al)O) is the less active catalyst and its activity increases with the calcination temperature due to the improvement of the basic strength [41].

***Table 2** Reaction time and yields in the reaction of 1-phenylethanol and DEC with La/Mg(Al)O catalysts calcined at 923 K*[a]

Catalyst	Reaction time (min)[b]	Alkyl carbonate yield (%)
Mg(Al)O	60	87
	60[c]	59[c]
La/Mg(Al)O(1)	30	90
La/Mg(Al)O(0.33)	15	91
La/Mg(Al)O(0.25)	15	81

[a] *Reaction conditions: 1-phenylethanol (2 mmol), DEC (33 mmol), catalyst (0.1 g), 403 K.*
[b] *to reach the highest conversion*
[c] *calcined at 723 K*

These results can be compared with those already reported in the same transesterification reaction with solid catalysts of different basic strengths [22]. The two most active CsF/α-Al_2O_3 and Mg/La mixed oxide catalysts reach full conversion in 45 min and 3.5 h, respectively. The catalysts of this study are therefore more active; nevertheless, their specific surface areas ranging from 130 to 230 m^2·g^{-1} (Table 1) are higher than those reported for CsF/α-Al_2O_3 and Mg/La, i.e. 7 and 37.6 m^2·g^{-1}, respectively. However, CsF/γ-Al_2O_3 and KF/γ-Al_2O_3, exhibiting specific surface areas of about 220 $m^2 \cdot g^{-1}$, comparable to those of La/Mg(Al)O(0.25) and La/Mg(Al)O(0.33), reach 57 and 36% alkyl carbonate yields in 12 h, being then less active [22].

Regarding the La-containing mixed oxides, it is noteworthy that La/Mg(Al)O(0.33) afforded the optimum activity which then decreases, on one hand, in La/Mg(Al)O(0.25) due to the lower density of sites, and on the other hand, in La/Mg(Al)O(1) due to the lower dispersion of La (Table 1).

4. Conclusions

In this work, preformed negatively charged guest La hydroxy citrate colloids were intercalated by anionic exchange into host Mg/Al LDH to give nanocomposites precursors of La/Mg(Al)O(x) mixed oxides. Different La loadings were obtained by controlling the colloids exchange rate in order to vary the dispersion of the cations and to tune the basic properties of the obtained materials. The TPD of CO_2 results indicate the generation of strong basic sites in the La/Mg(Al)O(x) mixed oxides. Accordingly, these mixed oxides were found highly active for the transesterification reaction of 1-phenylethanol with diethylcarbonate (DEC), which is known to be performed by strong basic catalysts. The unsymmetrical carbonate yields and the activities depend on the content and dispersion of the lanthanum oxide domains in the La-containing mixed oxides.

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Scientific article (Art 5)

La-containing mixed oxides obtained from LDH precursors as highly basic catalysts for double bond migration of olefins

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(in preparation)

La-containing mixed oxides obtained from LDH precursors as highly basic catalysts for double bond migration of olefins

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Abstract

Highly basic La-containing mixed oxides obtained from Mg/Al LDH by anionic exchange, are able to perform the double bond migration of olefins, a highly demanding basic reaction.

Keywords: Lanthanum, layered double hydroxides, mixed oxides, basic catalysis, olefin isomerization.

An increasing class of reactions is performed with $M^{II}(M^{III})O$ mixed oxides catalysts obtained by thermal decomposition of layered double hydroxides (LDH) precursors represented by the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][A^{n-}_{x/n}\cdot mH_2O]$, where M^{2+} and M^{3+} are di and trivalent metal cations and A^{n-} an interlayer compensating anion [1]. Several parameters, like the nature and the ratio of M^{2+} and M^{3+} in the brucite-type layers, the activation temperature of the LDH, allow a fine tuning of the acido-basic properties of the catalysts, mainly directed to the supplying of moderate basic solids [2, 3]. However, intrinsic limitations in the applications of these catalysts arise from the low density of strong basic sites available. So, further developments of $M^{II}(M^{III})O$ mixed oxides catalysts, nevertheless very attractive because of their easy preparation and high specific surface areas, require to rise the amount, the accessibility and the average negative charge on the low coordinated O^{2-} sites known to be the most basic [4, 5]. Though several routes are available, the one proceeding by introduction in LDH of well dispersed alkaline-earth (AE) or rare-earth (RE) cations was not thoroughly investigated so far, mainly because cations with large size which give rise to a strong distortion of the LDH layers cannot be accommodated.

Our goal was to implement an alternative route for the introduction of highly dispersed RE cations by intercalation of negatively charged guest complexes of lanthanum into the host Mg/Al LDH. Mg/Al LDH with good anion-exchange and expansion properties, and particularly high intrinsic basicity, are indeed well indicated host structures for immobilization of such species. Lanthanum containing-guest species are almost the most attractive choice, because lanthanum oxides as well as Mg/La mixed oxide, were already found strongly basic exhibiting initial heats of adsorption of CO_2 higher than 140 $kJ\cdot mol^{-1}$ [6-8]. A prerequisite of the suggested preparation route is to obtain negatively charged La-containing guest species. This was achieved by pre-chelation of La^{3+} with a strong complexing agent, i.e. citrate anion $(C_6O_7H_3)^{3-}$, and further hydrolysis. The intercalation of these species into NO_3-Mg/Al LDH by anionic exchange in competition with citrate anions leads to the hybrid material ($HTLa_{int}$) with controlled La content.

$HTLa_{int}$ is used as precursor for the requested basic catalysts ($La/Mg(Al)O_{int}$) actually obtained by thermal decomposition at 923 K. The low accessibility of the active sites is a main drawback of the catalysts obtained from LDH precursors, either in the mixed oxide or lamellar form. Vigorous mechanical stirring or sonication of the particles allows to produce their breakup, thus improving the accessibility of the catalytic sites for the reactants molecules [9-12]. An alternative approach was supplied in this work by exfoliation of $HTLa_{int}$ previously dispersed in dimethylformamide and then sonicated. This $HTLa_{int/us}$ sample, after drying was calcined at 923 K to give the $La/Mg(Al)O_{int/us}$ catalyst.

For sake of comparison two parents lanthanum-containing catalysts have been also synthesized following well known preparation routes. On one hand, a $La/Mg(Al)O_{imp}$ sample was obtained by impregnation with lanthanum salt of the Mg(Al)O mixed oxide support. On the other hand, a sample noted as Mg/La was obtained by co-precipitation of Mg and La nitrates in alkaline media as previously described [6].

Elemental analysis of NO_3-Mg/Al allows to establish the chemical formula $[Mg_{0.67}Al_{0.33}(OH)_2][(NO_3)_{0.29}(CO_3)_{0.024} \cdot 0.99H_2O]$ which agrees with the composition in solution (Table 1).

Table 1 *Elemental analysis of the samples*

Sample	Mg (%)	Al (%)	La (%)	C (%)	N (%)
NO_3-Mg/Al	16.71	9.06	-	0.30	4.18
$HTLa_{int}$	16.65	9.00	1.82	7.49	0.10
$La/Mg(Al)O_{imp}$	36.85	20.40	1.20	_	_
Mg/La	6.4	_	52.6	3.9	_

The complete exchange of the NO_3^- anions of NO_3-Mg/Al revealed by elemental analysis (Table 1), as well as the intercalation of the La-containing complexes in $HTLa_{int}$ are consistent with the shift to lower 2Θ angle values of the 00*l* peaks in the XRD pattern which corresponds to an expansion of the interlayer space from 0.88 to 1.13 nm (Figure 1).

The La and C contents of $HTLa_{int}$ (Table 1) which give rise to Al/La and C/La molar ratios of 25.0 and 47.7, respectively, show that the intercalation of the La-containing hydroxy citrate complexes and of the citrate anions concurrently occurs. Comparatively to $HTLa_{int}$, a broadening of the 00*l* peaks is observed in the XRD pattern of $HTLa_{int/us}$ (Figure 1).

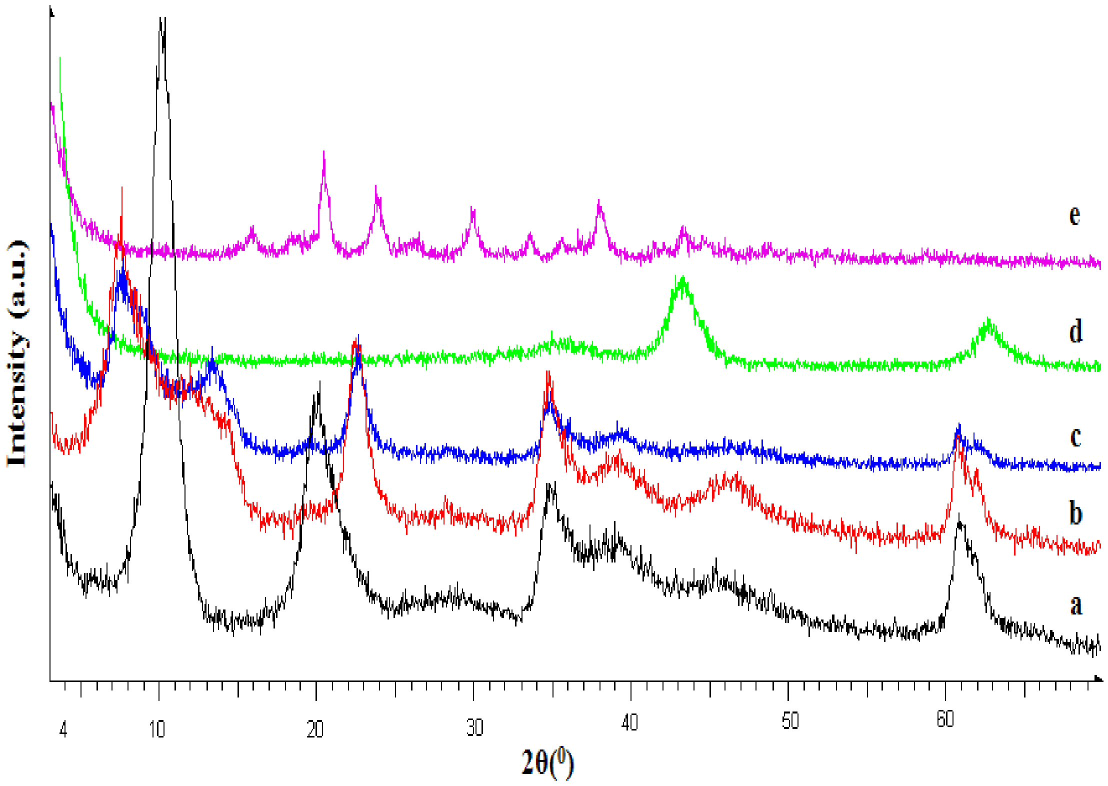

Figure 1. *XRD patterns of (a) NO_3-Mg/Al, (b) $HTLa_{int}$, (c) $HTLa_{int/us}$, (d) $La/Mg(Al)O_{imp}$ and (e) Mg/La samples.*

Accordingly, the specific surface area increases from 231 to 336 $m^2 \cdot g^{-1}$ when going from $La/Mg(Al)O_{int}$ to $La/Mg(Al)O_{int/us}$, the catalysts obtained by calcination at 923 K of $HTLa_{int}$ and $HTLa_{int/us}$ precursors, respectively (Table 2).

***Table 2** Specific surface areas, number and strength of basic sites, and conversions in the isomerisation reaction of DB-1 with the catalysts calcined at 923 K.*

		Number of sites[a]			Conversion (%)	
Catalyst	S.S.A. ($m^2 \cdot g^{-1}$)	Total ($\mu mol \cdot m^{-2}$)	With $\Delta H > 110$ $kJ \cdot mol^{-1}$ ($\mu mol \cdot m^{-2}$)	Initial rate ($mmol \cdot min^{-1} . g^{-1}$)	15 min	45 min
Mg(Al)O	137	0.75	0.00	5.70	47.6	46.8
La/Mg(Al)O_{int}	231	0.4	0.12	0.00	8.4	14
La/Mg(Al)$O_{int/us}$	336	-	-	30.53	80.1	77.8
La/Mg(Al)O_{imp}	40	2.2	0.00	0.00	0	86.9
Mg-LaMO	38	0.73	0.45	24.42	54.8	86.7

[a] *Number and enthalpy of adsorption of CO_2 molecules measured by microcalorimetry.*

These features confirm that the ultrasound treatment allows to break the aggregates and gives rise to a less ordered structure in $HTLa_{int/us}$ than in $HTLa_{int}$ [11, 13]. The previous catalysts, as well as La/Mg(Al)O_{imp}, exhibit the characteristic XRD pattern of the Mg(Al)O mixed oxide support. The low La loading in La/Mg(Al)O_{imp} (1.2 wt%) actually impedes the detection of a La-containing phase in the XRD pattern. It is noteworthy that the specific surface area of 137 $m^2 \cdot g^{-1}$ for Mg(Al)O decreases to 40 $m^2 \cdot g^{-1}$ into La/Mg(Al)O_{imp} (Table 2). This could result from the agglomeration of the Mg(Al)O support particles of La/Mg(Al)O_{imp} during the impregnation. $Mg(OH)_2$, $La_2(CO_3)_2(OH)_2$ and $La(OH)_3$ phases are identified in the XRD pattern of the Mg/La sample (Figure 1). The Mg-La mixed oxide (Mg-LaMO) obtained by calcination of this sample at 923 K possess a specific surface area of 38 $m^2 \cdot g^{-1}$ close to that of the impregnated sample (Table 2).

In this series of samples Mg-LaMO behaves as a strong base with an initial enthalpy of adsorption of CO_2 measured by microcalorimetry of 160 $kJ \cdot mol^{-1}$ and about 0.45 μmol·m^{-2} of molecules adsorbed with an enthalpy higher than 100 kJ·mol^{-1}. Comparatively, La/Mg(Al)O$_{imp}$ and La/Mg(Al)O$_{int}$ mixed oxides with initial enthalpies of adsorption of 108 and 135 kJ·mol^{-1}, respectively, exhibit weaker basic strength than Mg-LaMO. In contrast, their basicity is significantly higher than the Mg(Al)O support with an initial enthalpy of 85 kJ·mol^{-1}. If we assume that the strong basic sites are those adsorbing CO_2 with an enthalpy higher than 110 kJ·mol^{-1}, these sites are only present in La/Mg(Al)O$_{int}$ and Mg-LaMO with a density being about four times higher in the latter sample (Table 2). Though exhibiting a lower basic strength, the impregnated sample La/Mg(Al)O$_{imp}$ presents the highest total number of sites reaching 2.2 μmol·m^{-2}, which is by far higher than in the Mg(Al)O support.

Intercalation of La hydroxyl citrate complex in the Mg/Al LDH allows to obtain, after activation of the hybrid, a mixed oxide with stronger basic sites than the impregnation of a lanthanum salt on the Mg(Al)O support at similar lanthanum loading. Sites of close basic strength are found in La/Mg(Al)O$_{int}$ and Mg-LaMO, though with a lower density in the former sample. Mg-LaMO was earlier described as a layer of lanthanum oxide deposited on magnesia. It therefore behaves like a pure La_2O_3 with a higher thermal stability of the surface area [6, 14]. La_2O_3 activated at 673 K is indeed a strong basic oxide giving about 4.5 μmol·m^{-2} of sites with enthalpies of adsorption ranging from 100 to 150 kJ·mol^{-1}[8].

These features suggest that the presence of the strong basic sites into La/Mg(Al)O$_{int}$ is due to La_2O_3 clusters dispersed into the Mg(Al)O matrix. This allows to obtain basic sites of higher strength than when the lanthanum oxide domains result from an impregnation of a lanthanum salt, however with a lower number of accessible sites. Therefore, the dispersed La_2O_3 clusters into La/Mg(Al)O$_{int}$ are able to give basic sites of similar strength than the La_2O_3 layer formed on surface of Mg-LaMO, with obviously a lower density of sites.

The catalytic activity of the samples was evaluated in the isomerisation of 2,3-dimethyl-1-butene (DB-1) to more thermodynamically stable 2,3-dimethyl-2-butene. This reaction of double bond migration is known to proceed only by the action of strong basic sites [15]. It actually goes through the formation of an allylic anion intermediate by abstraction of a proton which is weakly acid. Results reported in Table 2 show that the catalysts behave very differently. La/Mg(Al)O$_{int/us}$ and Mg-LaMO exhibit similar initial reaction rate, higher than Mg(Al)O, while La/Mg(Al)O$_{int}$ and La/Mg(Al)O$_{imp}$ are initially inactive. An activity is indeed observed only after 5 and 15 min of reaction for La/Mg(Al)O$_{int}$ and La/Mg(Al)O$_{imp}$, respectively. Mg-LaMO and Mg(Al)O behave in opposite way in this series of samples, the former being largely most active. The result obtained with Mg(Al)O shows that basic sites adsorbing CO_2 with an enthalpy of about 80 kJ·mol^{-1} are able to abstract the allylic proton of DB-1. Accordingly, all the catalysts being more strongly basic than Mg(Al)O are active in the reaction. Mg-LaMO gives higher initial reaction rate and conversion after 15 min of reaction than La/Mg(Al)O$_{imp}$ with same specific surface area. This is due to the presence of sites of higher strength. They reach closer activity after 45 min reaction time. The very low activity of La/Mg(Al)O$_{int}$ accounts for the inaccessibility of the DB-1 molecules to the strong basic sites revealed by adsorption of CO_2. The ultrasonic treatment of this sample and the concurrent increase of the specific surface area, which gives access to the active sites, lead to the most active La/Mg(Al)O$_{int/us}$ sample.

Conclusions

In conclusion, the intercalation of RE-containing anionic complexes into of a host Mg/Al LDH, followed by an ultrasonic disaggregation of this hybrid, allows to create after thermal activation, strong basic sites which are not observed into Mg(Al)O. This probably results from the presence of highly dispersed RE oxide domains into the mixed oxide structure. This new preparation route offer a unique opportunity to overcome the basic strength limitations of the catalysts obtained from LDH precursors. The catalysts thus obtained are indeed able to perform the double bond migration of olefins, a highly demanding basic reaction.

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Notes and references

‡ The La hydroxyl citrate complexes (La$_{comp}$) were prepared by dissolution in water of the required amounts of $LaCl_3{\cdot}7H_2O$ and $Na_3C_6H_5O_7$ salts ($[C_6H_5O_7]/[La] = 1$) followed by hydrolysis with NaOH ($[OH]/[La] = 1$) under vigorous stirring for 0.5 h, leading to a clear solution. Anionic exchange of the initial NO_3^- anions of NO_3-Mg/Al to give the hybrid HTLa$_{int}$ material was carried out under hydrothermal conditions (50 bar N_2, 423 K, 4 h), using an aqueous solution containing a mixture of the previously prepared La$_{comp}$ and $Na_3C_6H_5O_7$ at $[La_{comp}]/[La_{comp} + C_6H_5O_7]$ molar ratios of 0.33. To obtain the HTLa$_{int/us}$ sample, 2 h of ultrasound treatment was applied to a mixture of 0.2 g of sample and 10 ml of dimethylformamide. The solid was separated by centrifugation, washed 3 times with water and dried at 423 K for 0.5 h.

The La/Mg(Al)O$_{imp}$ sample was obtained by impregnation of Mg(Al)O mixed oxide (0.4 g) calcined at 923 K under air flow for 18 h by the required amount of a solution of $La(NO_3)_3$ in ethanol followed by a calcination at 923 K for 18 h under air flow.

The DB-1 isomerization reaction was carried out into a quartz glass fixed-bed reactor where the catalyst (0.2 g) was previously calcined at 923 K for 18 h in order to avoid its exposure to air after activation. The DB-1 (≥ 98%, (GC), Fluka), without further purification, was fed by bubbling He (0.005 $l{\cdot}min^{-1}$) through a saturator at 175 K ($P_{DB-1} = 0.002$ kPa). This stream was then introduced in the reactor heated at 343 K and the reaction products were analyzed on line by gas chromatography using a 30 m HP-5 column.

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Scientific article (Art 6)

New synthesis route of hydrocalumite-type materials and their application as basic catalysts for aldol condensation

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New synthesis route of hydrocalumite-type materials and their application as basic catalysts for aldol condensation

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Abstract

Attempt was achieved to directly synthesize Brønsted-type catalyst based on the hydrocalumite-like structure by controlled hydrolysis of calcium and aluminium alkoxides. Solids belonging to the AFm and hydrogrossular families were obtained by dissolution of calcium methoxide and aluminium triethoxide precursors in water at a molar ratio $[Ca^{2+}]/[Al^{3+}] = 2.0$, followed by an aging of the precipitate at 273, 298 or 333 K. At 273 K, a mixture of gibbsite, layered hydrocalumite-like phase, and 3 dimensional cubic Si-free katoite compound is obtained. At 298 K, the XRD pattern reveals the presence of a hydrocalumite-like phase with two distinct 00*l* peaks corresponding to interlayer distances of 0.803 and 0.762 nm, assigned to the presence of intercalated OH^- and CO_3^{2-} species, respectively. At 333 K, the katoite phase only is observed. The presence of the OH^- and CO_3^{2-} compensating anions in the hydrocalumite-like sample is confirmed by IR spectroscopy. This as-prepared sample is able to perform the condensation reaction of benzaldehyde and acetone at 333 K yielding 100% of benzylideneacetone in 2 h. The hydroxylated hydrocalumite-like compound behaves then as an efficient Bronsted-type catalyst whose activity is comparable to that of meixnerite.

Keywords: hydrocalumite, layered double hydroxide, aldolisation, Brønsted catalysts.

1. Introduction

There is an increasing interest for more environmental friendly heterogeneous catalytic processes in the chemical industry. It particularly remains a continuous challenge to find highly active solid Brønsted-type basic catalysts able to perform with good selectivity C-C bond formation, i.e. different types of self- or cross-condensation reactions between aldehydes and ketones for the synthesis of pharmaceutical and fine chemicals [1, 2]. In most of the industrial processes, NaOH and KOH are used as catalysts. However, these homogeneous processes exhibit well known drawbacks, the main ones being separation difficulties, corrosion problems in the equipment and generation of large amounts of wastes. Consequently, in order to overcome the aforementioned disadvantages numerous efforts have been made to prepare new catalytic materials with controlled basic properties in order to increase the process efficiency.

Basic materials ranging from alkaline or alkaline-earth exchanged X zeolites with medium strength, to $Na/NaOH/Al_2O_3$ exhibiting very strong sites, cover a large range of strength [3-5]. Besides, the nature of the basic sites is less easily tailored, though Brønsted sites are known to be highly efficient in condensation reactions [6, 7]. This explains why layered double hydroxides (LDH), also called anionic clays or hydrotalcite-like compounds, have been the most extensively studied materials in the recent years, because they indeed offer the unique possibility to control the nature of the basic sites [1, 2, 8, 9]. Into the LDH family, meixnerite, which contains OH^- as compensating anions in the interlayer space, exhibits outstanding properties of Brønsted-type catalyst able to perform reactions requiring normally strong homogeneous bases such as NaOH [10]. But, meixnerite is difficult to prepare by co-precipitation or anionic exchange. It is likely prepared using a specific property of the Mg/Al LDH which is the memory effect, i.e. the ability to restore the lamellar structure with OH^- groups in the interlayer space by contacting with decarbonated water the Mg(Al)O mixed oxide obtained by thermal decomposition of the precursor Mg/Al LDH [10]. Other LDH structures may give highly basic Brønsted-type catalysts. It is particularly the case of hydrocalumite which belongs to the AFm phases, a group of hydrated compounds found in cement pastes and composed of positively charged main layers $[Ca_2M^{3+}(OH)_6]^+$ and a negatively charged interlayer $[X\cdot nH_2O]^-$ where X^- is a mineral anion [11]. Besides their interest as hydration product of cements, which has induced extensive investigations [12-14], they have been also recently studied as host structures for the intercalation of guest monomers and polymers [15]. In contrast, studies dealing with their use as catalysts are very scarce, in spite of the high potentialities resulting from the close composition of these materials to the highly basic CaO. Therefore, it will be interesting to prepare hydrocalumite-like compounds intercalated with OH^- species able to provide highly basic Bronsted-type solids.

However, the reconstruction method, advantageously used in the case of Mg/Al LDH to prepare the meixnerite-like phases, largely failed in the case of hydrocalumite. Vieille et al. [16] studied the reconstruction of hydrocalumites and they concluded that it is possible only for the samples calcined below 673 K. Nevertheless, the XRD pattern of the reconstructed sample reveals the presence of the initial hydrocalumite and of a residual amorphous phase, indicating that the restoration of the lamellar structure is not complete.

In the existing literature, hydrocalumites are prepared using the coprecipitation of metallic salts at controlled pH method; the hydrocalumites obtained using this method contain as compensation anion Cl^- [16-19] or NO_3^{2-} [19-21]. Therefore, the preparation of OH^--containing hydrocalumite can only be contemplated using a direct method which consists in performing a controlled hydrolysis of Ca^{2+} and Al^{3+} alkoxides.

One step synthesis protocol of OH^--containing hydrocalumite has been investigated in this work. The catalytic properties of the resulting solids have been tested in the aldolisation reaction of benzaldehyde and acetone, so far studied using meixnerite and then chosen for sake of comparison [22-24]. Furthermore, physical and chemical properties of the synthesized materials have been determined using different characterization techniques.

2. Experimental

2.1. Sample preparation

4.42×10^{-3} mol of calcium methoxide ($Ca(OCH_3)_2$) and 2.21×10^{-3} mol of aluminium triethoxide ($Al(OC_2H_5)_3$) (provided by Sigma Aldrich) were simultaneously dissolved in 15 ml of water at room temperature (molar ratio $[Ca^{2+}]/[Al^{3+}] = 2.0$). The mixture was then aged for 18 hours into a beaker at three different temperatures, i.e. 273, 298 and 333 K under vigorous stirring and inert atmosphere in order to avoid contamination with CO_2. The final pH of the solutions was around 13.4. The gel thus obtained was separated by centrifugation and washed several times with distilled water and finally with ethanol. All samples were dried at 343 K for 24 h. They were hereafter noted as HC_x where x is the aging temperature.

2.2. Characterization techniques

X-ray powder diffraction (XRD) patterns were recorded on a Siemens D5000 diffractometer with Bragg-Brentano geometry with nickel-filtered $Cu_{K\alpha}$ radiation (λ=0.1541 nm). Data were collected in the 2Θ range of 4 to 70^0 with an angular step of 0.05^0 at 3 s per step, resulting in a scan rate of $1^0 \cdot min^{-1}$.

N_2 adsorption experiments at 77 K were carried out on samples freshly prepared and previously degassed in vacuum at 523 K (10^{-4} Pa) with a Micromeritics ASAP 2000 instrument. Specific surface area was calculated using the BET method.

Thermogravimetric analysis (TGA) was performed in a Labsys/Setaram TG DTA/DSC thermobalance equipped with a programmable temperature furnace. The sample (150 mg) was heated from room temperature to 1173 K in air (80 cm^3 STP$\cdot min^{-1}$) at 5 $K \cdot min^{-1}$.

DRIFT spectra were recorded using a Bruker-Equinox-55 FTIR spectrometer in the region of 400–4000 cm^{-1} at the resolution of 4 cm^{-1}; the number of scans was equal to 64. The sample, freshly prepared was introduced into the DRIFT cell and dried in a helium stream (10 cm^3 STP·min^{-1}) at 373 K for 1 h. The sample was cooled at room temperature and the spectrum was measured.

2.3. Catalytic test reaction

The reactions were performed in a 100 ml batch reactor equipped with a condenser system, under inert atmosphere, in order to avoid CO_2. For a typical experimental procedure, to a stirred solution of benzaldehyde and acetone (molar ratio acetone/benzaldehyde= 4.4) freshly prepared catalyst (350 mg) was added, and the flask was maintained at 333 K. Samples were taken at regular time periods and analyzed by gas chromatography (GC) using a FID detector and a AG Ultra 2 column (15 m x 0.32 mm x 0.25 µm). Tetradecane was used as internal standard.

3. Results and discussion

3.1. Characterization of the materials

The XRD patterns of the samples are depicted in Figure 1. Well crystallized phases are obtained in all cases, as generally observed in the syntheses of the solids belonging to the AFm family of materials. Moreover, there is a clear influence of the aging temperature on the nature of phases.

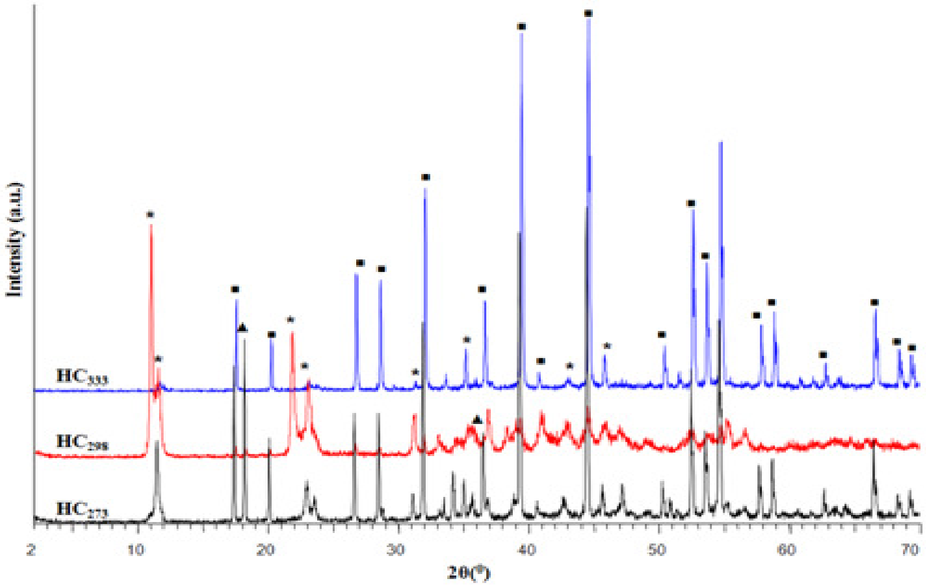

Figure 1. *XRD patterns of HC_{273}, HC_{298} and HC_{333}; (■) corresponds to the basal reflections of the katoite phase; (*) corresponds to the basal reflections of the hydrocalumite phase and (▲) corresponds to the reflections of gibbsite.*

A mixture of gibbsite, hydrocalumite-like phase and Si-free cubic katoite ($Ca_3Al_2(OH)_{12}$) is obtained for HC_{273} synthesized and aged at 273 K. The same mixture of phases was previously observed during hydration of a calcium aluminate cement paste, however after 1 day at 313 K [25]. The presence of different phases observed in HC_{273} sample, can account for a different hydrolysis rate of the Ca and Al alkoxide precursors. XRD pattern typical of layered hydrocalumite-like compound is observed for HC_{298} aged at 298 K. The splitting of the 00*l* peaks reveals the presence of two kinds of intercalated species giving interlayer distances of 0.803 and 0.762 nm, respectively. It is noteworthy that this is a different behavior than that observed for halide-containing Friedel's salts e.g. $[Ca_2Al(OH)_6]^+[Cl_{1-x}Br_x{\cdot}2H_2O]^-$ samples containing also two different compensating anions, i.e. Cl^- and Br^-. They give only one phase with an interlayer distance increasing regularly with the x value [11]. It is indeed a general tendency that anions of same charge and shape give solid solution in AFm phases, while ordering occurs between ions differing in both charge and shape [26]. Besides, the basal spacing 0.762 nm observed for HC_{298} is in close agreement with that of 0.755 nm previously reported for a carbonated hydrocalumite-like material [27]. Accordingly, AFm phases with carbonate show definite range of thermodynamic stability at 293 K [26]. That phase is in minor amount in HC_{298} because it results from the contamination by carbonate from air during preparation. This also reveals the intrinsic high basicity of these materials easily carbonated in the atmosphere. The basal spacing of 0.803 nm could account for the intercalation of alkoxide anions from the precursors. Nevertheless, when one considers the carbon content of 0.67% and the formation of the previous carbonated phase, this disagrees with the concurrent intercalation of alkoxide anions. Therefore, this basal spacing is likely assigned to the presence of intercalated OH^- species. It is in the range of previous results showing interlayer spacing of 0.778-0.783 nm for Friedel's salt (Ca_2Al-Cl) or 0.818 and 0.857 nm for Br^-- and NO_3^--containing AFm phases ($Ca_2Al(OH)_6Br\cdot2H_2O$ and $Ca_2Al(OH)_6NO_3\cdot4H_2O$), respectively [11, 17]. Nevertheless, the interlayer distance in these AFm phases depends on several parameters. It actually decreases above 303 K in the Friedel's salt when a transition from monoclinic to a rhombohedral structure occurs due to the displacement of Cl^- in the interlayer space [28]. It also decreases when nitrated AFm phase is dehydrated because layers are pillared by nitrate groups [29]. It must be underlined that ordering has been also previously reported in AFm phase containing OH^- and CO_3^{2-} anions [26]. Finally, it can be noted that the increase from 0.762 to 0.803 nm in the interlayer distance when going from the CO_3^{2-}- to the OH^--containing hydrocalumite-type phase of HC_{298} is in agreement with the behavior observed in the case of the hydrotalcite with interlayer distances of about 0.750 and 0.810 nm for the carbonated and hydroxylated forms, respectively [30, 31]. Elemental analysis of this sample, which gives 14.8% Al and 44.3% Ca, leads to the expected Ca/Al molar ratio of ~2, in agreement with the presence of hydrocalumite-like phase.

The XRD pattern of HC_{333} reveals the presence of the cubic Si-free katoite phase only. Katoite is a mineral with the structure of garnets, a group of silicate minerals whose structure is a 3D framework built of AlO_6 octahedra and SiO_4 tetrahedra joined by their O atom corners. 8-coordinated Ca atoms are situated in the interstice of this framework [32-34]. Garnets are potential hydrogen reservoirs because it is possible to obtain an hydrogrossular series going from grossular ($Ca_3Al_2(SiO_4)_3$) to katoite

($Ca_3Al_2(OH)_{12}$) by substitution of $(OH)_4$ for all the SiO_4 groups and intermediate partially substituted samples [32-34].

Remarkably, the evolution from a mixture of hydrocalumite-like, katoite and gibbsite phases to pure katoite phase was not observed during hydration in deionized water of a calcium aluminate cement paste at 313 K, but was in contrast observed after 6 days at 298 K in a 65% relative humidity and atmosphere of 5% CO_2. Katoite is actually more resistant to carbonation than Friedel's salts [26]. Therefore, the evolutions observed in function of the temperature for the HC samples prepared in this study from the alkoxide precursors account for the thermodynamically metastability of the phases, besides the progressive carbonation which cannot be easily avoided for these highly basic materials [25, 26].

It is worthy to note that the hydrocalumite phase obtained in this work by hydrolysis of calcium methoxide and aluminium ethoxide at room temperature can be advantageously compared, regarding the synthesis conditions, to the precipitation method described by Vieille et al. [16] using a mixture of calcium and aluminium salts in water and ethanol at 338 K and pH = 11.5. These conditions are obviously softer than those leading to single crystals using a mixture of $Ca(OH)_2$, $Al(OH)_3$ and $CaCO_3$ which involve hydrothermal treatment for 1 month at 393 K at 200 GPa [11, 27]. Similarly, the katoite phase obtained by aging at 333 K a mixture of alkoxides, involves less drastic conditions than those previously described from Al_2O_3 and $CaCO_3$ performed at 773 K and 2.0 GPa [35].

In the hydrated calcium aluminate cements (CAC) the stability of the Friedel's salt is very relevant for practical uses and appears pH-dependant. A mixture containing close amounts of Friedel's salt and katoite was obtained from a paste of water/CAC molar ratio 0.5 and 3% of Cl^- stored at 313 K for 18 days. These results show that alkoxide precursors are very interesting for the formation of the hydrocalumite-like and katoite phases and particularly for the formation of the former in its hydroxylated form.

The thermal behavior of HC_{298} and HC_{333} corresponding respectively to hydrocalumite-like and katoite structures, has been examined performing thermogravimetric analyses in the temperature range from 298 to 1273 K. The TGA curves of both samples exhibit the same general shape (Figure 2). Besides, they are similar to that obtained for the TG experiment carried out on the Friedel's salt [$(Ca_2Al(OH)_6]Cl\cdot 2H_2O$] in a static air atmosphere [16] and only slightly different from that obtained for the binitroaluminate [$(Ca_2Al(OH)_6]NO_3\cdot 2H_2O$] in an experiment carried out in a flux of dry N_2 [29].

HC_{298} and HC_{333} exhibit three mass losses in the temperature range $298 \leq T \leq 513$ K, $513 \leq T \leq 673$ K and $673 \leq T \leq 1273$ K. These mass losses are respectively assigned to dehydration, decomposition of the anions with also dehydroxylation of the layers, and finally concurrent release of water formed by recombination of hydroxyls and decomposition of remaining anions. The corresponding mass losses reach ca. 2, 19 and 7% for HC_{298}. The hydration water content is significantly lower than in the parents Friedel's salt and binitroaluminate where it reaches nearly 12.5% [16]. This accounts for a lower hydration state for HC_{298}. However, it is noticeable that the hydration-rehydration process is highly reversible in the temperature range 298-373 K for the Friedel's salt [16] and then the hydration state can depend on the ambient atmosphere. The second mass loss of ca. 19% in HC_{298} is in the same range than in the Friedel's salt and the binitroaluminate where it reaches ca. 16.4 and 15.5%, respectively, though the different nature of the compensating anions. As largely observed in the hydrotalcites, OH^-, Cl^- and NO_3^- anions due to their different polarizabilities and process of decomposition are removed at different temperatures. This explains that the third mass loss is almost similar in HC_{298} than in the Friedel's salt (8.4%), but significantly higher in the binitroaluminate (18%). Removal of Cl^- or OH^- with concurrent dehydroxylation of the layers occurs in the same temperature range, especially as the experiments on HC_{298} and the Friedel's salt are both achieved in air. In the experiment carried out on the binitroaluminate under N_2, the decomposition of nitrates is greatly delayed due to their intermediate reduction into nitrites. This enhances the third mass loss [29]. The total mass loss of 28% for HC_{298} compares well with that for the Friedel's salt (37.5%) with two water molecules per formula unit, but is lower than that of the binitroaluminate (46%) where, in addition to nitrate anions, four water molecules per formula unit are present.

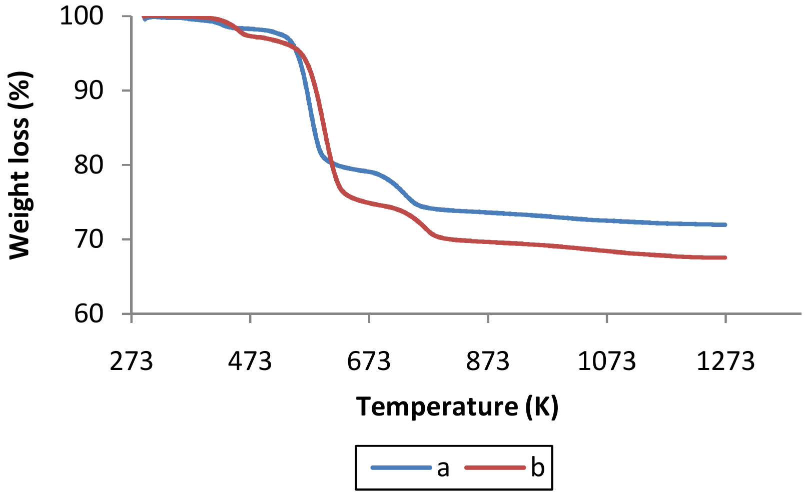

Figure 2. *TGA curve of: (a) HC_{298} and (b) HC_{333} samples.*

The three mass losses of ca. 3, 22 and 6% for HC_{333} must respectively correspond to a dehydration followed by a dehydroxylation occurring in two steps as this material does not contain compensating anions. It is worth noting that the total mass loss of 31% is in agreement with that expected i.e. 28.6% for the dehydroxylation of the katoite ($Ca_3Al_2(OH)_{12}$) to give the corresponding oxide.

The specific surface areas of the AFm phases have been scarcely examined probably because they always give large crystallites obviously leading to low surface areas. HC_{298} exhibits a type IV adsorption isotherm following the classification of Brunauer et al. [36] characteristic of mesoporous materials with a type H3 hysteresis loop attributed to aggregates of plate-like particles leading to slit-shaped pores. The specific surface area of 7.6 $m^2 \cdot g^{-1}$ is consistent with the high crystallinity of the sample (Figure 1).

IR spectrum of the as-prepared HC_{298} sample depicted in figure 3(a) is able to give information on the structure and the composition of this compound.

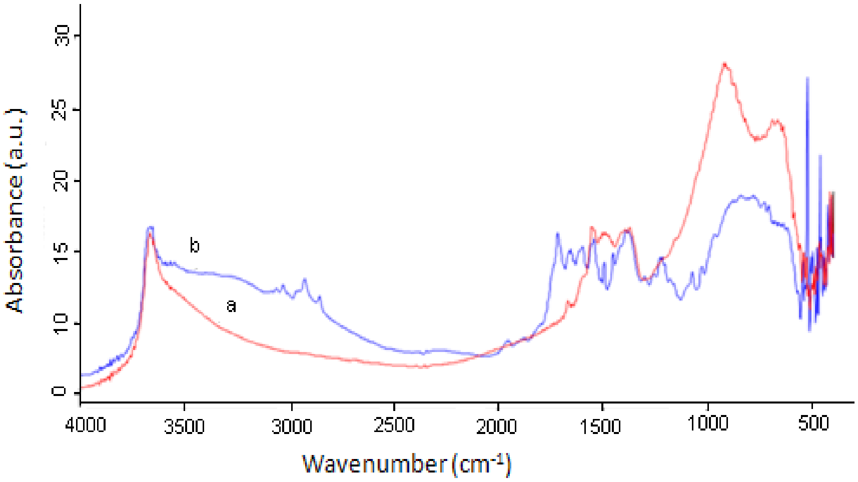

***Figure 3**. IR spectra of HC_{298} before (a) and after catalytic reaction (b).*

The low wavenumber region (< 800 cm^{-1}) normally containing several lattice vibrations characteristic of the hydroxide layer [16] is poorly informative due to the presence of a broad band in the 600-1400 cm^{-1} range giving three distinct maxima at 680, 910 and 1390 cm^{-1} attributed to the bending angular ν_4, the bending non-planar ν_2 and the antisymetrical stretching ν_3 mode of CO_3^{2-} species, respectively [30]. This is in agreement with the presence of a slight amount of CO_3^{2-}-containing hydrocalumite like phase previously detected by XRD. Notwithstanding, the high intensity of the previous bands in HC_{298} suggests that CO_2 is physisorbed on the external faces of the crystallites, though in slight amount, considering the low intensity of the ν_3 mode at 1390 cm^{-1} assigned to adsorbed CO_3^{2-}. As aforementioned, the band corresponding to $\nu_{Ca\text{-}O}$ at 420 cm^{-1} is weak, and the Al-O vibrations giving in Friedel's salt well defined bands around 780, 580 and 530 cm^{-1} [15, 16] are overlapped by the carbonate bands. The broad band extending from 3200 to 3600 cm^{-1} is due to the stretching vibrations of water molecules, also responsible for the bending vibration at 1620 cm^{-1}. They account for the first mass loss in the TG experiment and correspond to hydration water molecules. It is noteworthy that the intensity of this broad absorption band in HC_{298} almost corresponds to that observed in the Friedel's salt heated at 573 K and then highly dehydrated [16]. The hydration-rehydration process in the Friedel's salt is reversible in the temperature range 298-473 K, and irreversible above 473 K [16]. This is in agreement with the low hydration state of HC_{298} previously observed in the TG experiment, with a first mass loss amounting only 2%. Washing with ethanol carried out in the synthesis procedure allows to greatly dehydrate the sample. Then, we can suggest that the broad band centered at 3400 cm^{-1} accounts for the presence of the OH^- compensating anions in the interlayer space.

The sharp band at 3675 cm^{-1} is assigned to the stretching vibration of the hydroxyl groups of the layers.

3.2. Catalytic activity

The condensation reaction of benzaldehyde and acetone has been previously studied using respectively Mg(Al)O mixed oxide and meixnerite (Mg/Al-OH LDH) as catalysts [22-24]. The first step of the reaction is the deprotonation of an acetone molecule to give the enolate anion whose nucleophilic attack on the C=O group of benzaldehyde leads to the β-aldol. This latter is easily dehydrated on weak acid sites and by increasing the reaction temperature benzalacetone is obtained. The reaction is generally performed with a large excess of acetone to reduce side Canizzarro or Tishchenko reactions on benzaldehyde leading to benzyl alcohol or benzoic acid, whereas only weak amounts of self-condensation product of acetone are formed. Tichit et al. [22] carrying out the reaction at 383 K and an acetone/benzaldehyde molar ratio of 15 with Mg(Al)O reached a maximum of activity when 5 wt% of water is added in ethanol used as solvent. Concurrently, the lamellar structure of the catalyst has been restored at the end of the reaction, suggesting that the OH^- compensating anions are active sites for the aldolisation. Accordingly, Rao et al. [23] using previously rehydrated mixed oxides, i.e. meixnerite containing only OH^- anions and carrying out the reaction at 273 K and acetone/benzaldehyde molar ratio of 32, reached an aldol yield of 80% in 3 h. At this low reaction temperature dehydration of the aldol is greatly reduced and benzylideneacetone yield reaches only 5.6%. Besides, Campanati et al. [24] using also meixnerite at higher reaction temperature (318 K) and acetone/benzaldehyde molar ratio of 40, reached almost 50% yield of benzylideneacetone in 2 h.

Though achieved in different experimental conditions, all previous reports clearly establish that the Brønsted-type catalysts, containing OH basic sites are the most efficient for the aldolisation reaction.

The condensation of benzaldehyde and acetone carried out with the as-prepared HC_{298} catalyst at 333 K and acetone/benzaldehyde molar ratio of 4.4 leads to 72% conversion in 1 h and 100% in 2 h with benzylideneacetone as the only product (Figure 4).

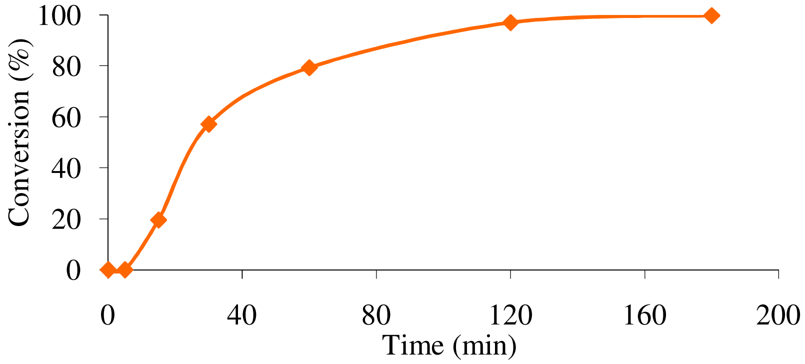

***Figure 4**. Catalytic activity of the HC_{298} sample in the aldolisation of benzaldehyde with acetone.*

After first run HC_{298} was separated from the reaction mixture, washed with water several times and re-used in a second run. No conversion was obtained after two hours of reaction time. Deactivation of the catalyst, moreover exhibiting a yellow color, is probably due to the adsorption of oligomers on the surface of the catalyst during the reaction. This hypothesis was checked doing the IR spectrum of HC_{298} after reaction (Figure 3(b)). A comparison with the spectrum of the as-prepared sample (Figure 3(a)) shows that contrary to this latter, the band at 420 cm^{-1} corresponding to $\nu_{Ca\text{-}O}$ is sharp and intense, and the Al-O vibrations give rise to a broad band in the 550-800 cm^{-1} range. This evolution is mainly due to the removal of the absorbed carbonate species. The sharp bands detected in the 1200-1700 cm^{-1} region and the weak bands localized at 2855 and 2925 cm^{-1} corresponding to the symmetric and antisymmetric stretching vibrations of CH modes can be assigned to oligomeric species adsorbed on the surface. It is noteworthy that the stretching vibration band of the OH^- groups of the layers is still observed at 3675 cm^{-1} showing that the interaction between the layers and the intercalated species is not modified.

In contrast to HC_{298}, HC_{333} is found totally inactive in the condensation of benzaldehyde and acetone. This is in agreement with its 3D structure containing no exchangeable OH^- in contrast to the hydrocalumite-like HC_{298} sample. This also confirms that the aldolisation is catalyzed by the OH^- anions of the hydrocalumite-like structure acting as Brønsted basic sites.

In summary, it is worthy to underline that the as-prepared and slightly carbonated hydrocalumite-like compound HC_{298} is able to catalyze the aldolisation, although meixnerite is more active. However, its preparation involves a more complex procedure with a calcination of the hydrotalcite precursor and rehydration of the obtained Mg(Al)O mixed oxide in liquid or vapor phase, avoiding contact with carbonate of the atmosphere. Further improvement of the catalytic activity of the hydrocalumite-like catalysts will result from the increase of their specific surface areas.

4. Conclusions

Solids belonging to AFm or hydrogrossular families can be obtained by hydrolysis of aluminium triethoxide and calcium methoxide. The nature of phases is thermodynamically controlled, thus hydrocalumite-like compound containing mainly OH^- as compensating anions and katoite are obtained after aging the precipitate at 298 and 333 K, respectively. The former layered material is particularly interesting to achieve catalytic reactions requiring Brønsted-type sites. The hydrocalumite-like compound (HC_{298}) actually leads to 100% yield into benzylideneacetone in 2 h by condensation of benzaldehyde and acetone at 333 K. This behavior compares well with that already found with meixnerite considered as a highly efficient Brønsted-type catalyst. We must emphasize that the preparation procedure of the hydroxylated hydrocalumite-like compound is simpler than that of the meixnerite. Moreover, the hydroxylated hydrocalumite-like sample is catalytically active, though slightly carbonated and exhibiting a low surface area. This reveals the high potentialities of these materials as Brønsted-type catalysts, particularly if surface areas can be greatly improved.

Acknowledgments

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Conclusions of chapter two

In this chapter, catalysts with increased basicity were obtained by intercalation of guest negatively charged M^{n+}-based colloids ($M^{n+} = Ca^{2+}$, Sr^{2+}, Ba^{2+}, La^{3+}) into the host Mg/Al LDHs, which were then used as precursors for mixed oxides. This preparation route takes advantage of the anionic exchange capacity and the ability to expand the interlayer space of the LDH. Good results were obtained in terms of conversions and selectivity when the mixed oxides obtained by thermal decomposition of these precursors were used in highly demanding basic reactions with interest for fine chemistry.

Also, an efficient and simple route for the synthesis of hydrocalumite, a new LDH structure with highly basic Brønsted-sites, was developed.

1. New basic mixed oxides catalysts were obtained when AE cations complexed with Edta and intercalated into Mg/Al LDH were used as precursors. An important feature is that the nature of the AE cations allows to finely control the basicity in order to perform reactions requiring different basic strength. Due to their larger content of strong basic sites, the AE-containing mixed oxides are able to perform the highly demanding isomerization reaction of DB-1.

2. Preformed negatively charged guest La hydroxy citrate colloids were introduced into host Mg/Al LDH structures to give nanocomposites precursors of La/Mg(Al)O(x) mixed oxides with different La loadings. These mixed oxides were found highly active for the transesterification reaction of 1-phenylehtanol with diethylcarbonate (DEC), which is known to be performed by strong basic catalysts. The unsymmetrical carbonate yields increase with the density of strong basic sites of the La-containing mixed oxides.

3. A comparison between several protocols of synthesis for La-containing LDHs was made. The intercalation of La-containing anionic complexes into a host Mg/Al LDH, followed by an ultrasonic disaggregation of the hybrid, allows to create after thermal activation, strong basic sites which are not observed into Mg(Al)O. This probably results from the presence of highly dispersed lanthanum oxide domains into the mixed oxide structure. The catalysts thus obtained are indeed able to perform the double bond migration of olefins, a highly demanding basic reaction.

4. A new synthesis route for hydrocalumite-type materials was developed. The nature of the obtained phases is thermodynamically controlled, thus hydrocalumite-like compound containing mainly OH^- as compensating anions and katoite are obtained after aging the precipitate at 298 and 333 K, respectively. The former layered material is particularly interesting to achieve catalytic reactions requiring Brønsted-type sites leading to 100% yield into benzylideneacetone in 2 h by condensation of benzaldehyde and acetone at 333 K. This behavior compares well with that already found with meixnerite considered as a highly efficient Brønsted-type catalyst. We must emphasize that the preparation procedure of the hydroxylated hydrocalumite-like compound is simpler than that of the meixnerite.

Chapter three

New short aliphatic chain ionic liquids: synthesis thermodynamics and catalytic activity in aldol condensation reactions.

3.1. Introduction

It is a continuous challenge to find new catalysts able to perform with good activities and selectivity condensation reactions for the synthesis of pharmaceutical and fine chemicals. In the last years room temperature ionic liquids (ILs) have received a lot of interest as environmental friendly or “green” alternatives to conventional molecular solvents. They differ from molecular solvents by their unique ionic character and their “structure and organization” which can lead to specific effects [1].

Room-temperature ILs have been used as clean solvents and catalysts for green chemistry, stabilizing agents for the catalysts or intermediates, electrolytes for batteries, in photochemistry and electrosynthesis etc [2-6]. Their success as environmental benign solvents or catalysts is described in numerous reactions [7-11], such as Diels-Alder reactions [12, 13], the Friedel-Crafts reaction [14-17], esterification [18-20], cracking rections [21], and so on.

3.2. Definition of ILs

ILs are defined as those ionic salts which have a melting point below 100^0C and are formed by positive and negative ions. There are many synonyms used in the literature for ILs, from which “molten salts” is the most common and most broadly applied term for ionic compounds in liquid state. The term of molten salts refers to high-temperature, viscous and highly corrosive media while an IL is a material fluid at ambient temperature, has a low viscosity and is easily handled [2]. There are also some fundamental features of ILs, such as strong ion-ion interactions that are not often seen in molten salts [22].

The link between ionic ILs and green chemistry is related to the solvent properties of ILs. Some of the properties that make ILs attractive media for catalysis are:

- they have no significant vapour pressure and thus create no volatile organic pollution during manipulation,

- ILs have good chemical and thermal stability, most ILs having liquid ranges for more than 300^0C,
- they are immiscible with some organic solvents and therefore can be used in two-phase systems,
- ILs polarity can be adjusted by a suitable choice of cation/anion,
- they are able to dissolve a wide range of organic, inorganic and organometallic compounds,
- ILs are often composed of weakly coordinating anions and therefore have the potential to be highly polar.

3.3. History of ILs

The first documented observation of ILs dates from the mild-19th century and refers to the so-called “red-oil” formed during Friedel-Crafts reactions. The structure of the red oil was identified as a salt having a cation that was the long-presumed stable intermediate in Friedel-Crafts reactions called the sigma complex [22].

In the early 20th century, simple alkylammonium nitrates were found to be liquids; for example ethylammonium nitrate which has a melting temperature of 12^0C would be considered IL if discovered today [22]. In the 1960s it was found that mixtures of copper (I) chloride and alkylammonium chlorides, for example triethylammonium chloride (Et_3NHCl), form a liquid at room temperature when mixed together [23].

In the 1970s the compounds known as liquids clathrates, today recognized as ILs, were discovered and characterized. Liquid clathrates are composed of a salt combined with an aluminium alkyl and they have been patented and used in coal liquefaction and petroleum recovery from tar sands [24].

The salts that were the transition between high temperature molten salts (like cryolite or LiCl-KCl) and the present ILs were the inorganic chloroaluminates (like sodium chloride-aluminium chloride eutectic) [22]. The alkali chloride-aluminium chloride system was applied as electrolyte for thermal batteries, but still the melting temperature was quite high (175^0C). In 1968 were assembled cells with aluminium and chlorine electrodes with various molten salt electrolytes, including a 1:2 ethylpyridinium bromide-$AlCl_3$ mixture [25].

The modern era of ILs started with the discovery and development of the 1-butylpyridinium chloride-aluminium chloride mixture (BPC-$AlCl_3$) [26, 27]. This new IL had two major drawbacks: first, the melting temperature of the equimolar composition is 40^0C, so it is not a room-temperature liquid at the composition that has the highest conductivity and secondly, in the basic compositions ($AlCl_3$ mole fraction < 0.5) the buthylpyridinium cation is easily reduced [22]. In the search for a salt with even lower melting temperatures new ILs made from a series of dialkylimidazolium chlorides with varying lengths of alkyl substituents were developed [28, 29]. For these new ILs measurements of phase transitions, densities, viscosities and conductivities were performed.

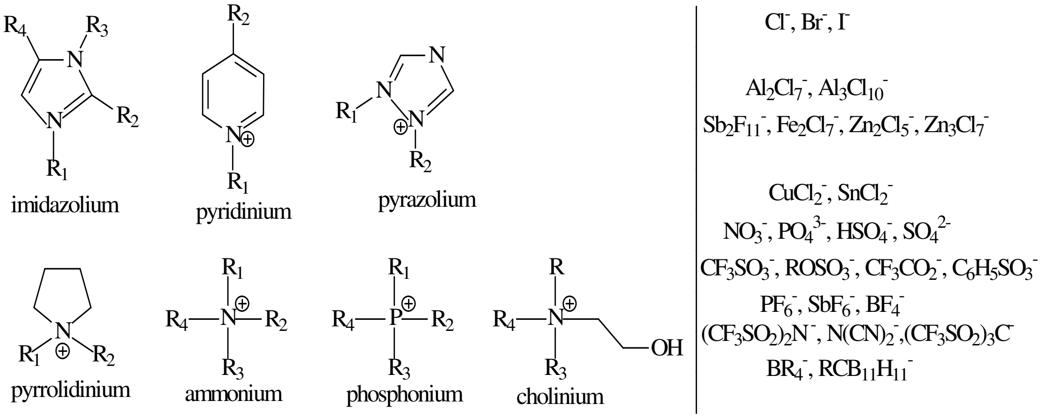
The pyridinium- and the imidazolium-based chloroaluminate ILs have a main disadvantage: they react with water giving as reaction product HCl, which means they can be handled only in a moisture free atmosphere. In order to overcome this disadvantage, in the 1990s new tetrafluoroborate, hexafluorophosphate, nitrate, sulfate, and acetate salts were prepared by metathesis reactions of the dialkylimidazolium halide with the appropriate silver salt. At room temperature, these new ILs were stable towards hydrolysis [30]. Around 1992 a large number of ILs were synthesized from the dialkylimidazolium and trialkylimidazolium cations combined with water stable anions mentioned above [31, 32].

During the last 20 years a numerous new ILs have been developed and applied as alternative reaction media [2, 7, 12] to conventional solvents and also as selective catalysts for different reactions [33-37]. The main drawback of using ILs in homogeneous catalysis is the separation and recycling of the catalyst. The solution to this problem is the heterogenisation of ILs on solid supports. Immobilization and supporting of ILs can be achieved by simple impregnation, covalent linking of the cation or the anion, polymerization etc [38-41]. Compared to ILs in homogeneous phase, immobilized ILs facilitate the recovery and re-use of the catalyst.

In the recent years several reports describe the immobilization of ILs by adsorption or grafting onto silica surface and their use as catalysts for reactions like Friedel-Crafts acylation [42], hydrogenation [43] and hydroformilation [44]. Organic polymers [37], natural polymers [44] and zeolites [46] have been also used as supports for ILs.

3.4. Types of ILs

The number of ILs has increased exponentially in the recent years. Many of them are based on the imidazolium cation and in a lesser proportion, alkyl pyridiniums and trialkylamines (Scheme 1). By changing the anion or the alkyl chain of the cation, a wide variety of ILs may be designed for specific applications. They can be of hydrophobic or hydrophilic nature depending on the chemical structures involved.



Scheme 1 *Main cations and anions described in literature [1].*

ILs can be divided into two broad categories:

- aprotic ionic liquids (AILs)
- protic ionic liquids (PILs).

AILs largely dominate the open literature due to their inertness relative to organometallic compounds and their potential of applications, particularly in catalysis. They are synthesized by transferring an alkyl group to the basic nitrogen site through S_N2 reactions [1].

PILs are formed through proton transfer from a Brønsted acid to a Brønsted base. Recently there has been an increasing interest in PILs due to their greater potential as environmental friendly solvents and promising applications. Moreover, they present the advantage of being cost-effective and easily prepared as their formation does not involve the formation of residual by-products. A specific feature of the PILs is that they are capable of developing a certain hydrogen bonding potency, including proton acceptance and proton donation and they are highly tolerant to hydroxylic media [47-49].

The application of new policies on terms of environment, health and safety deals towards minimizing or substituting organic volatile solvents by green alternatives, placing a renewed emphasis on research and development of lesser harmful compounds as ILs. On the other hand, recently has increased the interest in the use of PILs to tailor the water properties for cleaning applications in processes of minimization of CO_2/SO_2 emissions [50-52].

In the last years numerous studies report the use of ILs as selective catalysts for different reactions, as for aldol condensation reactions where several ILs have been successfully applied as homogeneous and heterogeneous catalysts [36, 53, 54, 55]. Abelló et al. [53] described the use of choline hydroxide as basic catalyst for adol condensation reactions between several ketones and aldehydes. Better conversions and selectivities were obtained when compared to other well known catalysts, such as rehydrated hydrotalcites, MgO and NaOH. In addition, higher performance was obtained when choline was immobilized on MgO.

Zhu et al. [36] described the use of 1,1,3,3-tetramethylguanidine lactate ([TMG] [Lac]) as recyclable catalyst for direct aldol condensation reactions at room temperature without any solvent. It was demonstrated that for each reaction only the aldol adduct was produced when the molar ratio of the IL and substrate was smaller than 1. Moreover after the reaction the IL was easily recovered and recycled without considerably decrease of activity.

Kryshtal et al. [54] described the application of tetraalkylammonium and 1,3-dialkylimidazolium perfluoro-borates and perfluoro-phosphates as recoverable phase-transfer catalysts in multiphase reactions of CH-acids, in particular in solid base-promoted cross-aldol condensations. The catalysts retained their catalytic activity over several reaction cycles.

In the study of Lombardo et al. [55] two onium ion-tagged prolines, imidazolium bis(trifluoromethylsulfonyl)imide-substituted proline and butyldimethylammonium bis(trifluoromethylsulfonyl) imide-substituted proline, were synthesized and their catalytic activity in the direct asymmetric aldol condensation was studied in ILs. The catalytic protocol developed by this group makes use of a 6-fold lower amount of catalyst with respect to the preceding reports [56, 57] and affords greater chemical yields and higher enantioselectivity.

Objectives of chapter three

The main objective of this chapter is to develop and study the applications of a new family of ILs based on substituted amine cations of the form R_XNH (X is the number of alkyl substitutions) combined with organic anions of the form $R'COO^-$ (being of different nature R and R'). The variations in the anion alkyl chain, in conjunction with different cations, lead to a large matrix of materials.

This kind of compounds show interesting properties for industrial use of ILs: low cost of preparation, simple synthesis and purification methods. Moreover, the very low toxicity and the degradability of this kind of ILs have been verified. Thus, sustainable processes can be originated with their use.

In order to determine the catalytic activity of the ILs several condensation reactions of carbonyl compounds were carried out. The products obtained from these reactions are applied in pharmacological and flavor and fragrance industry.

The first part (art. 7) of the present work deals with the synthesis, FT-infrared identification and thermodynamic characterization of different components. In order to obtain information related to internal organization (and data of industrial interest) density, ultrasonic velocity and ionic conductivity, were measured at a wide range of temperature (278.15 - 338.15 K). In the first paper we study the synthesis and characterization of 2-hydroxy ethylammonium formate (2-HEAF), 2-hydroxy diethylammonium formate (2-HDEAF) and 2-hydroxy triethylammonium formate (2-HTEAF). The studied ILs in terms of catalytic effect were 2-hydroxy ethylammonium formate (2-HEAF), 2-hydroxy diethylammonium formate (2-HDEAF), 2-hydroxy triethylammonium formate (2-HTEAF), 2-hydroxy ethylammonium acetate (2-HEAA), 2-hydroxy diethylammonium formate (2-HDEAA), 2-hydroxy triethylammonium acetate (2-HTEAA), 2-hydroxy ethylammonium propionate (2-HEAP), 2-hydroxy diethylammonium propionate (2-HDEAP) and 2-hydroxy triethylammonium propionate (2-HTEAP). Attending to the high melting point of 2-hydroxy triethylammonium formate (2-HTEAF), no experimental study was possible to develop.

In the second part (art. 8) of this work we study the physicochemical properties of a new serie of PILs and showed their catalytic potential. In order to obtain information related to internal organization and data of industrial interest, density, ultrasonic velocity, ionic conductivity, refractive index, viscosity and surface tension, are measured in a wide range of temperature of the following PILs: 2-hydroxy ethylammonium pentanoate (2-HEAPE), 2-hydroxy diethylammonium pentanoate (2-HDEAPE) and 2-hydroxy triethylammonium pentanoate (2-HTEAPE). We also describe the catalytic activity and recycling of 6 different PILs of the same family into a serie of aldol condensation processes.

In the third part of the work (art. 9) we describe the immobilization on alanine of the ILs studied in the previous two articles. Alanine was chosen as support because it’s a cheap, commercially available aminoacid able to form covalent bonds with the studied ILs. The catalytic activity of the alanine-supported ILs (a-ILs) is tested in the same reactions as the free ILs.

References of chapter three

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Scientific article (Art. 7)

New Short Aliphatic Chain Ionic Liquids: Synthesis, Thermodynamics and Catalytic Activity in Aldol Condensations

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New Short Aliphatic Chain Ionic Liquids: Synthesis, Thermodynamics and Catalytic Activity in Aldol Condensations

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Abstract

This paper reports on the synthesis of new short aliphatic chain ionic liquids and the study of the temperature dependence of density, ultrasonic velocities and ionic conductivity at the range 278.15 – 338.15 K. FT-IR spectra establishes their simple ionic salt structure. Due to their polarity, the ionic liquids are able to dissolve polar solvents and inorganic salts, all of them showing high tolerance into hydroxylic media. The observed temperature trend of the studied properties points out the special packing of these ionic liquids, as well as, the strong influence of the steric hindrance among linear aliphatic residues enclosed into anions and cations. One of them showed a very high melting temperature. A collection of slight basic ionic liquid was used to test their catalytic activity in several aldol condensation reactions of some carbonyl compounds. The best conversions and selectivity were obtained using single ionic liquids, no synergetic effects being observed when different concentrations of mixed ionic liquids were used as catalysts. At any case, the ionic liquid can also easily be recycled from reaction media and then it suggests a promising way of process design for this kind of reactions.

Keywords: ionic liquid; density; ultrasonic velocities; ionic conductivity; aldol condensation, catalysis

1. Introduction

Ionic liquids (ILs) are versatile new media for many chemical synthesis, enzymatic catalysis and green engineering processes [1]. They can be of hydrophobic or hydrophilic nature depending on the structure of the ions. In fact, the ILs consist solely of a collection of positive and negative ions. However, unlike conventional molten salts, these materials often melt at low temperature. This is achieved due to the incorporation of the bulky functional structures as anion and/or cation and the structure avoids the ions packing easily into an ordered electrostatic net structure and, then, solid phase at ambient conditions. ILs can be used as solvents due to their low melting point; and because of their ionic structure when ILs are used as solvents better selectivity is obtained when compared with other conventional organic solvents. In the last few years, room-temperature ILs have been also used as clean solvents and catalysts for green chemistry, as electrolytes for batteries, in photochemistry and electrosynthesis. Their potential interest rises from the necessities of cleaner processes and stronger environmental policies that will be applied. They have no significant vapour pressure and thus create no volatile organic pollution during manipulation of industrial operation. They also allow an easy separation of organic molecules by direct distillation without loss of the IL. Their liquid range can be as large as 300^0C allowing for large reaction kinetic control, which, coupled with their good solvent properties, allows minimization of reactor design. Salts based upon poor nucleophilic anions such as $[BF_4]^-$, $[PF_6]^-$, $[CF_3CO_2]^-$, $[CF_3SO_3]^-$, etc, are insensitive to water and air and possess remarkably high thermal stability. Until now, many of these materials are based on the imidazolium cation and in a lesser proportion, alkyl pyridiniums and trialkylamines. By changing the anion or the alkyl chain of the cation, a wide variation in properties such as hydrophobicity, viscosity, density and solvation power can be obtained and then a tailored-made IL may be designed for specific industrial applications. Although there have been done many studies concerning their thermodynamics, little is yet known about the possibilities of new structures (so-called IL chemical families), as well as mixing ILs thermodynamics. In what is referred to reaction media, in the last few years, ILs have been the subject of considerable interest in the context of green synthesis because of their wide acceptability as alternative reaction media [2, 3] and have been found to act as selective catalysts for different reactions.

With this fact in mind, and as a continuation of a wider project to develop and study the applications of new ILs [4, 5] the first part of the present work deals with the synthesis, FT-infrared identification and thermodynamic characterization of different components of a new family of ILs based on short organic chain acid and base (substituted amine) neutralization. This kind of compounds show interesting properties for industrial use of ILs: low cost of preparation, simple synthesis and purification methods. Besides, in order to obtain information related to internal organization (and data of industrial interest) density, ultrasonic velocity and ionic conductivity, were measured at a wide range of temperature (278.15 - 338.15 K). In this paper we have studied the synthesis and characterization of 2-hydroxy ethylammonium formate (2-HEAF), 2-hydroxy diethylammonium formate (2-HDEAF) and 2-hydroxy triethylammonium formate (2-HTEAF). As far as we know, open literature doesn't show publications related with these new ILs except to 2-HEAF which was synthesized by Bicak [6], and moreover no information about their thermodynamic characterization, phase behaviour, mixing trend or temperature dependence is available until now. The observed inverse dependence on temperature of density and ultrasonic velocity for these ILs points out the special trend of packing and the strong dependence on ion kinetics. The rising values of ionic conductivity versus temperature may be also ascribed to faster mobility of ions. The observed values are surprisingly lower than expected due to the strong influence of steric hindrance of aliphatic residues into ions during mixing process. For 2-HDEAF, only the range 323.15-338.15 K was studied due to its high value of melting point.

On the other hand, it is a continuous challenge to find new catalysts able to perform with good activities and selectivity condensation reactions for the synthesis of pharmaceutical and fine chemicals [7]. In the commercial production processes of the selected aldol condensations, NaOH and KOH are used as homogeneous catalysts [8]; however this kind of catalyst have numerous disadvantages as: loss of catalyst due to the separation difficulties, corrosion problems in the equipment and generation of large amounts of residues. Recently, because of the industrial importance of the process there is an interest in substituting conventional bases in homogeneous phase by heterogeneous catalysts such as alkali oxides, basic alumina and calcined hydrotalcites [9]. ILs have attracted growing interest in catalysis due to their physical and chemical properties. Recently, it was described [7] a new basic catalyst based on an IL (choline hydroxide).

In this study we describe the catalytic activity of a new family of ILs, which is characterized by a short aliphatic chain structure for the anion and different substitution for the cation. The studied ILs in terms of catalytic effect were 2-hydroxy ethylammonium formate (2-HEAF), 2-hydroxy diethylammonium formate (2-HDEAF), 2-hydroxy triethylammonium formate (2-HTEAF), 2-hydroxy ethylammonium acetate (2-HEAA), 2-hydroxy diethylammonium formate (2-HDEAA), 2-hydroxy triethylammonium acetate (2-HTEAA), 2-hydroxy ethylammonium propionate (2-HEAP), 2-hydroxy diethylammonium propionate (2-HDEAP) and 2-hydroxy triethylammonium propionate (2-HTEAP). Attending to the high melting point of 2-hydroxy triethylammonium formate (2-HTEAF), no experimental study was possible to develop. Those ILs which are not enclosed into this paper have been studied earlier [5].

In order to determine the catalytic activity of the ILs several condensation reactions of some carbonyl compounds were carried out. The products obtained from these reactions are applied in pharmacological and flavour and fragrance industry.

2. Experimental

2.1. Materials and equipment

During the course of the experiments, the purity of ILs was monitored by density and ultrasonic velocity measurements. The pure ILs were stored in sun light protected form, constant humidity and low temperature. Usual manipulation and purification in our experimental works was applied [10]. The molar mass and experimental results at standard condition for the ILs are shown in Table 1.

***Table 1** Experimental data for pure ionic liquids at 298.15 K and other relevant information*[a]

IL	Molecular Weight ($g\cdot mol^{-1}$)	Exp. Density ($g\cdot cm^{-3}$)	Exp. Ultrasonic Velocity (ms^{-1})	Exp. Conductivity ($\mu S\cdot cm^{-1}$)
2-HEAF	107.11	1.176489	1709.00	4197.6
2-HDEAF	157.17	1.194041	1798.54	973.17
2-HTEAF[b]	195.22	1.221864	1884.60	1843.38

[a] *Other experimental data for comparison are not available from the literature.*
[b] *323.15 K*

The densities and ultrasonic velocities of pure components were measured with an Anton Paar DSA-5000 vibrational tube densimeter and sound analyzer, with a resolution of 10^{-5} $g\cdot cm^{-3}$ and 1 ms^{-1}. Apparatus calibration was performed periodically in accordance with provider’s instructions using a double reference (Millipore quality water and ambient air at each temperature). Accuracy in the temperature of measurement was better than $\pm 10^{-2}$ K by means of a temperature control device that applied the Peltier principle to maintain isothermal conditions during the measurements.

The ion conductivity was measured by a Jenway Model 4150 Conductivity/TDS Meter with resolution of 0.01 μS to 1 mS and accuracy of ± 0.5% at the range temperature. The accuracy of temperature into the measurement cell was ± 0.5°C.

2.2. Preparation of the ILs

The amine compounds (monoethanolamine, diethanolamine or triethanolamine, Merck Synthesis, better than 99%) were placed in a threenecked flask all-made-in-glass equipped with a reflux condenser, a PT-100 temperature sensor for controlling temperature and a dropping funnel. The flask was mounted in a thermal bath. A slight heating is necessary for increasing miscibility between reactants and then allow reaction. The formic acid (Merck Synthesis, better than 99%) was added drop wise to the flask under stirring with a magnetic bar. Stirring was continued for 24 h at laboratory temperature, in order to obtain a final viscous liquid. Lower viscosity was observed in the final product by decreasing molecular weight of reactants. No solid crystals or precipitation was noticed when the liquid sample was purified or stored at freeze temperature for a few months after synthesis. The reaction is a simple acid–base neutralization creating the acetate or propionate salt of mono, di or tri ethanolamine, that in a general form should be expressed as follows:

$$(\mathrm{HOCH_2CH_2})_X\mathrm{NH}_Y + \mathrm{HOOCH} \rightarrow (\mathrm{HOCH_2CH_2})_X\mathrm{NH}^+_{Y+1}(^-\mathrm{OOCH})$$

where *x* is the number of ethanol substitutions into the amine compound, and *y* is the number of protons ($x + y = 3$). For example, when $x = 1$, $y = 2$, this equation shows the chemical reaction for the reactants monoethanolamine + formic acid, with 2-HEAF as neutralization product.

Because these chemical reactions are highly exothermic, an adequate control of temperature is essential throughout the chemical reaction; otherwise heat evolution may produce the dehydration of the salt to the corresponding amide, as in the case for nylon salts (salts of diamines with dicarboxy acids).

As observed in our laboratory during IL synthesis, dehydration begins around 423.15 K for the lightest ILs. The color varied in each case from transparent to dark yellow when the reaction process and purification (strong agitation and slight heating for the vaporization of residual nonreacted acid for at least for 24 h) were completed. 2-HTEAF shows a solid phase at room temperature, having a melting point of 321.15 K; for this reason, thermodynamical studies were carried out at 323.15-338.15 K for this IL.

2.3. Spectroscopy Test

An FT-IR spectrum was taken by a Jasco FT/IR 680 plus model IR spectrometer, using a NaCl disk. The broad band in the 3500-2400 cm^{-1} range exhibits a characteristic ammonium structure for all the neutralization products. The OH stretching vibration is embedded in this band. The broad band centered at 1600 cm^{-1} is a combined band of the carbonyl stretching and N-H plane bending vibrations. For example, Figure 1 shows the FT-IR spectrum corresponding to the neutralization product of 2-HEAA, which shows two characteristic bands at 3500-2400 cm^{-1} for NH_3^+ + OH^- and another wide band at 1600 cm^{-1} for COO^- + N-H plane bend.

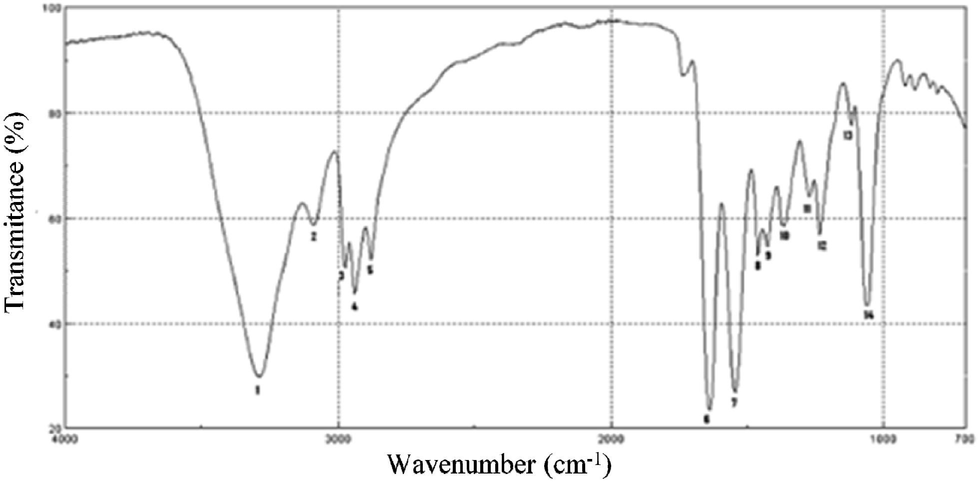


Figure 1. *FTIR spectra for 2-HDEAF.*

2.4. Catalytic Test

The reactions were performed in liquid phase using a 100 ml batch reactor equipped with a condenser system, under argon atmosphere, in order to avoid CO_2. To a stirred solution of substrate and ketone (ratio ketone / substrate = 4.4) was added 1 g of IL, and the flask was maintained at 333 K using a water bath. Samples were taken at regular time periods and analyzed by gas chromatography using a flame ionization detector and an AG Ultra 2 column (15 m x 0.32 mm x 0.25 μm). Tetradecane was used as the internal standard. Reagents were purchase from Aldrich and used without further purification.

2.5. Thermodynamic Data Treatment

For compact and smooth representation, the measured magnitudes of the ILs were correlated as a function of temperature in accordance to eq 1:

$$P = \sum_{i=0}^{N} A_i T^i \tag{1}$$

where P is density ($g \cdot cm^{-3}$), ultrasonic velocity (ms^{-1}), or ionic conductivity ($\mu S \cdot cm^{-1}$), A_i represents fitting parameters, and T is the absolute temperature. N stands for the extension of the mathematical series. The fitting parameters were obtained by the unweighted least-squared method applying a fitting Marquardt algorithm. The root-mean-square deviations were computed using eq 2, where z is the value of the property, and n_{DAT} is the number of experimental data:

$$\sigma = \left(\frac{\sum_{i=1}^{n_{DAT}} \left(z_{exp} - z_{pred} \right)^2}{n_{DAT}} \right)^{1/2} \tag{2}$$

Densities and ultrasonic velocities are given in Table 2, and ionic conductivity is given in Table 3. The fitting parameters and the corresponding deviations are gathered in Table 4, which were computed as explained above. In Figures 2-4, the temperature trends of these magnitudes are gathered. These figures show a decreasing trend in the packing efficiency of the ILs as the molecular weight rises. This tendency results in a continuous diminution of density and ultrasonic velocity versus temperature in each case. In Figure 4, the ionic conductivity of the ILs is enclosed, where a rising trend for higher temperatures could be observed. This fact may be ascribed to the increasing mobility of ions for rising temperatures.

TABLE 2: Densities (ρ), Ultrasonic Velocity (u), Isentropic Compressibilities (κ_S), and Isobaric Expansibilities (α) at 278.15−338.15 K

T (K)	ρ (g cm^{-3})	u (m s^{-1})	κ_S (T Pa^{-1})	$10^3\cdot\alpha$ (K^{-1})	T (K)	ρ (g cm^{-3})	u (m s^{-1})	κ_S (T Pa^{-1})	$10^3\cdot\alpha$ (K^{-}
2-Hydroxy Ethylammonium Formate (2-HEAF)									
338.15	1.148091	1613.59	334.53	0.6188	321.15	1.160154	1653.63	315.22	0.6124
337.90	1.148254	1614.14	334.26	0.6187	320.91	1.160330	1654.22	314.94	0.6124
337.66	1.148433	1614.71	333.97	0.6186	320.66	1.160509	1654.81	314.67	0.6123
337.40	1.148608	1615.30	333.67	0.6185	320.40	1.160688	1655.41	314.39	0.6122
337.15	1.148785	1615.87	333.39	0.6184	320.15	1.160863	1656.01	314.12	0.6121
336.91	1.148963	1616.46	333.09	0.6183	319.90	1.161042	1656.60	313.85	0.6120
336.66	1.149139	1617.04	332.80	0.6182	319.65	1.161218	1657.19	313.58	0.6119
336.41	1.149316	1617.63	332.51	0.6182	319.40	1.161398	1657.79	313.30	0.6118
336.16	1.149494	1618.22	332.21	0.6181	319.15	1.161574	1658.39	313.03	0.6117
335.90	1.149669	1618.81	331.92	0.6180	318.91	1.161750	1658.98	312.76	0.6116
335.65	1.149848	1619.38	331.64	0.6179	318.65	1.161930	1659.58	312.48	0.6115
335.40	1.150027	1619.96	331.35	0.6178	318.40	1.162110	1660.18	312.21	0.6114
335.16	1.150205	1620.55	331.05	0.6177	318.16	1.162286	1660.78	311.93	0.6113
334.90	1.150384	1621.13	330.77	0.6176	317.90	1.162462	1661.37	311.67	0.6112
334.66	1.150560	1621.71	330.48	0.6175	317.65	1.162643	1661.97	311.39	0.6111
334.40	1.150740	1622.30	330.19	0.6174	317.41	1.162820	1662.56	311.12	0.6110
334.16	1.150916	1622.89	329.90	0.6173	317.15	1.162998	1663.16	310.85	0.6109
333.90	1.151094	1623.48	329.61	0.6173	316.91	1.163174	1663.75	310.58	0.6108
333.65	1.151271	1624.06	329.32	0.6172	316.65	1.163352	1664.35	310.31	0.6107
333.41	1.151449	1624.64	329.03	0.6171	316.41	1.163529	1664.95	310.04	0.6106
333.16	1.151625	1625.23	328.75	0.6170	316.15	1.163706	1665.55	309.77	0.6105
332.90	1.151804	1625.82	328.46	0.6169	315.90	1.163885	1666.15	309.50	0.6104
332.65	1.151981	1626.41	328.17	0.6168	315.65	1.164062	1666.74	309.23	0.6103
332.41	1.152159	1626.99	327.88	0.6167	315.40	1.164240	1667.34	308.96	0.6102
332.15	1.152338	1627.58	327.59	0.6166	315.15	1.164417	1667.94	308.70	0.6101
331.90	1.152514	1628.16	327.31	0.6165	314.90	1.164597	1668.54	308.43	0.6100
331.65	1.152694	1628.75	327.02	0.6164	314.65	1.164774	1669.14	308.16	0.6099
331.40	1.152871	1629.34	326.74	0.6163	314.40	1.164951	1669.73	307.89	0.6098
331.16	1.153048	1629.93	326.45	0.6162	314.15	1.165128	1670.33	307.63	0.6097
330.90	1.153225	1630.52	326.16	0.6162	313.90	1.165305	1670.94	307.35	0.6096
330.65	1.153405	1631.11	325.88	0.6161	313.65	1.165485	1671.54	307.09	0.6095
330.41	1.153582	1631.69	325.59	0.6160	313.40	1.165661	1672.13	306.82	0.6094
330.15	1.153761	1632.29	325.30	0.6159	313.15	1.165839	1672.72	306.56	0.6093
329.90	1.153939	1632.88	325.02	0.6158	312.90	1.166018	1673.34	306.29	0.6092
329.65	1.154114	1633.47	324.73	0.6157	312.65	1.166194	1673.94	306.02	0.6091
329.41	1.154294	1634.06	324.45	0.6156	312.40	1.166372	1674.54	305.75	0.6090
329.15	1.154469	1634.65	324.17	0.6155	312.15	1.166549	1675.14	305.49	0.6089
328.91	1.154648	1635.24	323.88	0.6154	311.90	1.166726	1675.74	305.22	0.6088
328.65	1.154826	1635.84	323.59	0.6153	311.65	1.166903	1676.34	304.96	0.6086
328.40	1.155003	1636.43	323.31	0.6152	311.40	1.167085	1676.95	304.69	0.6085
328.15	1.155181	1637.02	323.03	0.6151	311.15	1.167260	1677.55	304.43	0.6084
327.90	1.155360	1637.61	322.75	0.6150	310.90	1.167437	1678.14	304.17	0.6083
327.66	1.155535	1638.20	322.47	0.6149	310.65	1.167617	1678.74	303.90	0.6082
327.40	1.155713	1638.79	322.18	0.6148	310.40	1.167794	1679.35	303.63	0.6081
327.16	1.155890	1639.38	321.90	0.6148	310.15	1.167970	1679.94	303.38	0.6080
326.91	1.156069	1639.97	321.62	0.6147	309.90	1.168149	1680.55	303.11	0.6079
326.66	1.156247	1640.57	321.34	0.6146	309.65	1.168325	1681.15	302.85	0.6078
326.41	1.156426	1641.16	321.06	0.6145	309.40	1.168502	1681.75	302.59	0.6077
326.16	1.156603	1641.75	320.78	0.6144	309.15	1.168680	1682.35	302.32	0.6076
325.91	1.156780	1642.34	320.50	0.6143	308.90	1.168859	1682.96	302.06	0.6075
325.65	1.156957	1642.94	320.21	0.6142	308.65	1.169036	1683.55	301.80	0.6074
325.40	1.157136	1643.53	319.93	0.6141	308.40	1.169213	1684.16	301.54	0.6073
325.16	1.157314	1644.12	319.66	0.6140	308.15	1.169391	1684.76	301.28	0.6072
324.90	1.157490	1644.72	319.37	0.6139	307.90	1.169567	1685.36	301.02	0.6071
324.65	1.157669	1645.32	319.09	0.6138	307.65	1.169742	1685.96	300.76	0.6070
324.40	1.157846	1645.91	318.81	0.6137	307.40	1.169922	1686.56	300.50	0.6069
324.15	1.158023	1646.50	318.54	0.6136	307.15	1.170102	1687.17	300.23	0.6068
323.90	1.158201	1647.09	318.26	0.6135	306.90	1.170276	1687.77	299.98	0.6067
323.65	1.158378	1647.68	317.98	0.6134	306.65	1.170454	1688.37	299.72	0.6066
323.40	1.158556	1648.28	317.70	0.6133	306.40	1.170632	1688.98	299.45	0.6065
323.15	1.158734	1648.90	317.42	0.6132	306.15	1.170810	1689.58	299.20	0.6064
322.90	1.158910	1649.47	317.15	0.6131	305.90	1.170986	1690.18	298.94	0.6063
322.66	1.159088	1650.06	316.87	0.6130	305.65	1.171165	1690.79	298.68	0.6062
322.41	1.159265	1650.66	316.59	0.6129	305.40	1.171343	1691.39	298.42	0.6060
322.16	1.159442	1651.25	316.32	0.6128	305.15	1.171518	1691.99	298.16	0.6059
321.91	1.159620	1651.85	316.04	0.6127	304.90	1.171699	1692.60	297.90	0.6058
321.65	1.159797	1652.43	315.77	0.6126	304.65	1.171876	1693.20	297.65	0.6057
321.40	1.159976	1653.03	315.49	0.6125	304.40	1.172053	1693.80	297.39	0.6056

TABLE 2 (Continued)

T (K)	ρ (g cm^{-3})	u (m s^{-1})	κ_S (T Pa^{-1})	$10^3\cdot\alpha$ (K^{-1})	T (K)	ρ (g cm^{-3})	u (m s^{-1})	κ_S (T Pa^{-1})	$10^3\cdot\alpha$ (K^{-1})
2-Hydroxy Ethylammonium Formate (2-HEAF)									
304.15	1.172230	1694.41	297.13	0.6055	291.15	1.181453	1726.18	284.06	0.5998
303.90	1.172408	1695.01	296.88	0.6054	290.90	1.181631	1726.80	283.81	0.5997
303.65	1.172587	1695.62	296.62	0.6053	290.65	1.181809	1727.43	283.56	0.5996
303.40	1.172764	1696.23	296.36	0.6052	290.40	1.181990	1728.05	283.32	0.5995
303.15	1.172937	1696.81	296.11	0.6051	290.15	1.182162	1728.67	283.07	0.5994
302.90	1.173120	1697.43	295.85	0.6050	289.90	1.182339	1729.29	282.83	0.5993
302.65	1.173295	1698.04	295.59	0.6049	289.65	1.182515	1729.91	282.58	0.5991
302.40	1.173473	1698.64	295.34	0.6048	289.39	1.182700	1730.84	282.24	0.5990
302.15	1.173648	1699.25	295.09	0.6047	289.15	1.182877	1731.59	281.95	0.5989
301.90	1.173826	1699.86	294.83	0.6046	288.89	1.183052	1732.13	281.73	0.5988
301.65	1.174003	1700.47	294.57	0.6045	288.64	1.183228	1732.78	281.48	0.5987
301.40	1.174180	1701.07	294.32	0.6043	288.39	1.183407	1733.34	281.25	0.5986
301.15	1.174361	1701.68	294.06	0.6042	288.15	1.183574	1733.91	281.03	0.5985
300.90	1.174535	1702.29	293.81	0.6041	287.90	1.183753	1734.51	280.79	0.5983
300.65	1.174714	1702.90	293.56	0.6040	287.64	1.183941	1735.04	280.58	0.5982
300.40	1.174891	1703.50	293.30	0.6039	287.40	1.184107	1735.67	280.33	0.5981
300.15	1.175070	1704.12	293.05	0.6038	287.15	1.184289	1736.27	280.10	0.5980
299.90	1.175247	1704.73	292.79	0.6037	286.90	1.184462	1736.82	279.88	0.5979
299.65	1.175425	1705.33	292.54	0.6036	286.65	1.184637	1737.45	279.63	0.5978
299.40	1.175602	1705.95	292.29	0.6035	286.40	1.184815	1738.07	279.39	0.5977
299.15	1.175780	1706.55	292.04	0.6034	286.15	1.184986	1738.68	279.16	0.5975
298.90	1.175955	1707.16	291.78	0.6033	285.90	1.185168	1739.24	278.93	0.5974
298.65	1.176133	1707.77	291.53	0.6032	285.65	1.185344	1739.86	278.69	0.5973
298.40	1.176311	1708.39	291.28	0.6030	285.40	1.185519	1740.47	278.46	0.5972
298.15	1.176489	1709.00	291.02	0.6029	285.15	1.185700	1741.08	278.22	0.5971
297.90	1.176666	1709.61	290.77	0.6028	284.90	1.185886	1741.82	277.94	0.5970
297.65	1.176842	1710.22	290.52	0.6027	284.64	1.186059	1742.42	277.71	0.5968
297.40	1.177019	1710.84	290.27	0.6026	284.40	1.186228	1742.99	277.49	0.5967
297.15	1.177201	1711.45	290.02	0.6025	284.15	1.186403	1743.61	277.25	0.5966
296.90	1.177373	1712.06	289.77	0.6024	283.90	1.186582	1744.21	277.02	0.5965
296.65	1.177553	1712.67	289.52	0.6023	283.65	1.186756	1744.84	276.78	0.5964
296.40	1.177729	1713.28	289.27	0.6022	283.40	1.186933	1745.46	276.54	0.5963
296.15	1.177905	1713.90	289.01	0.6021	283.15	1.187110	1746.08	276.30	0.5961
295.90	1.178085	1714.52	288.76	0.6019	282.90	1.187288	1746.70	276.06	0.5960
295.65	1.178265	1715.13	288.51	0.6018	282.65	1.187467	1747.32	275.82	0.5959
295.40	1.178438	1715.75	288.26	0.6017	282.40	1.187641	1747.95	275.59	0.5958
295.15	1.178617	1716.36	288.01	0.6016	282.15	1.187817	1748.57	275.35	0.5957
294.90	1.178798	1716.97	287.76	0.6015	281.90	1.187991	1749.20	275.11	0.5956
294.65	1.178971	1717.58	287.52	0.6014	281.65	1.188172	1749.83	274.87	0.5954
294.40	1.179148	1718.20	287.27	0.6013	281.40	1.188344	1750.39	274.66	0.5953
294.15	1.179325	1718.81	287.02	0.6012	280.90	1.188699	1751.60	274.19	0.5951
293.90	1.179505	1719.42	286.77	0.6011	280.65	1.188874	1752.24	273.95	0.5950
293.65	1.179682	1720.04	286.52	0.6009	280.40	1.189050	1752.86	273.72	0.5948
293.40	1.179858	1720.66	286.27	0.6008	280.15	1.189231	1753.49	273.48	0.5947
293.15	1.180037	1721.27	286.03	0.6007	279.90	1.189407	1754.12	273.24	0.5946
292.90	1.180210	1721.88	285.78	0.6006	279.65	1.189580	1754.75	273.01	0.5945
292.65	1.180390	1722.50	285.53	0.6005	279.40	1.189760	1755.38	272.77	0.5944
292.40	1.180568	1723.11	285.29	0.6004	279.15	1.189935	1756.03	272.53	0.5943
292.15	1.180744	1723.72	285.04	0.6003	278.90	1.190108	1756.62	272.31	0.5941
291.90	1.180923	1724.34	284.80	0.6002	278.65	1.190288	1757.23	272.08	0.5940
291.65	1.181104	1724.95	284.55	0.6000	278.40	1.190464	1757.88	271.83	0.5939
291.40	1.181278	1725.57	284.30	0.5999	278.15	1.190632	1758.50	271.60	0.5938
2-Hydroxy Diethylammonium Formate (2-HDEAF)									
338.148	1.167306	1697.99	297.13	0.6294	334.399	1.169947	1708.24	292.91	0.6139
337.898	1.167485	1698.67	296.85	0.6283	334.149	1.170124	1708.92	292.63	0.6129
337.649	1.167660	1699.35	296.56	0.6272	333.899	1.170294	1709.58	292.37	0.6119
337.400	1.167838	1700.05	296.27	0.6261	333.651	1.170470	1710.26	292.09	0.6110
337.149	1.168016	1700.75	295.99	0.6251	333.398	1.170646	1710.94	291.81	0.6100
336.899	1.168195	1701.43	295.70	0.6240	333.149	1.170816	1711.61	291.54	0.6091
336.650	1.168369	1702.12	295.42	0.6230	332.898	1.170991	1712.28	291.27	0.6081
336.398	1.168546	1702.81	295.14	0.6219	332.650	1.171163	1712.95	291.00	0.6072
336.147	1.168724	1703.51	294.85	0.6209	332.399	1.171336	1713.60	290.74	0.6063
335.898	1.168897	1704.18	294.57	0.6199	332.149	1.171510	1714.26	290.47	0.6053
335.649	1.169072	1704.86	294.29	0.6189	331.899	1.171683	1714.92	290.20	0.6044
335.399	1.169250	1705.54	294.01	0.6179	331.648	1.171853	1715.58	289.94	0.6035
335.149	1.169423	1706.22	293.74	0.6169	331.399	1.172025	1716.23	289.68	0.6026
334.899	1.169602	1706.90	293.46	0.6159	331.150	1.172199	1716.88	289.41	0.6017
334.650	1.169774	1707.57	293.18	0.6149	330.898	1.172371	1717.54	289.15	0.6008

TABLE 2 (Continued)

T (K)	ρ (g cm^{-3})	u (m s^{-1})	κ_S (T Pa^{-1})	$10^3\cdot\alpha$ (K^{-1})	T (K)	ρ (g cm^{-3})	u (m s^{-1})	κ_S (T Pa^{-1})	$10^3\cdot\alpha$ (K^{-1}
2-Hydroxy Diethylammonium Formate (2-HDEAF)									
330.648	1.172539	1718.21	288.88	0.6000	313.649	1.183936	1760.64	272.48	0.5564
330.400	1.172712	1718.85	288.62	0.5991	313.398	1.184098	1761.26	272.25	0.5560
330.149	1.172885	1719.50	288.36	0.5982	313.147	1.184263	1761.87	272.02	0.5556
329.899	1.173052	1720.15	288.10	0.5974	312.898	1.184428	1762.48	271.80	0.5552
329.648	1.173226	1720.80	287.84	0.5965	312.648	1.184593	1763.09	271.57	0.5548
329.399	1.173398	1721.46	287.58	0.5957	312.397	1.184759	1763.71	271.34	0.5544
329.149	1.173566	1722.08	287.33	0.5948	312.148	1.184922	1764.32	271.12	0.5541
328.899	1.173737	1722.72	287.08	0.5940	311.897	1.185086	1764.94	270.89	0.5537
328.649	1.173908	1723.35	286.83	0.5932	311.647	1.185251	1765.54	270.67	0.5533
328.399	1.174079	1723.99	286.57	0.5923	311.399	1.185413	1766.15	270.44	0.5530
328.149	1.174248	1724.62	286.32	0.5915	311.148	1.185575	1766.76	270.22	0.5527
327.897	1.174417	1725.26	286.07	0.5907	310.897	1.185743	1767.37	269.99	0.5523
327.647	1.174587	1725.89	285.82	0.5899	310.647	1.185907	1767.99	269.77	0.5520
327.399	1.174757	1726.52	285.57	0.5891	310.398	1.186071	1768.60	269.54	0.5517
327.148	1.174928	1727.15	285.32	0.5884	310.148	1.186236	1769.20	269.32	0.5514
326.898	1.175096	1727.78	285.07	0.5876	309.897	1.186398	1769.82	269.10	0.5511
326.649	1.175266	1728.41	284.82	0.5868	309.647	1.186561	1770.43	268.88	0.5508
326.398	1.175433	1729.05	284.57	0.5861	309.398	1.186725	1771.04	268.65	0.5505
326.148	1.175605	1729.68	284.32	0.5853	309.147	1.186891	1771.65	268.43	0.5502
325.898	1.175771	1730.32	284.07	0.5846	308.898	1.187053	1772.26	268.21	0.5499
325.649	1.175942	1730.95	283.82	0.5838	308.648	1.187216	1772.87	267.99	0.5496
325.398	1.176111	1731.58	283.57	0.5831	308.399	1.187384	1773.48	267.77	0.5494
325.148	1.176280	1732.21	283.33	0.5823	308.146	1.187545	1774.09	267.55	0.5491
324.898	1.176448	1732.85	283.08	0.5816	307.898	1.187709	1774.69	267.33	0.5489
324.648	1.176614	1733.47	282.84	0.5809	307.647	1.187875	1775.30	267.11	0.5486
324.398	1.176781	1734.11	282.59	0.5802	307.397	1.188037	1775.91	266.89	0.5484
324.147	1.176950	1734.74	282.34	0.5795	307.147	1.188200	1776.53	266.66	0.5482
323.898	1.177123	1735.37	282.09	0.5788	306.897	1.188361	1777.13	266.45	0.5479
323.649	1.177289	1736.00	281.85	0.5781	306.647	1.188527	1777.74	266.23	0.5477
323.398	1.177455	1736.63	281.61	0.5775	306.397	1.188692	1778.34	266.01	0.5475
323.148	1.177621	1737.25	281.36	0.5768	306.148	1.188850	1778.95	265.79	0.5473
322.899	1.177790	1737.87	281.12	0.5761	305.897	1.189012	1779.55	265.58	0.5471
322.649	1.177958	1738.50	280.88	0.5755	305.647	1.189178	1780.17	265.36	0.5469
322.398	1.178124	1739.12	280.64	0.5748	305.397	1.189346	1780.80	265.13	0.5468
322.147	1.178293	1739.73	280.40	0.5742	305.148	1.189506	1781.40	264.92	0.5466
321.897	1.178462	1740.36	280.16	0.5735	304.897	1.189665	1782.01	264.70	0.5464
321.648	1.178624	1740.97	279.93	0.5729	304.648	1.189827	1782.61	264.49	0.5463
321.399	1.178792	1741.59	279.69	0.5723	304.397	1.189991	1783.22	264.27	0.5461
321.148	1.178961	1742.21	279.45	0.5717	304.147	1.190159	1783.83	264.05	0.5460
320.898	1.179128	1742.83	279.21	0.5710	303.898	1.190318	1784.45	263.83	0.5458
320.649	1.179294	1743.44	278.97	0.5704	303.648	1.190481	1785.05	263.62	0.5457
320.397	1.179459	1744.06	278.74	0.5698	303.397	1.190645	1785.67	263.40	0.5456
320.149	1.179628	1744.67	278.50	0.5693	303.148	1.190807	1786.27	263.19	0.5454
319.898	1.179795	1745.29	278.26	0.5687	302.897	1.190966	1786.88	262.97	0.5453
319.648	1.179965	1745.90	278.03	0.5681	302.647	1.191134	1787.50	262.75	0.5452
319.398	1.180128	1746.51	277.80	0.5675	302.397	1.191295	1788.11	262.54	0.5451
319.148	1.180293	1747.14	277.56	0.5670	302.146	1.191456	1788.72	262.32	0.5450
318.897	1.180461	1747.75	277.33	0.5664	301.898	1.191616	1789.33	262.11	0.5450
318.648	1.180625	1748.37	277.09	0.5659	301.645	1.191779	1789.94	261.90	0.5449
318.398	1.180791	1748.99	276.85	0.5653	301.397	1.191946	1790.55	261.68	0.5448
318.148	1.180960	1749.60	276.62	0.5648	301.148	1.192106	1791.16	261.47	0.5447
317.898	1.181123	1750.21	276.39	0.5643	300.898	1.192269	1791.77	261.25	0.5447
317.648	1.181290	1750.83	276.16	0.5637	300.648	1.192428	1792.39	261.04	0.5446
317.397	1.181457	1751.44	275.93	0.5632	300.397	1.192595	1793.00	260.82	0.5446
317.147	1.181622	1752.06	275.69	0.5627	300.148	1.192754	1793.62	260.61	0.5446
316.898	1.181787	1752.68	275.46	0.5622	299.897	1.192914	1794.23	260.40	0.5445
316.646	1.181953	1753.29	275.23	0.5617	299.648	1.193072	1794.84	260.18	0.5445
316.398	1.182120	1753.91	274.99	0.5612	299.397	1.193240	1795.46	259.97	0.5445
316.148	1.182282	1754.52	274.77	0.5608	299.148	1.193403	1796.07	259.76	0.5445
315.897	1.182447	1755.13	274.54	0.5603	298.897	1.193563	1796.69	259.54	0.5445
315.648	1.182618	1755.75	274.30	0.5598	298.647	1.193724	1797.31	259.33	0.5445
315.397	1.182779	1756.36	274.07	0.5594	298.398	1.193889	1797.92	259.12	0.5445
315.148	1.182944	1756.97	273.85	0.5589	298.148	1.194041	1798.54	258.91	0.5445
314.898	1.183111	1757.58	273.62	0.5585	297.897	1.194211	1799.17	258.69	0.5446
314.648	1.183277	1758.20	273.39	0.5580	297.647	1.194365	1799.77	258.48	0.5446
314.398	1.183441	1758.81	273.16	0.5576	297.398	1.194529	1800.39	258.27	0.5446
314.148	1.183605	1759.42	272.93	0.5572	297.145	1.194689	1801.02	258.05	0.5447
313.897	1.183770	1760.03	272.70	0.5568	296.897	1.194853	1801.63	257.84	0.5447

TABLE 2 (Continued)

T (K)	ρ (g cm^{-3})	u (m s^{-1})	κ_S (T Pa^{-1})	$10^3 \cdot \alpha$ (K^{-1})	T (K)	ρ (g cm^{-3})	u (m s^{-1})	κ_S (T Pa^{-1})	$10^3 \cdot \alpha$ (K^{-1})
2-Hydroxy Diethylammonium Formate (2-HDEAF)									
296.647	1.195012	1802.25	257.63	0.5448	287.145	1.201254	1826.68	249.48	0.5523
296.397	1.195176	1802.87	257.42	0.5449	286.895	1.201421	1827.35	249.27	0.5526
296.146	1.195335	1803.50	257.20	0.5449	286.647	1.201589	1827.98	249.06	0.5529
295.897	1.195495	1804.12	256.99	0.5450	286.395	1.201757	1828.65	248.84	0.5533
295.647	1.195653	1804.76	256.78	0.5451	286.146	1.201924	1829.30	248.63	0.5536
295.396	1.195819	1805.38	256.56	0.5452	285.897	1.202093	1829.97	248.41	0.5540
295.146	1.195977	1806.02	256.35	0.5453	285.647	1.202258	1830.61	248.21	0.5544
294.897	1.196138	1806.66	256.13	0.5454	285.396	1.202428	1831.29	247.99	0.5547
294.647	1.196296	1807.32	255.91	0.5455	285.146	1.202594	1831.96	247.77	0.5551
294.397	1.196455	1807.97	255.69	0.5457	284.897	1.202763	1832.62	247.56	0.5555
294.147	1.196617	1808.61	255.48	0.5458	284.646	1.202928	1833.29	247.34	0.5559
293.896	1.196776	1809.26	255.26	0.5459	284.395	1.203095	1833.93	247.14	0.5563
293.647	1.196937	1809.92	255.04	0.5461	284.144	1.203261	1834.65	246.91	0.5567
293.397	1.197094	1810.56	254.83	0.5462	283.894	1.203428	1835.36	246.68	0.5571
293.147	1.197254	1811.20	254.61	0.5464	283.645	1.203596	1836.04	246.46	0.5576
292.896	1.197415	1811.83	254.40	0.5466	283.395	1.203761	1836.72	246.25	0.5580
292.647	1.197569	1812.48	254.19	0.5467	283.143	1.203931	1837.43	246.02	0.5584
292.396	1.197728	1813.12	253.97	0.5469	282.895	1.204097	1838.10	245.81	0.5589
292.146	1.197893	1813.76	253.76	0.5471	282.646	1.204263	1838.77	245.60	0.5593
291.896	1.198060	1814.40	253.55	0.5473	282.395	1.204429	1839.48	245.37	0.5598
291.647	1.198230	1815.03	253.33	0.5475	282.145	1.204596	1840.18	245.15	0.5602
291.397	1.198397	1815.67	253.12	0.5477	281.896	1.204763	1840.87	244.94	0.5607
291.147	1.198567	1816.31	252.91	0.5479	281.645	1.204932	1841.56	244.72	0.5612
290.897	1.198735	1816.95	252.69	0.5481	281.395	1.205098	1842.24	244.50	0.5617
290.647	1.198902	1817.59	252.48	0.5484	281.145	1.205262	1842.96	244.28	0.5622
290.395	1.199069	1818.23	252.27	0.5486	280.896	1.205430	1843.66	244.06	0.5627
290.146	1.199239	1818.89	252.05	0.5488	280.645	1.205596	1844.35	243.84	0.5632
289.896	1.199407	1819.53	251.83	0.5491	280.397	1.205766	1845.06	243.62	0.5637
289.647	1.199575	1820.18	251.62	0.5493	280.146	1.205932	1845.77	243.40	0.5642
289.396	1.199742	1820.81	251.41	0.5496	279.896	1.206098	1846.49	243.18	0.5647
289.146	1.199912	1821.48	251.19	0.5499	279.647	1.206263	1847.20	242.96	0.5652
288.896	1.200079	1822.12	250.98	0.5501	279.398	1.206429	1847.90	242.74	0.5658
288.645	1.200248	1822.76	250.77	0.5504	279.143	1.206595	1848.72	242.49	0.5663
288.396	1.200415	1823.41	250.55	0.5507	278.894	1.206764	1849.50	242.25	0.5669
288.146	1.200583	1824.08	250.33	0.5510	278.645	1.206928	1850.24	242.03	0.5674
287.895	1.200751	1824.72	250.12	0.5513	278.398	1.207096	1850.97	241.80	0.5680
287.647	1.200919	1825.36	249.91	0.5516	278.153	1.207250	1851.77	241.56	0.5686
287.396	1.201085	1826.02	249.70	0.5520					
2-Hydroxy Triethylammonium Formate (2-HTEAF)									
338.145	1.212896	1841.05	243.25	0.5350944	330.646	1.217655	1863.53	236.48	0.50054876
337.895	1.213056	1841.81	243.01	0.53473476	330.396	1.217805	1864.27	236.27	0.49855042
337.645	1.213219	1842.58	242.78	0.53432049	330.145	1.217959	1864.99	236.06	0.49648913
337.395	1.213378	1843.35	242.54	0.53385159	329.895	1.218108	1865.71	235.84	0.4943813
337.146	1.213544	1844.12	242.31	0.53333026	329.645	1.218259	1866.43	235.63	0.49221885
336.896	1.213708	1844.88	242.07	0.53275232	329.397	1.218404	1867.15	235.42	0.49001972
336.645	1.213868	1845.63	241.85	0.53211711	329.145	1.218554	1867.87	235.21	0.48773006
336.396	1.214032	1846.42	241.61	0.53143254	328.896	1.218703	1868.59	235.00	0.48541312
336.146	1.214193	1847.15	241.38	0.53069071	328.646	1.218852	1869.31	234.79	0.48303237
335.895	1.214351	1847.91	241.15	0.52989095	328.397	1.219001	1870.02	234.59	0.48060683
335.646	1.214509	1848.66	240.93	0.52904314	328.146	1.219150	1870.74	234.38	0.47810696
335.394	1.214673	1849.43	240.69	0.52812995	327.896	1.219292	1871.45	234.17	0.47556231
335.146	1.214836	1850.18	240.47	0.52717706	327.644	1.219438	1872.13	233.97	0.47294202
334.895	1.214998	1850.94	240.24	0.5261579	327.394	1.219578	1872.86	233.77	0.47028767
334.646	1.215155	1851.69	240.01	0.52509245	327.144	1.219719	1873.58	233.56	0.4675787
334.396	1.215312	1852.43	239.79	0.5239682	326.894	1.219862	1874.29	233.35	0.46481509
334.146	1.215469	1853.19	239.56	0.52278932	326.645	1.220003	1874.99	233.15	0.46200823
333.896	1.215629	1853.93	239.34	0.52155581	326.144	1.220277	1876.42	232.75	0.45619648
333.646	1.215784	1854.69	239.11	0.52026767	325.896	1.220417	1877.12	232.55	0.45323842
333.395	1.215943	1855.43	238.89	0.51891941	325.646	1.220557	1877.82	232.35	0.45020209
333.146	1.216101	1856.17	238.67	0.51752749	325.395	1.220700	1878.52	232.15	0.44709866
332.895	1.216262	1856.90	238.45	0.51606954	325.145	1.220843	1879.22	231.94	0.44395286
332.644	1.216419	1857.67	238.22	0.51455651	324.896	1.220977	1879.93	231.74	0.44076533
332.395	1.216577	1858.41	238.00	0.51300114	324.647	1.221112	1880.63	231.55	0.43752361
332.145	1.216728	1859.14	237.78	0.51138499	324.396	1.221251	1881.31	231.35	0.43420101
331.895	1.216882	1859.88	237.56	0.50971422	324.148	1.221380	1881.98	231.16	0.43086403
331.645	1.217039	1860.62	237.35	0.50798881	323.894	1.221502	1882.65	230.98	0.42739059
331.396	1.217189	1861.35	237.13	0.506216	323.646	1.221627	1883.34	230.78	0.42394479
331.146	1.217344	1862.07	236.92	0.50438155	323.397	1.221756	1884.00	230.60	0.42043101
330.896	1.217498	1862.80	236.70	0.50249247	323.151	1.221864	1884.60	230.43	0.41690634

Table 3 *Values of ionic conductivity ($\mu S\cdot cm^{-1}$) of the ILs in the range 278.15 – 338.15 K*

Temperature	2-HEAF	2-HDEAF	Temperature	2-HTEAF
278.15 K	2158.20	452.76	323.15 K	1843.38
288.15 K	3069.00	676.17	325.65 K	1975.05
298.15 K	4197.60	973.17	328.15 K	2108.7
308.15 K	5623.20	1314.72	330.65 K	2316.6
318.15 K	6959.70	1707.75	333.15 K	2494.8
328.15 K	8563.50	2108.70	335.65 K	2643.3
338.15 K	10404.90	2395.80	338.15 K	2811.6

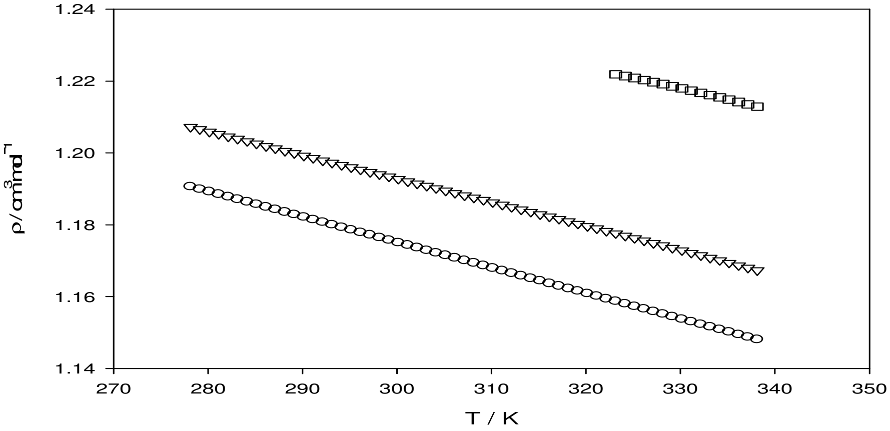


Figure 2. *Curves of density ($g\cdot cm^{-3}$) of the studied ILs, (○) 2-HEAF, (▽) 2-HDEAF and (□) 2-HTEAF at the range of temperature 278.15 – 338.15 K.*

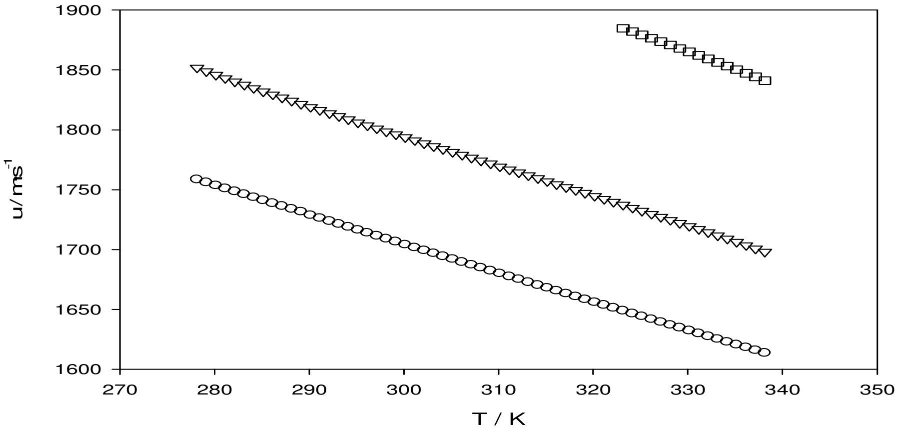


Figure 3. *Curves of ultrasonic velocity (ms^{-1}) of the studied ILs, (○) 2-HEAF, (▽) 2-HDEAF and (□) 2-HTEAF at the range of temperature 278.15 – 338.15 K*

Table 4 *Fitting parameters for density, ultrasonic velocity and conductivity of Eq. 1 in the range 278.15 – 338.15 K and root-mean-square deviations (σ) in accordance to Eq 2 for pure ILs*

	2-HEAF	
	ρ/(g·cm^{-3})	σ
A_0	1.3553	$2.551\cdot10^{-6}$
A_1	-4.0096e-4	
A_2	-9.6623e-7	
A_3	1.0048e-9	
	u/(ms^{-1})	σ
A_0	2654.5515	0.065
A_1	-4.1691	
A_2	4.2548e-3	
A_3	-3.0446e-6	
	C/(μS·cm^{-1})	σ
A_0	48576.9035	45.817
A_1	-443.1112	
A_2	1.0691	
A_3	-2.7428e-4	
	2-HDEAF	
	ρ/(g·cm^{-3})	σ
A_0	1.8296	$1.795\cdot10^{-5}$
A_1	-5.0300e-3	
A_2	1.4476e-5	
A_3	-1.5950e-8	
	u/(ms^{-1})	σ
A_0	6693.4496	0.058
A_1	-42.7907	
A_2	0.1302	
A_3	-1.3999e-4	
	C/(μS·cm^{-1})	σ
A_0	182372.1191	12.493
A_1	-1804.0674	
A_2	5.8659	
A_3	-6.2241e-3	
	2-HTEAF [a]	
	ρ/(g·cm^{-3})	σ
A_0	-5.5873	$4.959\cdot10^{-3}$
A_1	0.0614	
A_2	-1.8296e-4	
A_3	1.7976e-7	
	u/(ms^{-1})	σ
A_0	-2426.8628	0.018
A_1	40.8934	
A_2	-0.1208	
A_3	1.1000e-4	
	C/(μS·cm^{-1})	σ
A_0	5610627.3132	11.158
A_1	-50905.4365	
A_2	153.7971	
A_3	-0.1547	

[a] *Within a temperature range of 338.15 - 323.15 K.*

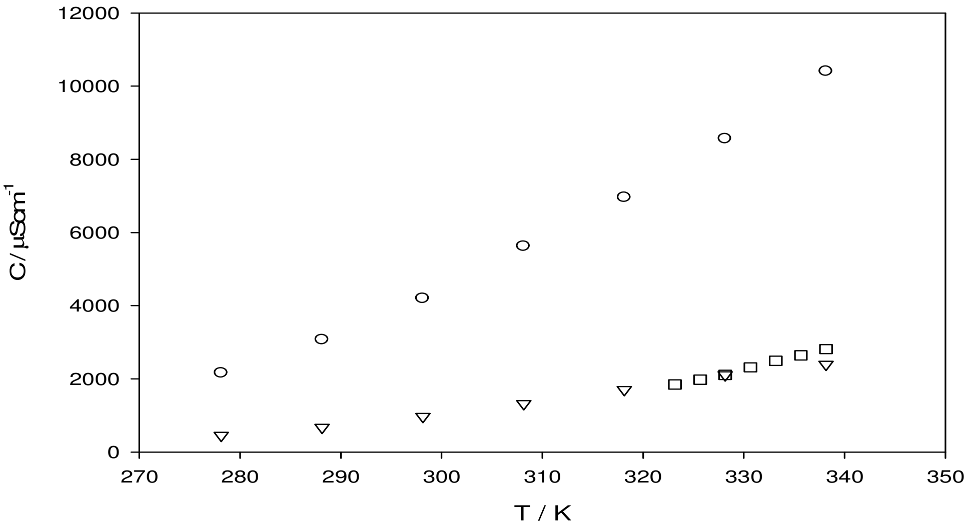


Figure 4. *Curves of ionic conductivity (µS·cm^{-1}) of the studied ILs, (○) 2-HEAF, (▽) 2-HDEAF and (□) 2-HTEAF at the range of temperature 278.15 – 338.15 K.*

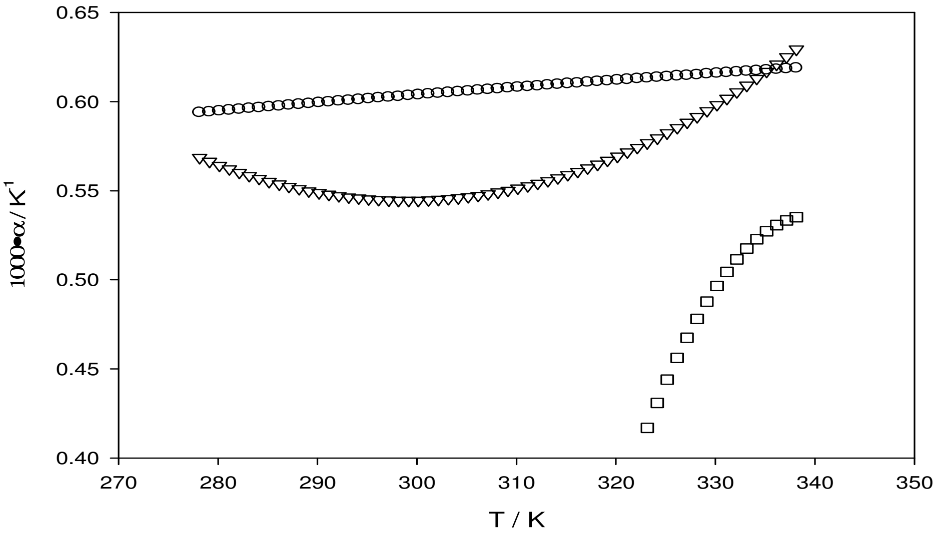


Figure 5. *Curves of isobaric expansibility (K^{-1}) of the studied ILs (○) 2-HEAF, (▽) 2-HDEAF and (□) 2-HTEAF at the range of temperature 278.15 – 338.15 K.*

A frequently applied derived magnitude for industrial mixtures is the temperature dependence of volumetry, which is expressed as isobaric expansibility or a thermal expansion coefficient (α). The data reported in literature normally give only values of thermal expansion coefficients both of pure compounds and their mixtures, showing the relative changes in density, calculated by means of $(-\Delta\rho/\rho)$ as a function of temperature and assuming that α remains constant in any thermal range. As in the case of pure chemicals, it can be computed by way of the expression:

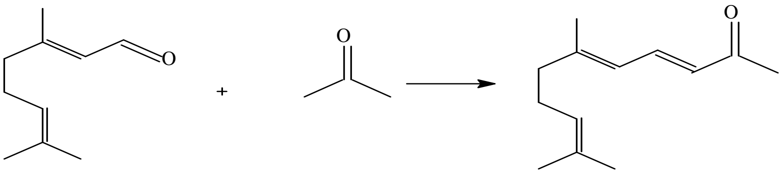
$$\alpha = -\left(\frac{\partial \ln \rho}{\partial T}\right)_{P,x} \tag{3}$$

taking into account the temperature dependence of density. These values are included in Table 2 and show a rising trend for each case (Figure 5). 2-HDEAF shows a minimum at 298.90 K. The other ILs show a rising tendency with temperature.

2.6. Catalytic Studies

In order to determine the catalytic activity of these ILs, three model reactions were employed: citral and acetone, benzaldehyde and acetone, and benzaldehyde and heptanal condensations. The ILs studied were those included in this work (2-HEAF and 2-HDEAF; no experiments were realized with 2-HTEAF), as commented above, and others of the same family (2-HEAA, 2-HDEAA, 2-HTEAA, 2-HEAP, 2-HDEAP, and 2-HTEAP). Experimental data related to these compounds could be obtained from an earlier work.

The condensation reaction between citral and acetone (Scheme 1) leads to the formation of pseudoionone, which is an intermediate in the commercial production of vitamin A. Citral consists of two isomers, neral and geranial, caused by the cis-trans isomerism at the C=C bond near the aldehyde group [8].



***Scheme 1** Condensation reaction between citral and acetone.*

The two isomers of citral can be converted into the corresponding pseudoionone with good selectivity (between 63% and 82%, Figure 6); the most active IL for this reaction is 2-HEAA, which gives a conversion of 52.3%, and the less active IL is 2-

HEAF, which gives a conversion of 34.8%. 2-HEAP gives an intermediate conversion of 40.2%. Other compounds observed were those from the condensation of two citral molecules or of pseudoionone isomers and one acetone molecule [11].

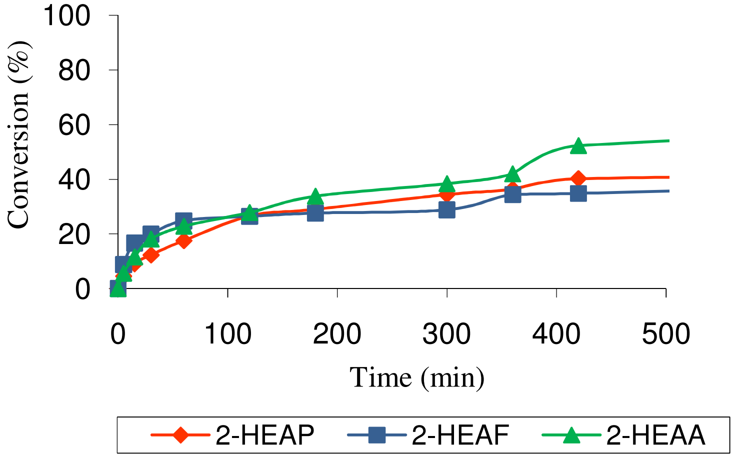
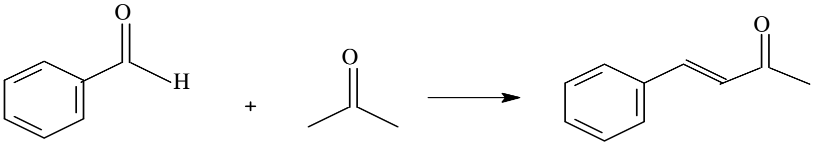


Figure 6. *Conversion of citral in the citral and acetone condensation.*

The catalytic activity of the ILs was also tested in the production of benzylidenacetone (Scheme 2) from the condensation between benzaldehyde and acetone.



Scheme 2 *Condensation reaction between benzaldehyde and acetone.*

After 3 h, a conversion of 100% and a selectivity of 86% were obtained using 2-HEAP as the catalyst. Good conversions were also obtained with 2-HEAF (94.1%) and 2 HEAA (99.4%), with selectivities of 82% and 85%, respectively, after 4 h of reaction time (Figure 7). In these reactions, good conversions were obtained with all the ILs in a relatively short time.

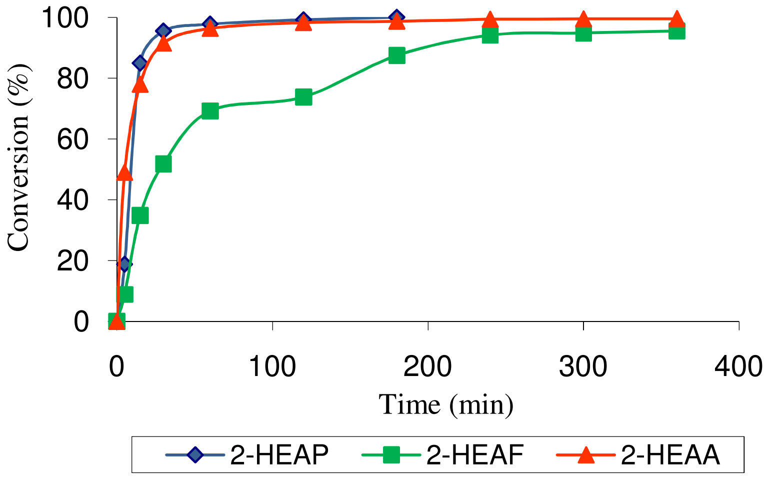
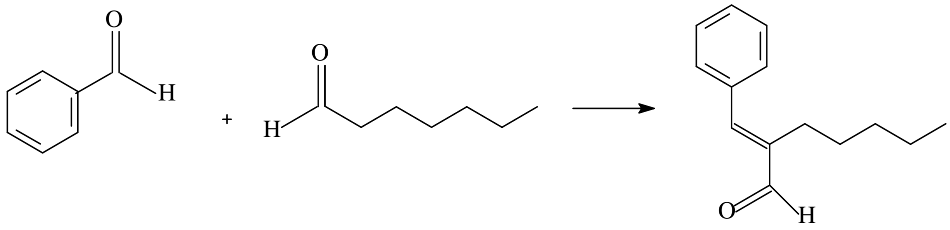


Figure 7. *Conversion of benzaldehyde in the benzaldehyde-acetone condensation.*

The third reaction for which the catalytic activity was studied was the synthesis of jasminaldhyde from the condensation between benzaldehyde and heptanal (Scheme 3).



Scheme 3 *Condensation reaction between benzaldehyde and heptanal.*

In this reaction, good conversion was obtained with 2-HEAF (77.8%) and 2-HEAA (63.3%), while, with 2-HEAP, a lower conversion (18.5%) was obtained (Figure 8). The selectivity was low (between 13.7% and 30.7%) because of the formation of a secondary product. The undesired product comes from the self-condensation of heptanal to 2-*n*-pentyl-2- nonenal, and this secondary reaction can be inhibited to some extent by the slow addition of heptanal.

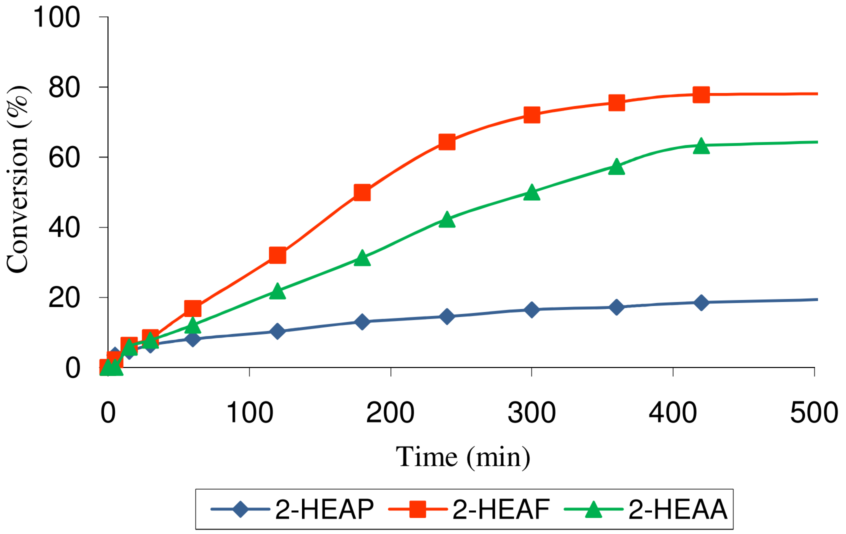


Figure 8. *Conversion of benzaldehyde in the benzaldehyde-heptanal condensation.*

We can conclude that, with this new synthesized ILs family, good results were obtained in terms of conversion and selectivity for aldol condensation reactions. The ILs are not soluble in the reaction mixture and therefore, at the end of the reaction, these catalysts are easily to separated. For future work, we intend to study the optimized recovery process of the catalysts and their reuse in repeated runs of experiments, which makes accurate experimental data on liquid-liquid-phase equilibrium among all related chemicals necessary.

3. Results and Discussion

The basic physicochemical data of ILs are important for the design of cleaner technological processes and a better understanding of the interactions in this kind of compound. In the present paper, we have presented a new synthesis and experimental data of the densities, ultrasonic velocities, and ionic conductivities of 2-HEAF, 2-HDEAF, and 2-HTEAF, which show IL characteristics according to the FT-IR results. No information on all these compounds is gathered in the literature as far as we know.

From these results, the following was found:

1. An increase in temperature diminishes the interaction among ions, lower values of density and ultrasonic velocity being gathered for rising temperatures in each case. At the same temperature, higher viscosity was observed when the salt was of higher molecular weight. The effect of the temperature is similar for all salts.

2. The organic residual chain in the cation forming the IL has strong effects on the physicochemical properties, with the steric hindrance being a key factor for accommodation into a liquid structure. The ions enclosed are of two types: linear (the anion) and globular (the cation), and the factors studied were the substitution and then the bulk power character. The degree of their influence depends on the nature of cation, but the influence of anion residue is higher [4, 5] because of its linear and longer structure. This factor produces a higher disturbation in terms of the accommodation of ions. For these ions, the bulk cation develops lower steric hindrance influence than the linear anion. This fact may be observed in terms of higher values of densities and ultrasonic velocities for those salts of the lighter anion (in each case) and the heavier cation (for the same anion) [5].

3. The influence of molecular structure in terms of conductivity produces the lowest values for 2-HDEAF and 2-HTEAF and the largest for 2-HEAF. The effect of temperature in this magnitude produces a considerable increment toward high values by ion mobility.

4. As observed in Figure 5, the longer the size of the cation (triethylamine cation), the lower the value of isobaric expansibility obtained.

5. On the basis of these experimental observations and as explained above, because of the low cost and simplicity of synthesis, the potential interest of these liquid salts is great due to the possibility of a tailored-designed IL or IL mixture, which shows those physicochemical properties more adequate for industrial applications, such as unit operations or cosolvents for catalysis reactions, which are being studied in our laboratories.

6. As observed from the experimental data, the studied solvents used in homogeneous catalysis play a unique role in dissolving and stabilizing the reactants of

the studied aldol condensations, but must not react or compete with the reactants. An important feature of homogeneous systems enclosing ILs is that they are highly efficient and highly specific chemo-, stereo-, regio-, and enantioselectivities can be attained. The disadvantage, however, is the need to separate the solvent and catalyst from the product and remaining reactants at the end of the reaction. ILs offer the opportunity of combining the advantages of both homogeneous and heterogeneous catalysis in one system, because some of them show sharp immiscibility in polar reaction media. The development of applications of three-dimensional heterogeneous catalysis using ILs as supports should present challenges for the next decades. At the present time, several urgent questions regarding basic aspects of ILs need to be addressed. Among them, the physicochemical principles of the liquid properties and solubility of ILs remains a research subject of IL study today.

4. Conclusions

A new protocol for the synthesis of short aliphatic chain ILs has been developed. For this new family of ILs, a series of characterization has been carried out: the temperature dependence of density and the study of ultrasonic velocities and conductivity. Good results were obtained in terms of conversion and selectivity when these ILs were used as catalysts for a series of aldol condensation reactions with interest for the fine chemistry industry.

Acknowledgment

Joan Rosell, Sergi Paredes, and Bruno Sersante (Departament d’Enginyeria Quimica, Universitat Rovira i Virgili, España) are gratefully acknowledged for providing experimental support to complete this research, and the Ministerio de Educacio´n y Ciencia CTQ2006-08196/PPQ and Generalitat de Catalunya (2004FI-IQUC1/00137) are acknowledged for financial support.

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Scientific article (Art 8)

Brønsted ionic liquids: Study of physico-chemical properties and catalytic activity in aldol condensations

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Brønsted ionic liquids: Study of phyisco-chemical properties and catalytic activity in aldol condensations

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Abstract

A serie of trisubstituted amines-based ionic liquids was prepared using an aliphatic linear carboxylic acid (pentanoic acid). The ionic liquids synthesised are 2-hydroxy ethylammonium pentanoate (2-HEAPE), 2-hydroxy diethylammonium pentanoate (2-HDEAPE) and 2-hydroxy triethylammonium pentanoate (2-HTEAPE). FT-IR spectra establishes their simple ionic salt structure. The influence of structural variations on their thermodynamic properties (density, ultrasonic velocity, ionic conductivity, refractive index, viscosity and surface tension) was investigated, as a function of temperature in the range 278.15 – 338.15 K. In the serie studied here, the anion has strong effect on the properties if compared with previous studies of the authors, when shorter chains were used. It was found that the elongation of the alkyl chain causes the pronounced depression of fluidity and ionic conductivity. The observed temperature trend of the studied properties points out the special packing of these ionic liquids, as well as, the strong influence of the steric hindrance among linear aliphatic residues. We also describe the catalytic activity of these type of ionic liquids for a representative serie of aldol condensation processes. Conversions higher than 98% and selectivities higher than 85% were obtained. Moreover the catalysts are easily separated from reaction mixture and re-used, obtaining good conversions for at least three consecutive cycles. As a conclusion, it was found that simple structural modifications into anion length and degree of substitution provide a mechanism to manipulate the catalytic potency of these ionic liquids, as well as, tailor physicochemical properties for potential end-use applications.

Keywords: Protic Ionic liquid; physical properties; temperature; catalysis; aldol condensation.

1. Introduction

Ionic liquids (ILs) are a class of new solvents which are increasingly being used in a wide variety of applications in the last years due to an amazing number of desirable properties [1-4]. Their field of potential study is growing at a very fast rate, as their beneficial properties are identified and then applied into processes. ILs are defined as those ionic salts which have a melting point below 100^0C and are formed by positive and negative ions. Typically, these compounds have excellent chemical and thermal stability, negligible vapour pressure and many of them are described as environmentally friendly. They provide an attractive alternative to traditional nonionic organic solvents in a wide spectrum of applications and therefore, are considered highly promising neoteric solvents. ILs can be divided into two broad categories: aprotic ionic liquids (AILs) and protic ionic liquids (PILs). The later are produced through proton transfer from a Brønsted acid to a Brønsted base. The former have received far greater attention, nevertheless, recently there has been an increasing interest in PILs or Brønsted ILs due to their greater potential as environmental friendly solvents and promising applications [5-7].

The application of new policies on terms of environment, health and safety deals towards minimizing or substituting organic volatile solvents by green alternatives, placing a renewed emphasis on research and develop of lesser harmful compounds as ILs. In the past few years, room-temperature ILs have found numerous applications as clean solvents and catalysts for green chemistry, in photochemistry, in electrosynthesis [8-12] and other applictions as lubricants, electrolytes for batteries, new procedures for cheaper solar cells or cleaning applications in processes of minimization of CO_2/SO_2 emissions [13-18].

With this fact in mind, and as a continuation of a wider project to develop and study applications of new ILs, in this work we present the study of physical-chemical properties and the catalytic potential of a new family of PILs. These PILs consist of substituted amine cations of the form R_XNH (X is the number of alkyl substitutions) combined with organic anions of the form $R'COO^-$ (being of different nature R and

R'). These kind of compounds have low cost of preparation and simple synthesis/purification [5-7]. Moreover, the very low toxicity and the degradability of this kind of ILs has been verified [19]. Thus, sustainable processes can be originated with their use. The variations in the anion alkyl chain, in conjunction with different cations, lead to a large matrix of ILs.

In order to obtain information related to internal organization, density, ultrasonic velocity, ionic conductivity, refractive index, viscosity and surface tension, were measured in a wide range of temperature for the following PILs: 2-hydroxy ethylammonium pentanoate (2-HEAPE), 2-hydroxy diethylammonium pentanoate (2-HDEAPE) and 2-hydroxy triethylammonium pentanoate (2-HTEAPE). As far as we know, open literature doesn't show publications related with these new PILs, therefore no information is available about their thermodynamic data, phase behaviour, mixing trend or temperature dependence until now.

We also describe the catalytic activity and recycling of 9 different PILs of the same family into a serie of aldol condensation processes. Our work is now being oriented towards phase studies of ILs, industrial applications related to separation and energy and heterogeneous catalysis .

2. Experimental

2.1. Preparation of the ILs

The amine compounds (monoethanolamine, diethanolamine or triethanolamine, Merck Synthesis, better than 99%) were placed in a threenecked flask all-made-in-glass equipped with a reflux condenser, a PT-100 temperature sensor for controlling temperature and a dropping funnel. The flask was mounted in a thermal bath. A slight heating and strong agitation are necessary to increase miscibility between reactants and then allow reaction. The organic acid (pentanoic acid, Merck Synthesis, better than 99%) was added dropwise to the flask under stirring with a magnetic bar. Stirring was continued for 24 h at laboratory temperature, in order to obtain a final viscous liquid. Lower viscosity was observed in the final product by decreasing molecular weight of reactants. No solid crystals or precipitation was noticed when the liquid sample was purified (purification step explained below) or was stored at freeze temperature for a few months after synthesis. The reaction is an acid–base neutralization creating a pentanoate salt of mono, di or tri ethanolamine, that in a general form should be expressed as follows:

$$(\mathrm{HOCH_2CH_2})_X\,\mathrm{NH}_Y + \mathrm{HOOC(CH_2)_3(CH_3)} \rightarrow (\mathrm{HOCH_2CH_2})_X\,\mathrm{NH}^+_{Y+1}\left({}^-\mathrm{OOC(CH_2)_3(CH_3)}\right)$$

where X is the number of ethanol substitutions into the amine compound and Y the protons (X+Y=3). For example, when X=1 and Y=2, this equation shows the chemical reaction for the reactants monoethanolamine + pentanoic acid, and 2-hydroxy ethylammonium pentanoate (2-HEAPE) as neutralization product.

2.2. *Stability at room temperature*

For many of these fused ammonium salts, exists the possibility to undergo a condensation reaction and form an amide compound. Therefore, an adequate control of temperature is essential throughout the chemical reaction of salt formation; otherwise heat evolution may produce the dehydration of the salt to give the corresponding amide as in the case for nylon salts (salts of diamines with dicarboxy acids). As observed in our laboratory during IL synthesis, dehydration starts around 150^0C, for the lightest ILs from this family. The colour varies in each case from transparent to dark brown when reaction process and purification (strong agitation and slight heating for vaporization of residual non-reacted acid at least for 72 h) was completed.

There was no detectable decomposition for the ILs studied here when left for over 12 months at laboratory temperature. Less than 1% amide was detected after this period of time. On the basis of these results it appears obvious that the probability of amide formation is low for this kind of structures.

2.3. Spectroscopy test

FT-IR spectrum was taken by a Jasco FT/IR 680 plus model IR spectrometer, using a NaCl disk.

2.4. Physical properties equipment

During the course of the experiments, the purity of ILs was monitored by different physical properties measurements. The pure ILs were stored in sun light protected form, constant humidity and low temperature. Usual manipulation and purification in our experimental work was applied [5]. The molar mass and experimental results at standard condition for the ILs are shown in Table 1.

The densities and ultrasonic velocities of pure components were measured with an Anton Paar DSA-5000 vibrational tube densimeter and sound analyzer, with a resolution of 10^{-5} g·cm^{-3} and 1 ms^{-1}. Apparatus calibration was performed periodically in accordance with provider's instructions using a double reference (Millipore quality water and ambient air at each temperature). Accuracy in the temperature of measurement was better than ± 10^{-2} K by means of a temperature control device that applies the Peltier principle to maintain isothermal conditions during the measurements.

The ion conductivity was measured by a Jenway Model 4150 Conductivity/TDS Meter with resolution of 0.01 μS to 1 mS and accuracy of ± 0.5% at the range temperature. The accuracy of temperature into the measurement cell was ± 0.5^0C.

The kinematic viscosity (ν) was determined from the transit time of the liquid meniscus through a capillary viscosimeter supplied by Schott (Cap N° 0c, 0.46 (0.01 mm internal diameter, *K*) 0.003201 mm^2·s^{-1}) measured with an uncertainty of (0.00008 mm^2·s^{-1}) using eq 1.

$$\nu = K(t - \theta) \qquad (1)$$

where t is the efflux time, K is the characteristic constant of the capillary viscosimeter, and θ is a correction value to prevent the final effects. An electronic stopwatch accurate within ± 0.01 s was used for measuring efflux time

The capillary viscometer was immersed in a bath controlled to ± 0.1^0C. The viscometer was a Shott-Geräte AVS 350 Ubbelohde viscometer. Each measurement was repeated at least 10 times. The dynamic viscosity (η) was obtained by the product of kinematic viscosity (ν) and the corresponding density (ρ) of the mixture in terms of eq 2 for each temperature and mixture composition.

$$\eta = \rho \cdot \nu \tag{2}$$

The surface tensions of the mixtures were measured using a Kruss K-9 tensiometer, which employs the Wilhelmy plate principle. The surface tensions of the pure components were determined and compared with literature values to calibrate the tensiometer. The uncertainty of the measurement was ± 0.03 $mN{\cdot}m^{-1}$. In general, each surface tension value reported was an average of five measurements. The samples were thermostated in a closed vessel before surface tension measurements to prevent evaporation.

Refractive index was determined within ± $1{\cdot}10^{-6}$ using an Atago RX-1000 refractometer. Before measurements, the refractometer was calibrated using distilled-deionized water in accordance with the instrument instructions. Water was circulated into the instrument through a thermostatically controlled bath maintained constant to ± 0.1^0C. The samples were directly injected from the stock solution stored at work temperature to avoid evaporation. The refractive index measurements were done after the liquid samples reached the constant temperature of the refractometer. The detailed experimental procedure has been described into previous works of the authors [5, 6].

2.5. Catalytic studies

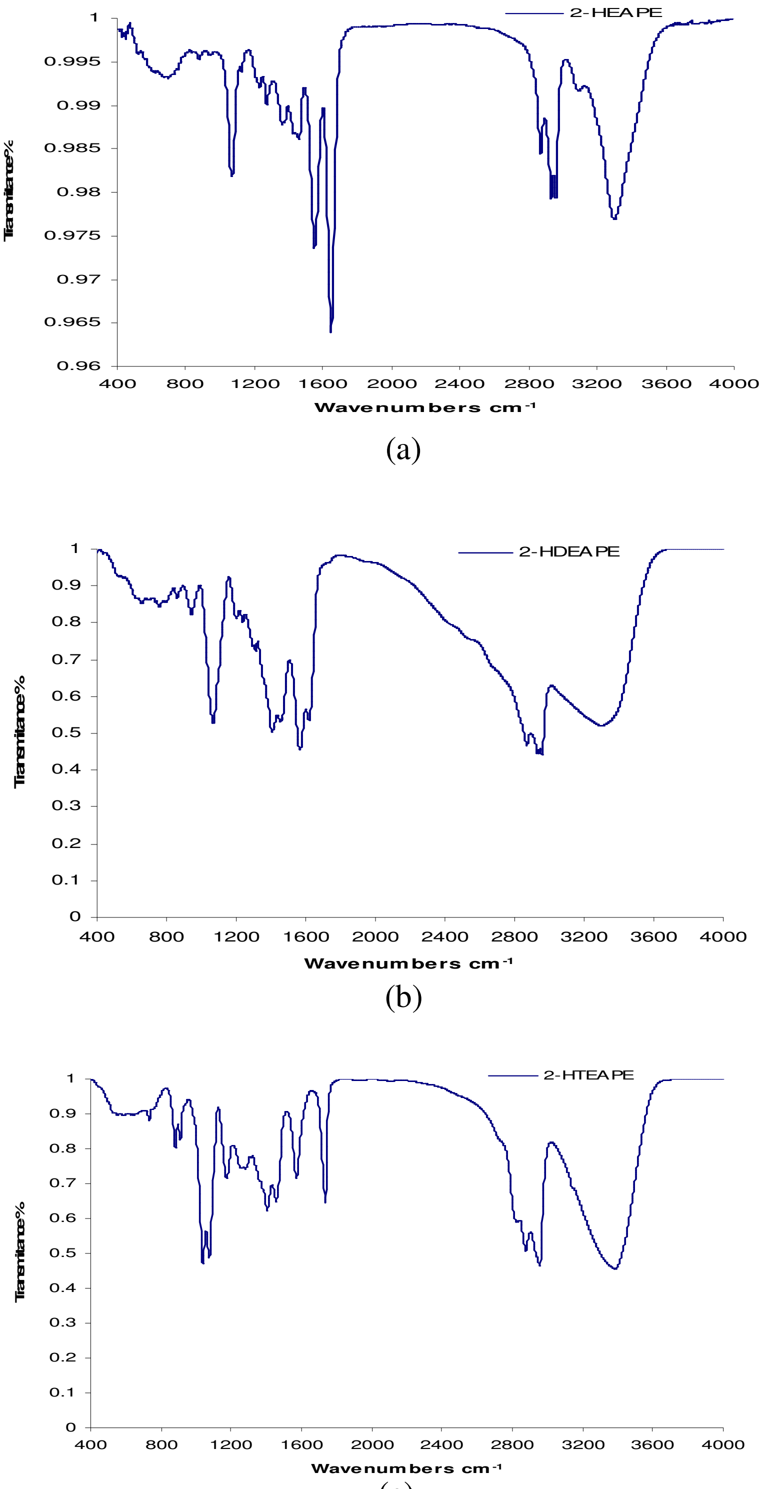
Recently, many studies [20-25] dealing with the application of ILs in organic synthesis and catalysis have been published, pointing out the vast interest in this type of compounds. With these facts in mind, we studied the catalytic potential of the serie of ILs gathered before and 6 ILs belonging to the same compounds family[26].

The studied reactions were the condensation between citral and acetone and between benzaldehyde and acetone . The reactions were performed in liquid phase using a 100 mL batch reactor equipped with a condenser system. To a stirred solution of substrate and ketone (molar ratio ketone/substrate = 4.4) was added 1 g of IL, and the flask was maintained at 333 K using an oil bath. Samples were taken at regular time periods and analyzed by gas chromatography using a flame ionization detector and an AG Ultra 2 column (15 m x 0.32 mm x 0.25 μm). Tetradecane was used as the internal standard. Reagents were purchase from Aldrich and used without further purification

In order to separate the ILs from the reaction mixture, at the end of the reaction 6 mL of H_2O were added. The mixture was stirred for 2 h and then left 15 h to repose. Two phases were separated: the organic phase which contains the reaction products and the aqueous phase which contains the IL. In order to separate the IL, the aqueous phase was heated up to 393 K under vacuum.

3. Results

As Figure 1 (a, b and c) shows, the broad band in the 3500-2400 cm^{-1} range exhibits characteristic ammonium structure for all the neutralization products. The OH stretching vibration is embedded in this band. The broad band centred at 1600 cm^{-1} is a combined band of the carbonyl stretching and N-H plane bending vibrations.



(a)

(b)

(c)

Figure 1. *FT-IR spectra for(a) 2-hydroxy ethylammonium propionate (2-HEAPE), (b) 2-hydroxy diethylammonium propionate (2-HDEAPE) and (c) 2-hydroxy triethylammonium propionate (2-HTEAPE)).*

The variation with the temperature of different thermodynamic properties measured in this work are gathered in Figures 2-8. These figures show an increasing trend in the packing efficiency of the ILs as the molecular weight increases.

This tendency shows a continuous decrease of the density and ultrasonic velocity versus temperature in each case (Figures 2 and 3).

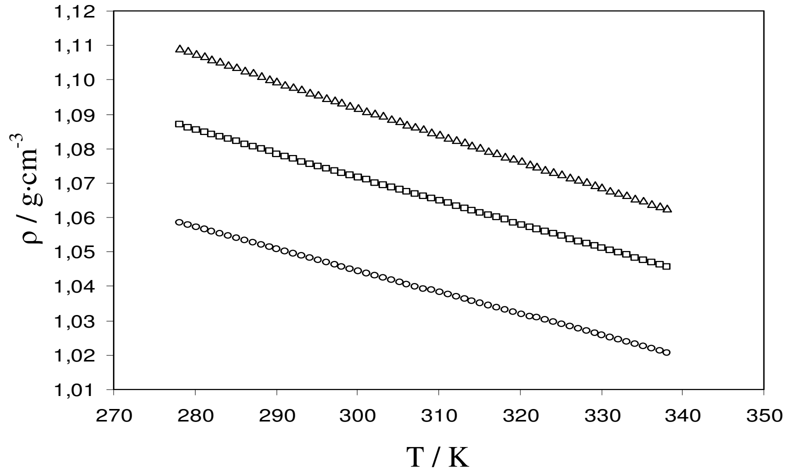


Figure 2. *Curves of density (g·cm^{-3}) for the studied ILs in the temperature range 278.15 – 338.15 K ((O) 2-hydroxy ethylammonium propionate (2-HEAPE), (□) 2-hydroxy diethylammonium propionate (2-HDEAPE) and (Δ) 2-hydroxy triethylammonium propionate (2-HTEAPE)).*

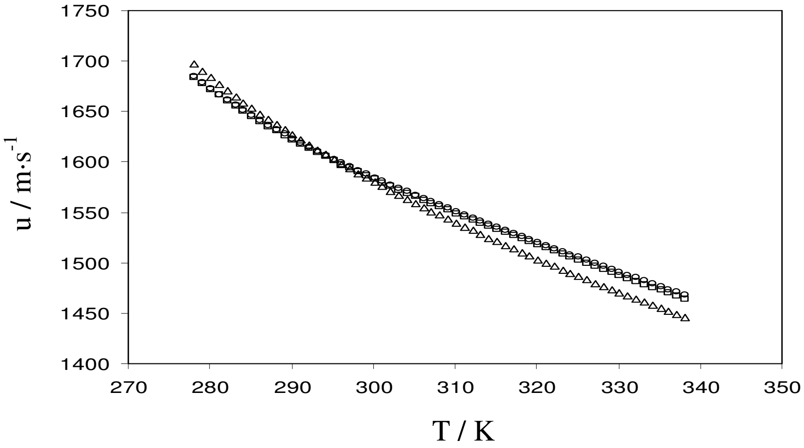


Figure 3. *Curves of ultrasonic velocity (m·s^{-1}) for the studied ILs in the temperature range 278.15 – 338.15 K ((O) 2-hydroxy ethylammonium propionate (2-HEAPE), (□) 2-hydroxy diethylammonium propionate (2-HDEAPE) and (Δ) 2-hydroxy triethylammonium propionate (2-HTEAPE)).*

A frequently applied derived property for industrial mixtures is the isobaric expansibility or thermal expansion coefficient (α), expressed as the temperature dependence of density. Thermal expansion coefficients are calculated by means of $(-\Delta\rho/\rho)$ as a function of temperature and assuming that α remains constant in any thermal range. As in the case of pure chemicals it can be computed by way of the expression:

$$\alpha = -\left(\frac{\partial \ln \rho}{\partial T}\right)_{P,x} \tag{5}$$

taking into account the temperature dependence of density. These α values showed a minimum (in terms of negative values) for each case at 333.41 K (Figure 4).

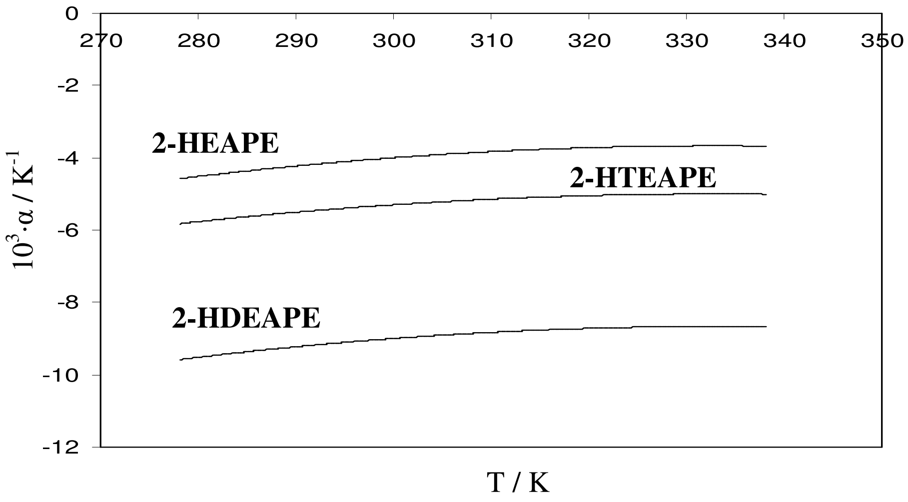


Figure 4. *Curves of isobaric expansibility (K^{-1}) for the studied ILs in the temperature range 278.15 – 338.15 K.*

In Figure 5, the ionic conductivity of the ILs is depicted, and it can be observed an increasing trend for higher temperatures in each case. This fact may be ascribed to the increasing mobility of the ions for increased temperatures. At the same time, the ionic conductivity values decrease when the cation's ramification increases. So the influence of molecular structure, in terms of conductivity, produces the lowest values for 2-HTEAPE and the highest for 2-HEAPE, but all of them have a lower ionic conductivity than 2-hydroxy ethylammonium formate (2-HEAF) (the shortest member of this IL family) [6].

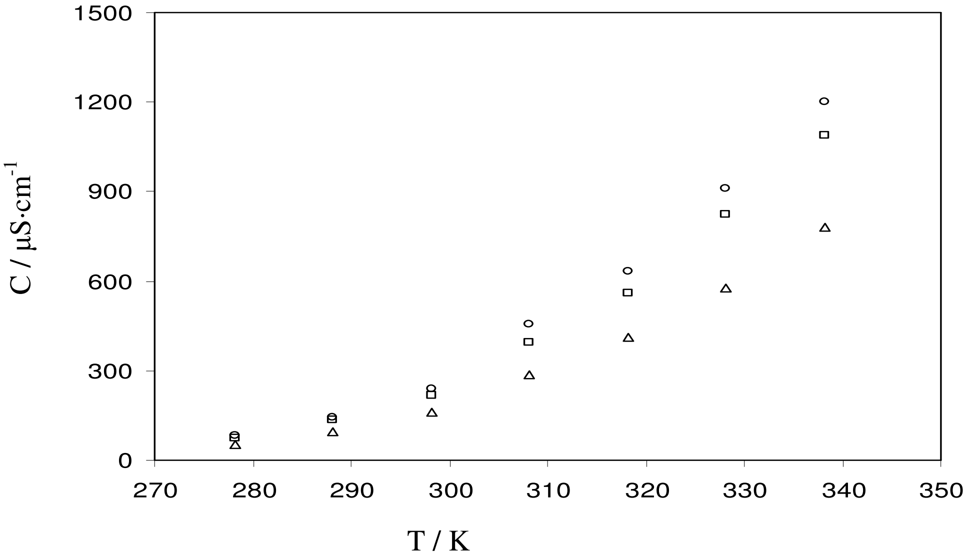
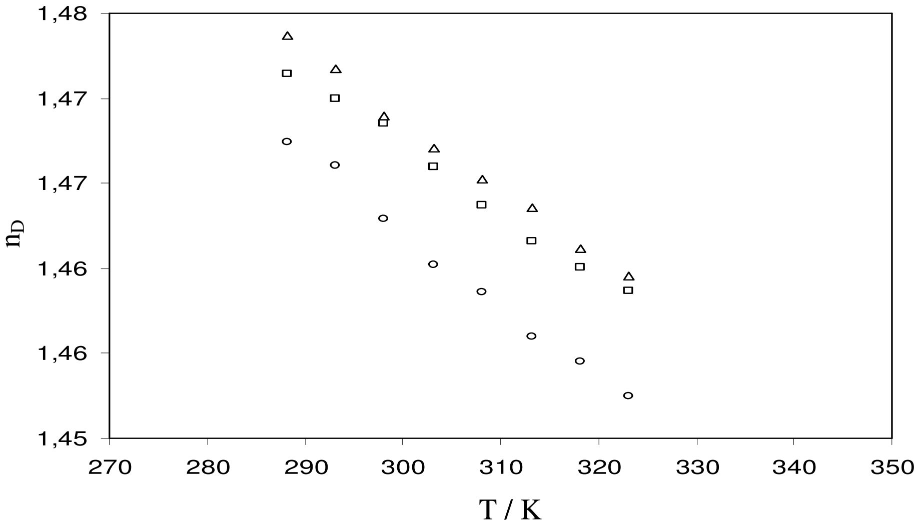


Figure 5. *Curves of ionic conductivity (μS·cm^{-1}) for the studied ILs in the temperature range 278.15 – 338.15 K ((O) 2-hydroxy ethylammonium propionate (2-HEAPE), (□) 2-hydroxy diethylammonium propionate (2-HDEAPE) and (Δ) 2-hydroxy triethylammonium propionate (2-HTEAPE)).*

In Figures 6-8, the variation with the temperature of the refraction, viscosity and surface tension are depicted. In each case, it can be observed a decreasing tendency for increasing temperatures and molar weight decrease.



Firure 6. *Curves of refractive index for the studied ILs in the temperature range 278.15 – 338.15 K ((O) 2-hydroxy ethylammonium propionate (2-HEAPE), (□) 2-hydroxy diethylammonium propionate (2-HDEAPE) and (Δ) 2-hydroxy triethylammonium propionate (2-HTEAPE)).*

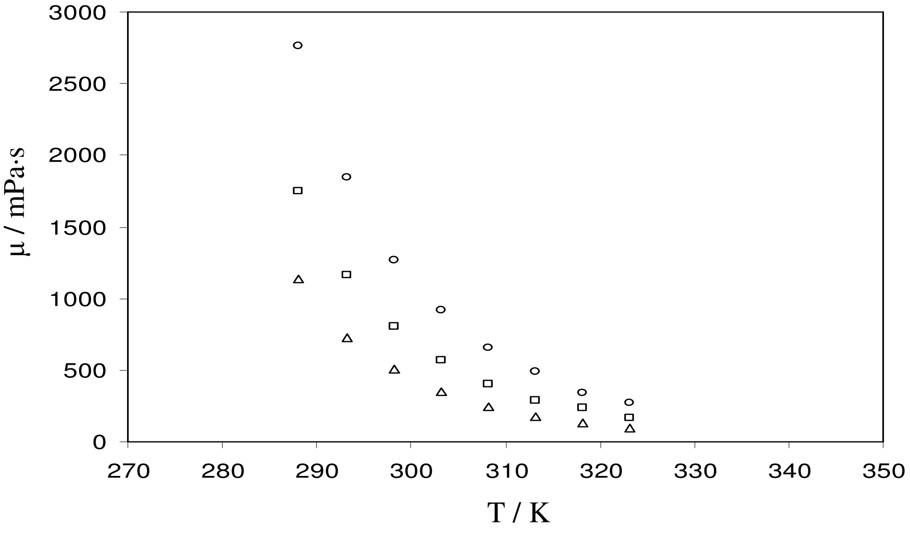


Figure 7. *Curves of dynamic viscosities (mPa·s^{-1}) for the studied ILs in the temperature range 278.15 – 338.15 K ((O) 2-hydroxy ethylammonium propionate (2-HEAPE), (□) 2-hydroxy diethylammonium propionate (2-HDEAPE) and (Δ) 2-hydroxy triethylammonium propionate (2-HTEAPE)).*

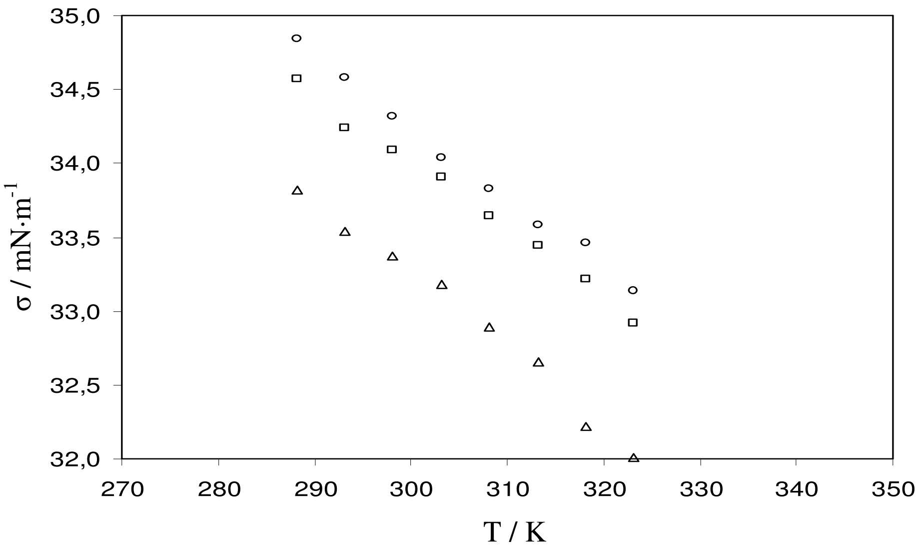


Figure 8. *Curves of surface tension (mN·m^{-1}) for the studied ILs in the temperature range 278.15 – 338.15 K ((O) 2-hydroxy ethylammonium propionate (2-HEAPE), (□) 2-hydroxy diethylammonium propionate (2-HDEAPE) and (Δ) 2-hydroxy triethylammonium propionate (2-HTEAPE)).*

The ions enclosed in this study are of two types: linear the anion and linear (mono), plane (di) or globular (tri substitution) the cation. The factors studied here are the chain length of the anion (comparatively with earlier results of the authors) and the substitution into the cation (bulk degree), respectively. The influence of anion residue is higher in terms of steric hindrance, due to its longer structure [6,8]. This factor produces a higher disturbation on ion package. For these ions, the bulk cation develops a lower steric hindrance influence than the anion. Ion's mobility and progressively higher kinetics, make more and more difficult the ion-ion interaction and then weaker structures into liquid phase.

For compact and smooth representation, the measured magnitudes of the ILs were correlated as a function of temperature in accordance to the eq. S1. Equation S1, fitting parameters and the values for Figures 2-8 are found in supplementary material.

Catalytic activity

In the present work the studied ILs were 2-hydroxi (mono, di or tri) ethylammonium butanoate (2-HEAB, 2-HDEAB and 2-HTEAB, respectively), 2-hydroxi (mono, di or tri) ethylammonium isobutanoate (2-HEAiB, 2-HDEAiB and 2-HTEAiB, respectively) and 2-hydroxi (mono, di or tri) ethylammonium pentanoate (2-HEAPE, 2-HDEAPE, and 2-HTEAPE, respectively). The synthesis and characterization of these ILs of butanoate and isobutanoate anions were presented earlier [26].

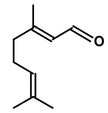
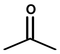
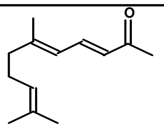
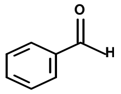
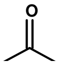
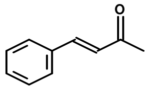
At industrial level aldol condensations are catalyzed by homogeneous alkaline bases (KOH or NaOH) [27, 28] but with this kind of catalysts numerous disadvantages arise such as loss of catalysts due to separation difficulties, corrosion problems in the equipment and generation of large amounts of residual effluents which must be subsequently treated to minimize their environmental impact. Consequently, new technological solutions have to be developed in order to generate new and more environmental friendly processes.

The condensation reaction between citral and acetone leads to the formation of pseudoionones which are precursors in the commercial production of vitamin A. In the last years, the aldol condensation between citral and acetone has been studied by several groups employing different types of catalysts: rehydrated hydrotalcites [29], mixed oxides derived from hydrotalcites [30, 31], organic molecules [32], ionic liquids [25] etc.

Using the mixed oxides derived from hydrotalcites Climent et al. [30, 31] obtained a conversion of 83% and selectivity to pseudoionones of 82% in 1 h. Abello et al. obtained a citral conversion of 81% in only 5 min employing rehydrated hydrotalcites as catalysts [29] highlighting that Brønsted basic sites are more active than Lewis sites for aldol condensation reactions. In the study of Cota et al. [32] it was shown that 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) which has Lewis basic properties, is inactive for aldol condensation reactions; however when it reacts with equimolar amounts of water, this molecule transforms towards a complex that shows Brønsted basic properties and becomes active giving a conversion of 89.17% and a selectivity of 89.6% in 6 h. When choline hydroxide (ionic liquid) was used as catalyst a citral conversion of 93% and selectivity of 98.2% were obtained [25] in 1 h.

Among the ILs studied in this work, for citral and acetone condensation (entry 1, Table 1) the most active IL is 2-HEAPE, which gives a conversion of 37.6%, the less active is 2-HEAiB which gives a conversion of 10.4% while 2-HEAB gives an intermediate conversion of 33.2%. The selectivity obtained in this reaction ranges between 49.5-59.7%. No traces of diacetone alcohol derived from the self-condensation of acetone were found but other secondary products coming from the self condensation of citral and oligomers derived from citral are detected in small quantities in the reaction mixture.

Table 1 *Condensation reactions catalyzed by the studied ILs*

Entry	**Substrate**	**Ketone**	**Product**	**Catalyst**	**Time (h)**	**Conversion (%)**	**Selectivity (%)**
1				2-HEAB	7	33.2	59.7
				2-HEAiB		10.4	53.4
				2-HEAPE		37.6	49.5
2				2-HEAB	2	98.8	85.6
				2-HEAiB		93.1	85.3
				2-HEAPE		98.4	77.2

For the production of benzylideneacetone from the aldol condensation between acetone and benzaldehyde, Cota et al. [32] obtained a conversion of 99.9% and 93.97 selectivity in 2 h. When choline hydroxide was employed as catalyst [25] the total conversion was obtained in 0.1 hours but due to the production of dibenzylidenacetone the selectivity to benzylidenacetone decreased around 77%.

When ILs presented in this study were employed for this reaction (entry 2, Table 1) after 2 h of reaction a conversion of 98.8% and a selectivity of 85.6% are obtained when using 2-HEAB as catalyst. Good conversion was also obtained with 2-HEAiB (93.1%) and 2-HEAPE (98.4%) with selectivity of 85.3% and 77.2% respectively.

The decrease in the selectivity to benzylidenacetone is due to the formation of secondary products which include products of aldolisation of benzylidenacetone, like dibenzylidenacetone and other oligomers.

The di- and tri- substituted ILs (2-HDEAB, 2-HTEAB, 2-HDEAiB, 2-HTEAiB, 2-HDEAPE, 2-HTEAPE) gave low conversions for the studied reactions. This low catalytic activity can be explained by the inaccessibility of the active sites of the catalyst due to the steric impediments produced by the ramification of the cation.

From the comparison made with the aforementioned basic catalysts employed for these two aldol condensation reactions we can conclude that the ILs presented in this study are not the most active catalysts for these reactions but due to their green character and easy separation from the reaction media represent a convenient and environmental friendly alternative for the traditional homogeneous catalysts.

For the repeated runs experiments, we used 2-HEAB in the condensation reaction between acetone and benzaldehyde. The catalyst was recycled 3 times, and in all runs a very good conversion was obtained. The results are presented in Figure 9.

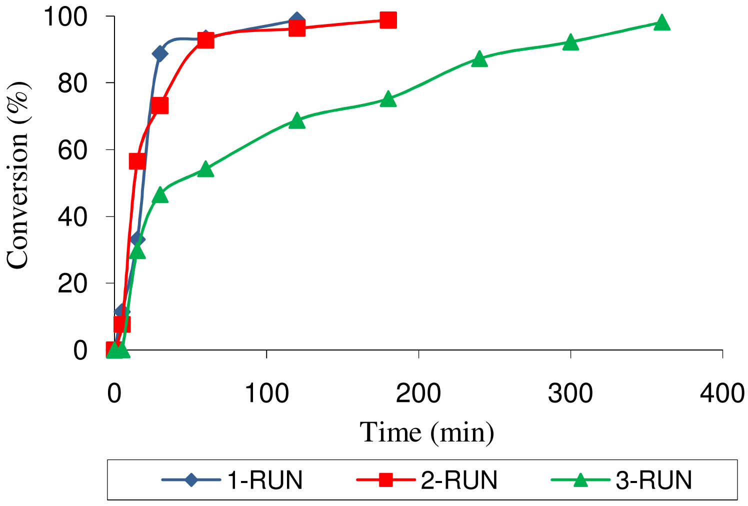


Figure 9. *Repeated runs experiments using 2-HEAB in benzylideneacetone synthesis.*

The loss of activity noticed in the second and third run can be attributed, on one hand to the loss of IL during the separation process and on the other hand due to the absorption of reaction products on the active sites of the catalyst. IL is partially soluble in the reaction product therefore during the separation procedure small quantities of IL can be dissolved in the organic phase and therefore lost during the separation process. This hypothesis is sustained by the evolution of the specific bands of the ILs which appear in the range 3500-2400 cm^{-1}, almost disappearing in the re-used sample as Figure 10 shows.

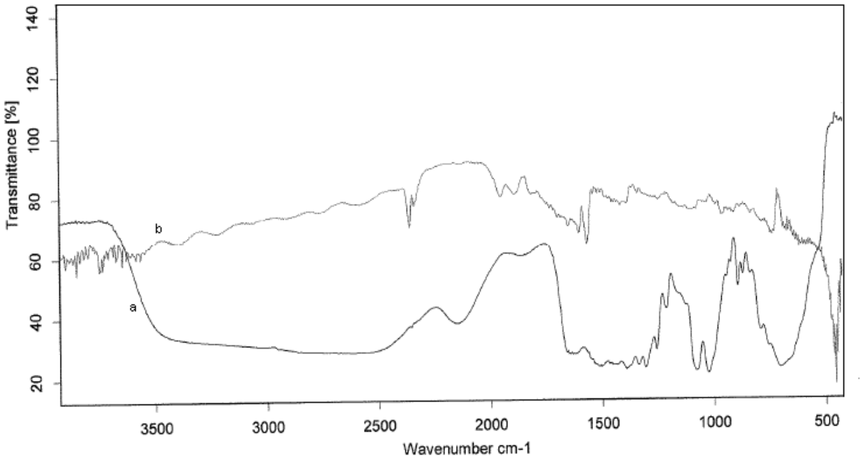


Figure 10. *FT-IR spectra for (a) 2-HEAB before reaction, (b) 2-HEAB after reaction (3 consecutive runs).*

A weak band around 1591 cm^{-1} is present in the re-used sample accounting for the carbonyl stretching and N-H plane bending vibrations. On the other hand, deactivation of the catalyst, moreover exhibiting a dark yellow colour, is probably due to the adsorption of oligomers and other secondary products on the surface of the catalyst during the reaction. This hypothesis is supported by the appearance of new bands in the re-used IL spectrum. The bands detected in the 1700-1200 cm^{-1} region corresponding to the symmetric and stretching vibrations of CH modes, can be assigned to oligomeric species adsorbed on the surface. On the other hand in the 1260-700 cm^{-1} region bands which are normally weak appear and can be assigned to the C-C skeletal vibrations.

Conclusions

In the present paper, we present a novel synthesis protocol for a new family of protic ionic liquids. The ionic structure was determined by FT-IR. An extensive study containing experimental data for density, ultrasonic velocity, ionic conductivity, viscosity, surface tension and refractive index of the liquid salts 2-hydroxy ethylammonium pentanoate (2-HEAPE), 2-hydroxy diethylammonium pentanoate (2-HDEAPE) and 2-hydroxy triethylammonium pentanoate (2-HTEAPE) is also presented. The physicochemical data of ILs are important for both, designing cleaner technological processes and understanding the interactions in this kind of compounds.

It was found that increased temperature diminishes the interaction among ions and therefore lower values of density, ultrasonic velocity, viscosity, surface tension and refractive index are obtained for increased temperatures in each case. The contrary effect is observed for conductivity.

The organic residual chain into both ions forming the IL has strong effects on the physicochemical properties, being the steric hindrance a key factor for accommodation into a liquid structure.

The catalytic potential of this new ILs was tested for two aldol condensation reactions; good results in terms of conversion and selectivity were obtained. Moreover an efficient recovery process was developed, the catalysts being recycled and reused for three consecutive cycles without significant loss of activity.

Based on these experimental observations and as explained above, because of the low cost and simplicity of synthesis, the potential interest of these liquid salts is amazing for industrial applications, as unit operations or cosolvents for catalytic reactions.

Acknowledgment

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Supplementary Information

Correlation

For compact and smooth representation, the measured magnitudes of the ILs were correlated as a function of temperature in accordance to the eq. S1:

$$\mathrm{P} = \sum_{i=1}^{N} \mathrm{A}_{\mathrm{i}} T^{i} \qquad \text{(S1)}$$

where P is the physical property (density ($g \cdot cm^{-3}$), ultrasonic velocity ($m \cdot s^{-1}$), ionic conductivity ($\mu S \cdot cm^{-1}$), refractive index, viscosity ($mPa \cdot s^{-1}$) and surface tension ($mN \cdot m^{-1}$)), and, A_i fitting parameters and T absolute temperature. N stands for the extension of the mathematical series. The fitting parameters were obtained by the unweighted least squared method applying a fitting Marquardt algorithm. The root mean square deviations were computed using eq. S2, where z is the value of the property, and n_{DAT} is the number of experimental data.

$$\sigma = \left(\frac{\sum_{i=1}^{n_{DAT}} \left(z_{exp} - z_{pred} \right)^2}{n_{DAT}} \right)^{1/2} \qquad \text{(S2)}$$

The physical properties are given in Table S1 (density and ultrasonic velocity) and Table S2-S5 (ionic conductivity, refractive index, viscosity and surface tension). The fitting parameters and the corresponding deviations are gathered in Table S6 and S7, which were computed as explained above.

Table S1 *Densities (ρ), ultrasonic velocity (u), isentropic compressibilities (κ_S), isobaric expansibilities (α), of pure ILs in the range of temperature 278.15-338.15 K*

2-hydroxy ethylammonium pentanoate (2-HEAPE)

T (K)	ρ (g·cm^{-3})	u (m·s^{-1})	κ_S (TPa^{-1})	$10^3 \cdot \alpha$ (K^{-1})	T (K)	ρ (g·cm^{-3})	u (m·s^{-1})	κ_S (TPa^{-1})	$10^3 \cdot \alpha$ (K^{-1})
338.15	1.020672	1468.15	454.54	-3.6736	307.90	1.039467	1558.18	396.24	-3.8607
337.90	1.020820	1468.77	454.09	-3.6729	307.65	1.039618	1558.99	395.77	-3.8646
337.65	1.020969	1469.46	453.60	-3.6723	307.40	1.039772	1559.78	395.31	-3.8684
337.40	1.021126	1470.18	453.08	-3.6716	307.15	1.039925	1560.61	394.83	-3.8723
337.15	1.021280	1470.87	452.59	-3.6710	306.90	1.040077	1561.44	394.35	-3.8763
336.90	1.021436	1471.58	452.09	-3.6705	306.65	1.040230	1562.25	393.89	-3.8803
336.65	1.021593	1472.29	451.58	-3.6700	306.40	1.040384	1563.08	393.41	-3.8843
336.40	1.021745	1473.00	451.08	-3.6695	306.15	1.040533	1563.89	392.94	-3.8883
336.15	1.021898	1473.73	450.56	-3.6690	305.90	1.040687	1564.73	392.47	-3.8924
335.90	1.022052	1474.42	450.07	-3.6686	305.65	1.040839	1565.55	392.00	-3.8966
335.65	1.022205	1475.12	449.58	-3.6683	305.40	1.040991	1566.38	391.52	-3.9007
335.40	1.022364	1475.83	449.08	-3.6679	305.15	1.041143	1567.19	391.06	-3.9050
335.15	1.022520	1476.54	448.58	-3.6677	304.90	1.041297	1568.03	390.59	-3.9092
334.90	1.022671	1477.24	448.09	-3.6674	304.65	1.041450	1568.87	390.11	-3.9135
334.65	1.022828	1477.95	447.59	-3.6672	304.40	1.041602	1569.72	389.63	-3.9178
334.40	1.022986	1478.66	447.09	-3.6670	304.15	1.041753	1570.56	389.16	-3.9222
334.15	1.023146	1479.37	446.59	-3.6669	303.90	1.041907	1571.39	388.69	-3.9266
333.90	1.023305	1480.07	446.10	-3.6668	303.65	1.042059	1572.25	388.21	-3.9310
333.65	1.023463	1480.78	445.60	-3.6667	303.40	1.042209	1573.09	387.74	-3.9355
333.40	1.023622	1481.49	445.11	-3.6667	303.15	1.042363	1573.94	387.26	-3.9400
333.15	1.023780	1482.20	444.61	-3.6667	302.90	1.042516	1574.79	386.79	-3.9445
332.90	1.023940	1482.92	444.11	-3.6667	302.65	1.042668	1575.65	386.31	-3.9491
332.65	1.024100	1483.63	443.62	-3.6668	302.40	1.042820	1576.51	385.83	-3.9537
332.40	1.024257	1484.34	443.12	-3.6669	302.15	1.042972	1577.39	385.34	-3.9584
332.15	1.024414	1485.06	442.63	-3.6671	301.90	1.043124	1578.23	384.88	-3.9631
331.90	1.024574	1485.77	442.13	-3.6673	301.65	1.043277	1579.11	384.39	-3.9678
331.65	1.024732	1486.48	441.64	-3.6675	301.40	1.043429	1579.97	383.92	-3.9726
331.40	1.024890	1487.19	441.15	-3.6678	301.15	1.043579	1580.82	383.45	-3.9774
331.15	1.025050	1487.90	440.66	-3.6681	300.90	1.043732	1581.71	382.96	-3.9822
330.90	1.025207	1488.62	440.17	-3.6684	300.65	1.043883	1582.58	382.49	-3.9871
330.65	1.025363	1489.35	439.67	-3.6688	300.40	1.044037	1583.48	382.00	-3.9920
330.40	1.025523	1490.05	439.19	-3.6692	300.15	1.044188	1584.38	381.51	-3.9970
330.15	1.025679	1490.79	438.69	-3.6697	299.90	1.044340	1585.27	381.02	-4.0020
329.90	1.025838	1491.51	438.20	-3.6702	299.65	1.044492	1586.16	380.54	-4.0070
329.65	1.025997	1492.23	437.71	-3.6707	299.40	1.044644	1587.08	380.04	-4.0121
329.40	1.026153	1492.96	437.21	-3.6713	299.15	1.044809	1587.96	379.56	-4.0172
329.15	1.026310	1493.70	436.71	-3.6719	298.90	1.044973	1588.87	379.07	-4.0224
328.90	1.026467	1494.41	436.23	-3.6726	298.65	1.045148	1589.78	378.57	-4.0275
328.65	1.026627	1495.14	435.74	-3.6732	298.40	1.045311	1590.70	378.07	-4.0328

T (K)	ρ (g·cm^{-3})	u (m·s^{-1})	κ_S (TPa^{-1})	$10^3 \cdot \alpha$ (K^{-1})	T (K)	ρ (g·cm^{-3})	u (m·s^{-1})	κ_S (TPa^{-1})	$10^3 \cdot \alpha$ (K^{-1})
328.15	1.026940	1496.60	434.75	-3.6747	297.90	1.045642	1592.53	377.09	-4.0433
327.90	1.027097	1497.32	434.27	-3.6755	297.65	1.045807	1593.44	376.60	-4.0487
327.65	1.027255	1498.06	433.77	-3.6764	297.40	1.045975	1594.39	376.09	-4.0540
327.40	1.027411	1498.78	433.29	-3.6772	297.15	1.046142	1595.32	375.59	-4.0594
327.15	1.027568	1499.51	432.80	-3.6781	296.90	1.046304	1596.24	375.10	-4.0649
326.90	1.027725	1500.24	432.32	-3.6791	296.65	1.046470	1597.18	374.60	-4.0704
326.65	1.027883	1500.98	431.82	-3.6801	296.40	1.046642	1598.12	374.10	-4.0759
326.40	1.028039	1501.70	431.34	-3.6811	296.15	1.046804	1599.08	373.59	-4.0814
326.15	1.028194	1502.44	430.85	-3.6821	295.90	1.046975	1600.00	373.10	-4.0870
325.90	1.028352	1503.16	430.38	-3.6832	295.65	1.047135	1600.95	372.60	-4.0927
325.65	1.028508	1503.88	429.90	-3.6844	295.40	1.047303	1601.93	372.08	-4.0983
325.40	1.028665	1504.64	429.40	-3.6855	295.15	1.047465	1602.89	371.58	-4.1041
325.15	1.028822	1505.36	428.92	-3.6868	294.90	1.047628	1603.86	371.07	-4.1098
324.90	1.028976	1506.11	428.43	-3.6880	294.65	1.047795	1604.81	370.58	-4.1156
324.65	1.029135	1506.84	427.95	-3.6893	294.40	1.047960	1605.78	370.07	-4.1214
324.40	1.029289	1507.58	427.47	-3.6906	294.15	1.048125	1606.77	369.56	-4.1273
324.15	1.029445	1508.32	426.98	-3.6920	293.90	1.048288	1607.74	369.05	-4.1332
323.90	1.029602	1509.05	426.50	-3.6934	293.65	1.048451	1608.73	368.54	-4.1391
323.65	1.029757	1509.79	426.02	-3.6948	293.40	1.048614	1609.75	368.02	-4.1451
323.40	1.029914	1510.53	425.54	-3.6963	293.15	1.048781	1610.72	367.52	-4.1511
323.15	1.030071	1511.28	425.05	-3.6978	292.90	1.048944	1611.75	366.99	-4.1571
322.90	1.030226	1512.02	424.57	-3.6993	292.65	1.049105	1612.77	366.47	-4.1632
322.65	1.030381	1512.75	424.10	-3.7009	292.40	1.049271	1613.76	365.96	-4.1693
322.40	1.030537	1513.50	423.62	-3.7025	292.15	1.049433	1614.77	365.45	-4.1755
322.15	1.030693	1514.23	423.14	-3.7042	291.90	1.049593	1615.76	364.94	-4.1817
321.90	1.030846	1514.98	422.66	-3.7059	291.65	1.049759	1616.79	364.42	-4.1879
321.65	1.031002	1515.72	422.18	-3.7076	291.40	1.049921	1617.83	363.90	-4.1942
321.40	1.031159	1516.46	421.71	-3.7094	291.15	1.050082	1618.87	363.37	-4.2005
321.15	1.031314	1517.21	421.23	-3.7112	290.90	1.050244	1619.95	362.83	-4.2068
320.90	1.031468	1517.96	420.75	-3.7130	290.65	1.050407	1620.99	362.31	-4.2132
320.65	1.031625	1518.71	420.27	-3.7149	290.40	1.050566	1622.02	361.80	-4.2196
320.40	1.031780	1519.46	419.79	-3.7168	290.15	1.050730	1623.16	361.23	-4.2261
320.15	1.031934	1520.22	419.31	-3.7188	289.90	1.050889	1624.19	360.72	-4.2326
319.90	1.032088	1520.97	418.83	-3.7208	289.65	1.051050	1625.29	360.18	-4.2391
319.65	1.032243	1521.73	418.35	-3.7228	289.40	1.051211	1626.38	359.64	-4.2457
319.40	1.032399	1522.49	417.87	-3.7249	289.15	1.051372	1627.47	359.10	-4.2523
319.15	1.032553	1523.24	417.40	-3.7270	288.90	1.051531	1628.60	358.55	-4.2590
318.90	1.032709	1524.00	416.92	-3.7292	288.65	1.051691	1629.70	358.01	-4.2656
318.65	1.032862	1524.77	416.44	-3.7313	288.40	1.051853	1630.82	357.46	-4.2724
318.40	1.033016	1525.53	415.96	-3.7336	288.15	1.052010	1631.92	356.93	-4.2791
318.15	1.033171	1526.28	415.49	-3.7358	287.90	1.052170	1633.05	356.38	-4.2859
317.90	1.033327	1527.05	415.01	-3.7381	287.65	1.052330	1634.18	355.83	-4.2928

T (K)	ρ ($g\cdot cm^{-3}$)	u ($m\cdot s^{-1}$)	κ_S (TPa^{-1})	$10^3\cdot\alpha$ (K^{-1})	T (K)	ρ ($g\cdot cm^{-3}$)	u ($m\cdot s^{-1}$)	κ_S (TPa^{-1})	$10^3\cdot\alpha$ (K^{-1})
317.40	1.033635	1528.57	414.06	-3.7428	287.15	1.052647	1636.52	354.71	-4.3065
317.15	1.033790	1529.33	413.59	-3.7452	286.90	1.052803	1637.66	354.16	-4.3135
316.90	1.033943	1530.10	413.11	-3.7477	286.65	1.052964	1638.82	353.61	-4.3205
316.65	1.034098	1530.86	412.64	-3.7502	286.40	1.053121	1639.97	353.06	-4.3275
316.40	1.034253	1531.63	412.16	-3.7527	286.15	1.053282	1641.17	352.49	-4.3345
316.15	1.034406	1532.39	411.69	-3.7552	285.90	1.053440	1642.36	351.93	-4.3416
315.90	1.034559	1533.16	411.22	-3.7578	285.65	1.053595	1643.59	351.35	-4.3488
315.65	1.034714	1533.92	410.75	-3.7605	285.40	1.053757	1644.76	350.80	-4.3559
315.40	1.034867	1534.71	410.26	-3.7631	285.15	1.053914	1645.91	350.25	-4.3632
315.15	1.035022	1535.47	409.80	-3.7659	284.90	1.054069	1647.20	349.65	-4.3704
314.90	1.035175	1536.22	409.34	-3.7686	284.65	1.054227	1648.38	349.10	-4.3777
314.65	1.035330	1536.99	408.86	-3.7714	284.40	1.054384	1649.68	348.50	-4.3850
314.40	1.035483	1537.77	408.39	-3.7742	284.15	1.054542	1650.96	347.91	-4.3924
314.15	1.035638	1538.53	407.92	-3.7771	283.90	1.054697	1652.23	347.32	-4.3998
313.90	1.035792	1539.30	407.46	-3.7800	283.65	1.054853	1653.49	346.74	-4.4072
313.65	1.035945	1540.06	406.99	-3.7829	283.40	1.055012	1654.78	346.15	-4.4147
313.40	1.036100	1540.83	406.53	-3.7859	283.15	1.055166	1656.17	345.52	-4.4222
313.15	1.036252	1541.60	406.06	-3.7889	282.90	1.055325	1657.46	344.93	-4.4297
312.90	1.036406	1542.37	405.60	-3.7919	282.65	1.055479	1658.73	344.35	-4.4373
312.65	1.036558	1543.14	405.13	-3.7950	282.40	1.055637	1660.17	343.70	-4.4449
312.40	1.036711	1543.91	404.67	-3.7981	282.15	1.055795	1661.49	343.10	-4.4526
312.15	1.036865	1544.69	404.20	-3.8013	281.90	1.055948	1662.83	342.50	-4.4603
311.90	1.037019	1545.47	403.73	-3.8045	281.65	1.056104	1664.24	341.87	-4.4680
311.65	1.037171	1546.25	403.26	-3.8077	281.40	1.056260	1665.61	341.26	-4.4758
311.40	1.037325	1547.02	402.80	-3.8110	281.15	1.056416	1667.01	340.63	-4.4836
311.15	1.037479	1547.82	402.33	-3.8143	280.90	1.056572	1668.41	340.01	-4.4914
310.90	1.037631	1548.60	401.86	-3.8176	280.65	1.056727	1669.88	339.36	-4.4993
310.65	1.037785	1549.39	401.39	-3.8210	280.40	1.056883	1671.29	338.74	-4.5072
310.40	1.037938	1550.17	400.93	-3.8244	280.15	1.057038	1672.76	338.10	-4.5152
310.15	1.038089	1550.96	400.46	-3.8279	279.90	1.057192	1674.21	337.46	-4.5232
309.90	1.038244	1551.75	400.00	-3.8314	279.65	1.057349	1675.59	336.86	-4.5312
309.65	1.038396	1552.56	399.52	-3.8349	279.40	1.057504	1677.18	336.17	-4.5393
309.40	1.038550	1553.36	399.05	-3.8385	279.15	1.057659	1678.69	335.52	-4.5474
309.15	1.038704	1554.16	398.58	-3.8421	278.90	1.057816	1680.20	334.86	-4.5556
308.90	1.038856	1554.95	398.12	-3.8458	278.65	1.057971	1681.62	334.25	-4.5637
308.65	1.039008	1555.77	397.64	-3.8494	278.40	1.058124	1683.11	333.61	-4.5720
308.40	1.039161	1556.55	397.18	-3.8532	278.15	1.058279	1684.75	332.91	-4.5802
308.15	1.039313	1557.36	396.71	-3.8569					

2-hydroxy diethylammonium pentanoate (2-HDEAPE)

T (K)	ρ ($g\cdot cm^{-3}$)	u ($m\cdot s^{-1}$)	κ_S (TPa^{-1})	$10^3\cdot\alpha$ (K^{-1})	T (K)	ρ ($g\cdot cm^{-3}$)	u ($m\cdot s^{-1}$)	κ_S (TPa^{-1})	$10^3\cdot\alpha$ (K^{-1})
338.15	1.045572	1464.17	446.13	-8.6736	307.90	1.066247	1556.31	387.21	-8.8607
337.90	1.045741	1464.80	445.68	-8.6729	307.65	1.066416	1557.13	386.74	-8.8646
337.65	1.045910	1465.50	445.18	-8.6723	307.40	1.066584	1557.97	386.27	-8.8684
337.40	1.046085	1466.22	444.67	-8.6716	307.15	1.066753	1558.79	385.80	-8.8723
337.15	1.046255	1466.93	444.16	-8.6710	306.90	1.066923	1559.62	385.33	-8.8763
336.90	1.046428	1467.66	443.65	-8.6705	306.65	1.067093	1560.47	384.85	-8.8803
336.65	1.046599	1468.39	443.14	-8.6700	306.40	1.067261	1561.30	384.38	-8.8843
336.40	1.046772	1469.13	442.62	-8.6695	306.15	1.067430	1562.14	383.90	-8.8883
336.15	1.046942	1469.86	442.11	-8.6690	305.90	1.067599	1562.98	383.43	-8.8924
335.90	1.047115	1470.58	441.60	-8.6686	305.65	1.067768	1563.85	382.94	-8.8966
335.65	1.047287	1471.30	441.09	-8.6683	305.40	1.067936	1564.66	382.49	-8.9007
335.40	1.047460	1472.04	440.58	-8.6679	305.15	1.068105	1565.50	382.01	-8.9050
335.15	1.047627	1472.78	440.07	-8.6677	304.90	1.068274	1566.37	381.53	-8.9092
334.90	1.047805	1473.51	439.56	-8.6674	304.65	1.068442	1567.19	381.07	-8.9135
334.65	1.047968	1474.25	439.05	-8.6672	304.40	1.068612	1568.07	380.58	-8.9178
334.40	1.048140	1474.98	438.54	-8.6670	304.15	1.068779	1568.91	380.12	-8.9222
334.15	1.048318	1475.72	438.03	-8.6669	303.90	1.068948	1569.78	379.63	-8.9266
333.90	1.048485	1476.45	437.52	-8.6668	303.65	1.069115	1570.63	379.16	-8.9310
333.65	1.048658	1477.19	437.01	-8.6667	303.40	1.069286	1571.48	378.69	-8.9355
333.40	1.048828	1477.92	436.51	-8.6667	303.15	1.069452	1572.35	378.22	-8.9400
333.15	1.049001	1478.67	436.00	-8.6667	302.90	1.069620	1573.20	377.75	-8.9445
332.90	1.049169	1479.40	435.50	-8.6667	302.65	1.069788	1574.08	377.27	-8.9491
332.65	1.049337	1480.14	434.99	-8.6668	302.40	1.069957	1574.96	376.79	-8.9537
332.40	1.049508	1480.87	434.49	-8.6669	302.15	1.070126	1575.82	376.32	-8.9584
332.15	1.049686	1481.61	433.98	-8.6671	301.90	1.070292	1576.69	375.84	-8.9631
331.90	1.049857	1482.35	433.48	-8.6673	301.65	1.070463	1577.58	375.36	-8.9678
331.65	1.050023	1483.10	432.97	-8.6675	301.40	1.070630	1578.44	374.89	-8.9726
331.40	1.050194	1483.83	432.48	-8.6678	301.15	1.070799	1579.34	374.40	-8.9774
331.15	1.050362	1484.57	431.98	-8.6681	300.90	1.070966	1580.22	373.93	-8.9822
330.90	1.050532	1485.32	431.47	-8.6684	300.65	1.071134	1581.10	373.45	-8.9871
330.65	1.050703	1486.05	430.98	-8.6688	300.40	1.071302	1582.01	372.97	-8.9920
330.40	1.050872	1486.80	430.47	-8.6692	300.15	1.071470	1582.90	372.49	-8.9970
330.15	1.051040	1487.53	429.98	-8.6697	299.90	1.071638	1583.79	372.01	-9.0020
329.90	1.051211	1488.29	429.47	-8.6702	299.65	1.071804	1584.70	371.53	-9.0070
329.65	1.051381	1489.03	428.98	-8.6707	299.40	1.071973	1585.60	371.05	-9.0121
329.40	1.051551	1489.77	428.48	-8.6713	299.15	1.072140	1586.50	370.57	-9.0172
329.15	1.051721	1490.52	427.98	-8.6719	298.90	1.072308	1587.43	370.08	-9.0224
328.90	1.051888	1491.27	427.48	-8.6726	298.65	1.072477	1588.34	369.59	-9.0275
328.65	1.052060	1492.01	426.99	-8.6732	298.40	1.072643	1589.25	369.11	-9.0328
328.40	1.052227	1492.76	426.49	-8.6740	298.15	1.072811	1590.19	368.62	-9.0380

T (K)	ρ ($g·cm^{-3}$)	u ($m·s^{-1}$)	κ_S (TPa^{-1})	$10^3 \cdot \alpha$ (K^{-1})	T (K)	ρ ($g·cm^{-3}$)	u ($m·s^{-1}$)	κ_S (TPa^{-1})	$10^3 \cdot \alpha$ (K^{-1})
328.15	1.052394	1493.50	426.00	-8.6747	297.90	1.072979	1591.10	368.14	-9.0433
327.65	1.052738	1495.00	425.01	-8.6764	297.40	1.073314	1592.99	367.15	-9.0540
327.40	1.052901	1495.75	424.52	-8.6772	297.15	1.073481	1593.92	366.67	-9.0594
327.15	1.053075	1496.50	424.02	-8.6781	296.90	1.073648	1594.85	366.18	-9.0649
326.90	1.053234	1497.24	423.54	-8.6791	296.65	1.073815	1595.81	365.69	-9.0704
326.65	1.053409	1497.99	423.04	-8.6801	296.40	1.073984	1596.77	365.19	-9.0759
326.40	1.053575	1498.74	422.55	-8.6811	296.15	1.074153	1597.71	364.70	-9.0814
326.15	1.053744	1499.49	422.06	-8.6821	295.90	1.074318	1598.66	364.21	-9.0870
325.90	1.053917	1500.24	421.57	-8.6832	295.65	1.074485	1599.63	363.71	-9.0927
325.65	1.054080	1500.99	421.09	-8.6844	295.40	1.074652	1600.57	363.23	-9.0983
325.40	1.054248	1501.75	420.59	-8.6855	295.15	1.074820	1601.56	362.73	-9.1041
325.15	1.054420	1502.49	420.11	-8.6868	294.90	1.074987	1602.52	362.23	-9.1098
324.90	1.054593	1503.25	419.62	-8.6880	294.65	1.075155	1603.50	361.74	-9.1156
324.65	1.054766	1503.99	419.14	-8.6893	294.40	1.075322	1604.46	361.25	-9.1214
324.40	1.054939	1504.73	418.65	-8.6906	294.15	1.075488	1605.44	360.75	-9.1273
324.15	1.055113	1505.49	418.16	-8.6920	293.90	1.075657	1606.44	360.24	-9.1332
323.90	1.055287	1506.24	417.68	-8.6934	293.65	1.075836	1607.44	359.74	-9.1391
323.65	1.055460	1507.00	417.19	-8.6948	293.40	1.076021	1608.46	359.22	-9.1451
323.40	1.055632	1507.75	416.71	-8.6963	293.15	1.076209	1609.45	358.71	-9.1511
323.15	1.055807	1508.50	416.22	-8.6978	292.90	1.076392	1610.45	358.21	-9.1571
322.90	1.055981	1509.25	415.74	-8.6993	292.65	1.076570	1611.47	357.70	-9.1632
322.65	1.056154	1510.02	415.25	-8.7009	292.40	1.076757	1612.48	357.19	-9.1693
322.40	1.056326	1510.77	414.77	-8.7025	292.15	1.076944	1613.52	356.66	-9.1755
322.15	1.056500	1511.53	414.28	-8.7042	291.90	1.077124	1614.54	356.15	-9.1817
321.90	1.056672	1512.28	413.80	-8.7059	291.65	1.077306	1615.54	355.65	-9.1879
321.65	1.056845	1513.04	413.32	-8.7076	291.40	1.077493	1616.60	355.12	-9.1942
321.40	1.057019	1513.79	412.84	-8.7094	291.15	1.077675	1617.64	354.61	-9.2005
321.15	1.057190	1514.55	412.36	-8.7112	290.90	1.077859	1618.70	354.08	-9.2068
320.90	1.057365	1515.31	411.88	-8.7130	290.65	1.078041	1619.77	353.56	-9.2132
320.65	1.057536	1516.06	411.41	-8.7149	290.40	1.078225	1620.83	353.03	-9.2196
320.40	1.057708	1516.83	410.92	-8.7168	290.15	1.078411	1621.89	352.51	-9.2261
320.15	1.057879	1517.59	410.45	-8.7188	289.90	1.078588	1623.01	351.97	-9.2326
319.90	1.058053	1518.35	409.97	-8.7208	289.65	1.078774	1624.08	351.44	-9.2391
319.65	1.058224	1519.12	409.49	-8.7228	289.40	1.078954	1625.20	350.90	-9.2457
319.40	1.058399	1519.88	409.01	-8.7249	289.15	1.079132	1626.29	350.37	-9.2523
319.15	1.058571	1520.65	408.53	-8.7270	288.90	1.079315	1627.42	349.83	-9.2590
318.90	1.058741	1521.41	408.05	-8.7292	288.65	1.079497	1628.53	349.29	-9.2656
318.65	1.058914	1522.17	407.58	-8.7313	288.40	1.079678	1629.66	348.75	-9.2724
318.40	1.059086	1522.95	407.10	-8.7336	288.15	1.079857	1630.78	348.21	-9.2791
318.15	1.059259	1523.73	406.61	-8.7358	287.90	1.080038	1631.93	347.66	-9.2859
317.90	1.059430	1524.49	406.14	-8.7381	287.65	1.080216	1633.09	347.11	-9.2928

T (K)	ρ ($g \cdot cm^{-3}$)	u ($m \cdot s^{-1}$)	κ_S (TPa^{-1})	$10^3 \cdot \alpha$ (K^{-1})	T (K)	ρ ($g \cdot cm^{-3}$)	u ($m \cdot s^{-1}$)	κ_S (TPa^{-1})	$10^3 \cdot \alpha$ (K^{-1})
317.65	1.059601	1525.27	405.66	-8.7405	287.40	1.080398	1634.24	346.56	-9.2996
317.40	1.059774	1526.03	405.19	-8.7428	287.15	1.080575	1635.41	346.01	-9.3065
316.90	1.060115	1527.58	404.24	-8.7477	286.65	1.080932	1637.77	344.90	-9.3205
316.65	1.060285	1528.34	403.77	-8.7502	286.40	1.081110	1638.95	344.35	-9.3275
316.40	1.060458	1529.13	403.29	-8.7527	286.15	1.081290	1640.13	343.80	-9.3345
316.15	1.060631	1529.91	402.81	-8.7552	285.90	1.081465	1641.32	343.24	-9.3416
315.90	1.060801	1530.70	402.33	-8.7578	285.65	1.081641	1642.52	342.69	-9.3488
315.65	1.060971	1531.47	401.86	-8.7605	285.40	1.081818	1643.81	342.09	-9.3559
315.40	1.061145	1532.26	401.38	-8.7631	285.15	1.081999	1645.02	341.53	-9.3632
315.15	1.061314	1533.03	400.92	-8.7659	284.90	1.082174	1646.22	340.98	-9.3704
314.90	1.061486	1533.82	400.44	-8.7686	284.65	1.082348	1647.45	340.41	-9.3777
314.65	1.061658	1534.60	399.97	-8.7714	284.40	1.082526	1648.74	339.83	-9.3850
314.40	1.061826	1535.38	399.50	-8.7742	284.15	1.082700	1649.92	339.29	-9.3924
314.15	1.061997	1536.18	399.02	-8.7771	283.90	1.082876	1651.24	338.69	-9.3998
313.90	1.062170	1536.98	398.54	-8.7800	283.65	1.083050	1652.56	338.09	-9.4072
313.65	1.062339	1537.75	398.08	-8.7829	283.40	1.083225	1653.84	337.52	-9.4147
313.40	1.062510	1538.55	397.60	-8.7859	283.15	1.083400	1655.22	336.90	-9.4222
313.15	1.062680	1539.34	397.13	-8.7889	282.90	1.083573	1656.53	336.31	-9.4297
312.90	1.062850	1540.14	396.65	-8.7919	282.65	1.083748	1657.87	335.71	-9.4373
312.65	1.063023	1540.93	396.18	-8.7950	282.40	1.083922	1659.21	335.12	-9.4449
312.40	1.063189	1541.71	395.72	-8.7981	282.15	1.084095	1660.62	334.50	-9.4526
312.15	1.063360	1542.51	395.24	-8.8013	281.90	1.084270	1661.97	333.90	-9.4603
311.90	1.063530	1543.32	394.76	-8.8045	281.65	1.084441	1663.38	333.28	-9.4680
311.65	1.063702	1544.10	394.30	-8.8077	281.40	1.084612	1664.76	332.68	-9.4758
311.40	1.063872	1544.92	393.82	-8.8110	281.15	1.084788	1666.20	332.05	-9.4836
311.15	1.064042	1545.72	393.35	-8.8143	280.90	1.084959	1667.66	331.41	-9.4914
310.90	1.064212	1546.52	392.88	-8.8176	280.65	1.085133	1669.07	330.80	-9.4993
310.65	1.064382	1547.32	392.41	-8.8210	280.40	1.085303	1670.59	330.15	-9.5072
310.40	1.064552	1548.13	391.94	-8.8244	280.15	1.085475	1672.05	329.52	-9.5152
310.15	1.064721	1548.93	391.47	-8.8279	279.90	1.085647	1673.53	328.89	-9.5232
309.90	1.064892	1549.75	390.99	-8.8314	279.65	1.085819	1675.09	328.22	-9.5312
309.65	1.065061	1550.57	390.52	-8.8349	279.40	1.085988	1676.62	327.57	-9.5393
309.40	1.065230	1551.37	390.05	-8.8385	279.15	1.086160	1678.10	326.94	-9.5474
309.15	1.065400	1552.20	389.58	-8.8421	278.90	1.086331	1679.73	326.26	-9.5556
308.90	1.065569	1553.02	389.10	-8.8458	278.65	1.086502	1681.23	325.62	-9.5637
308.65	1.065740	1553.84	388.63	-8.8494	278.40	1.086672	1682.86	324.94	-9.5720
308.40	1.065907	1554.66	388.16	-8.8532	278.15	1.086841	1684.36	324.31	-9.5802
308.15	1.066076	1555.48	387.69	-8.8569					

2-hydroxy triethylammonium pentanoate (2-HTEAPE)

T (K)	ρ ($g\cdot cm^{-3}$)	u ($m\cdot s^{-1}$)	κ_S (TPa^{-1})	$10^3 \cdot \alpha$ (K^{-1})	T (K)	ρ ($g\cdot cm^{-3}$)	u ($m\cdot s^{-1}$)	κ_S (TPa^{-1})	$10^3 \cdot \alpha$ (K^{-1})
338.15	1.062539	1445.65	450.33	-5.0063	307.90	1.085772	1548.05	384.32	-5.1747
337.90	1.062705	1446.28	449.87	-5.0056	307.65	1.085966	1549.01	383.77	-5.1781
337.65	1.062896	1447.00	449.34	-5.0050	307.40	1.086160	1549.99	383.22	-5.1816
337.40	1.063083	1447.74	448.80	-5.0045	307.15	1.086353	1550.97	382.67	-5.1851
337.15	1.063273	1448.47	448.27	-5.0039	306.90	1.086547	1551.96	382.11	-5.1887
336.90	1.063462	1449.23	447.72	-5.0034	306.65	1.086740	1552.95	381.56	-5.1922
336.65	1.063653	1449.98	447.17	-5.0030	306.40	1.086934	1553.96	380.99	-5.1959
336.40	1.063843	1450.73	446.63	-5.0025	306.15	1.087126	1554.93	380.45	-5.1995
336.15	1.064028	1451.49	446.09	-5.0021	305.90	1.087319	1555.95	379.88	-5.2032
335.90	1.064219	1452.23	445.55	-5.0018	305.65	1.087512	1556.95	379.33	-5.2069
335.65	1.064414	1452.99	445.00	-5.0014	305.40	1.087706	1557.95	378.78	-5.2107
335.40	1.064601	1453.76	444.45	-5.0012	305.15	1.087900	1558.96	378.22	-5.2145
335.15	1.064795	1454.53	443.90	-5.0009	304.90	1.088090	1559.98	377.66	-5.2183
334.90	1.064988	1455.30	443.35	-5.0007	304.65	1.088284	1561.00	377.10	-5.2221
334.65	1.065176	1456.06	442.81	-5.0005	304.40	1.088477	1562.03	376.53	-5.2260
334.40	1.065369	1456.82	442.27	-5.0003	304.15	1.088669	1563.05	375.97	-5.2300
334.15	1.065560	1457.60	441.72	-5.0002	303.90	1.088862	1564.07	375.42	-5.2339
333.90	1.065751	1458.38	441.17	-5.0001	303.65	1.089053	1565.11	374.85	-5.2379
333.65	1.065946	1459.15	440.62	-5.0000	303.40	1.089247	1566.14	374.29	-5.2419
333.40	1.066134	1459.93	440.07	-5.0000	303.15	1.089439	1567.17	373.74	-5.2460
333.15	1.066327	1460.70	439.53	-5.0000	302.90	1.089632	1568.22	373.17	-5.2501
332.90	1.066516	1461.48	438.98	-5.0001	302.65	1.089823	1569.26	372.61	-5.2542
332.65	1.066708	1462.27	438.43	-5.0001	302.40	1.090015	1570.32	372.04	-5.2584
332.40	1.066899	1463.02	437.90	-5.0002	302.15	1.090207	1571.38	371.47	-5.2625
332.15	1.067091	1463.82	437.34	-5.0004	301.90	1.090400	1572.43	370.91	-5.2668
331.90	1.067287	1464.63	436.78	-5.0006	301.65	1.090592	1573.46	370.36	-5.2710
331.65	1.067474	1465.40	436.24	-5.0008	301.40	1.090785	1574.54	369.79	-5.2753
331.40	1.067667	1466.18	435.70	-5.0010	301.15	1.090976	1575.60	369.23	-5.2797
331.15	1.067854	1466.98	435.15	-5.0013	300.90	1.091169	1576.66	368.66	-5.2840
330.90	1.068052	1467.77	434.60	-5.0016	300.65	1.091358	1577.74	368.10	-5.2884
330.65	1.068238	1468.56	434.06	-5.0019	300.40	1.091551	1578.80	367.54	-5.2928
330.40	1.068430	1469.37	433.50	-5.0023	300.15	1.091742	1579.91	366.96	-5.2973
330.15	1.068624	1470.16	432.96	-5.0027	299.90	1.091935	1580.97	366.40	-5.3018
329.90	1.068811	1470.95	432.42	-5.0032	299.65	1.092126	1582.08	365.82	-5.3063
329.65	1.069004	1471.75	431.87	-5.0037	299.40	1.092319	1583.18	365.25	-5.3109
329.40	1.069193	1472.55	431.32	-5.0042	299.15	1.092511	1584.24	364.70	-5.3155
329.15	1.069383	1473.33	430.79	-5.0047	298.90	1.092700	1585.39	364.11	-5.3201
328.90	1.069578	1474.13	430.25	-5.0053	298.65	1.092894	1586.48	363.54	-5.3248
328.65	1.069770	1474.94	429.70	-5.0059	298.40	1.093084	1587.60	362.96	-5.3295
328.40	1.069960	1475.73	429.16	-5.0066	298.15	1.093275	1588.71	362.39	-5.3342

T (K)	ρ ($g \cdot cm^{-3}$)	u ($m \cdot s^{-1}$)	κ_S (TPa^{-1})	$10^3 \cdot \alpha$ (K^{-1})	T (K)	ρ ($g \cdot cm^{-3}$)	u ($m \cdot s^{-1}$)	κ_S (TPa^{-1})	$10^3 \cdot \alpha$ (K^{-1})
327.90	1.070341	1477.34	428.07	-5.0080	297.65	1.093659	1590.96	361.24	-5.3438
327.65	1.070530	1478.13	427.54	-5.0087	297.40	1.093850	1592.11	360.66	-5.3486
327.40	1.070720	1478.94	427.00	-5.0095	297.15	1.094042	1593.22	360.09	-5.3535
327.15	1.070915	1479.74	426.46	-5.0103	296.90	1.094232	1594.35	359.52	-5.3584
326.90	1.071102	1480.54	425.92	-5.0112	296.65	1.094423	1595.49	358.94	-5.3633
326.65	1.071295	1481.34	425.38	-5.0121	296.40	1.094614	1596.62	358.37	-5.3683
326.40	1.071488	1482.16	424.84	-5.0130	296.15	1.094806	1597.77	357.80	-5.3733
326.15	1.071676	1482.97	424.30	-5.0139	295.90	1.094997	1598.93	357.21	-5.3783
325.90	1.071872	1483.78	423.76	-5.0149	295.65	1.095186	1600.05	356.65	-5.3834
325.65	1.072055	1484.59	423.22	-5.0159	295.40	1.095379	1601.24	356.06	-5.3885
325.40	1.072255	1485.41	422.68	-5.0170	295.15	1.095570	1602.39	355.49	-5.3937
325.15	1.072442	1486.22	422.14	-5.0181	294.90	1.095762	1603.56	354.91	-5.3988
324.90	1.072634	1487.04	421.60	-5.0192	294.65	1.095951	1604.72	354.33	-5.4040
324.65	1.072821	1487.87	421.06	-5.0204	294.40	1.096142	1605.91	353.75	-5.4093
324.40	1.073014	1488.68	420.53	-5.0215	294.15	1.096333	1607.07	353.17	-5.4145
324.15	1.073205	1489.51	419.98	-5.0228	293.90	1.096523	1608.26	352.59	-5.4198
323.90	1.073393	1490.33	419.45	-5.0240	293.65	1.096713	1609.43	352.02	-5.4252
323.65	1.073587	1491.16	418.90	-5.0253	293.40	1.096905	1610.64	351.43	-5.4306
323.40	1.073776	1491.98	418.37	-5.0266	293.15	1.097096	1611.84	350.84	-5.4360
323.15	1.073972	1492.84	417.81	-5.0280	292.90	1.097286	1613.03	350.26	-5.4414
322.90	1.074155	1493.65	417.29	-5.0294	292.65	1.097477	1614.22	349.69	-5.4469
322.65	1.074345	1494.49	416.74	-5.0308	292.40	1.097669	1615.44	349.10	-5.4524
322.40	1.074538	1495.33	416.20	-5.0323	292.15	1.097859	1616.63	348.52	-5.4579
322.15	1.074727	1496.18	415.66	-5.0338	291.90	1.098050	1617.88	347.92	-5.4635
321.90	1.074918	1497.00	415.13	-5.0353	291.65	1.098238	1619.06	347.36	-5.4691
321.65	1.075106	1497.83	414.59	-5.0369	291.40	1.098430	1620.28	346.77	-5.4748
321.40	1.075296	1498.70	414.04	-5.0384	291.15	1.098620	1621.54	346.18	-5.4804
321.15	1.075488	1499.54	413.50	-5.0401	290.90	1.098812	1622.78	345.59	-5.4862
320.90	1.075681	1500.40	412.95	-5.0417	290.65	1.099018	1624.03	344.99	-5.4919
320.65	1.075865	1501.25	412.42	-5.0434	290.40	1.099221	1625.27	344.40	-5.4977
320.40	1.076053	1502.12	411.87	-5.0452	290.15	1.099435	1626.54	343.80	-5.5035
320.15	1.076244	1503.00	411.31	-5.0469	289.90	1.099641	1627.83	343.19	-5.5093
319.90	1.076436	1503.87	410.76	-5.0487	289.65	1.099849	1629.09	342.59	-5.5152
319.65	1.076626	1504.74	410.22	-5.0506	289.40	1.100069	1630.42	341.96	-5.5211
319.40	1.076812	1505.64	409.65	-5.0524	289.15	1.100275	1631.64	341.39	-5.5271
319.15	1.077003	1506.52	409.10	-5.0543	288.90	1.100484	1632.95	340.78	-5.5331
318.90	1.077198	1507.42	408.54	-5.0562	288.65	1.100691	1634.27	340.16	-5.5391
318.65	1.077392	1508.31	407.99	-5.0582	288.40	1.100901	1635.61	339.54	-5.5451
318.40	1.077588	1509.18	407.44	-5.0602	288.15	1.101110	1636.91	338.94	-5.5512
318.15	1.077784	1510.08	406.88	-5.0622	287.90	1.101318	1638.20	338.34	-5.5573
317.90	1.077982	1510.96	406.33	-5.0643	287.65	1.101528	1639.55	337.72	-5.5635
317.65	1.078178	1511.84	405.79	-5.0664	287.40	1.101732	1640.87	337.11	-5.5697

T (K)	ρ ($g \cdot cm^{-3}$)	u ($m \cdot s^{-1}$)	κ_S (TPa^{-1})	$10^3 \cdot \alpha$ (K^{-1})	T (K)	ρ ($g \cdot cm^{-3}$)	u ($m \cdot s^{-1}$)	κ_S (TPa^{-1})	$10^3 \cdot \alpha$ (K^{-1})
317.15	1.078569	1513.62	404.69	-5.0707	286.90	1.102147	1643.52	335.90	-5.5821
316.90	1.078762	1514.49	404.15	-5.0729	286.65	1.102356	1644.86	335.29	-5.5884
316.65	1.078959	1515.40	403.59	-5.0752	286.40	1.102561	1646.21	334.68	-5.5947
316.40	1.079155	1516.29	403.04	-5.0774	286.15	1.102772	1647.58	334.06	-5.6011
316.15	1.079352	1517.19	402.49	-5.0797	285.90	1.102970	1648.93	333.45	-5.6075
315.90	1.079547	1518.10	401.94	-5.0821	285.65	1.103177	1650.33	332.82	-5.6139
315.65	1.079742	1519.01	401.38	-5.0844	285.40	1.103385	1651.74	332.19	-5.6204
315.40	1.079937	1519.92	400.83	-5.0868	285.15	1.103587	1653.13	331.57	-5.6268
315.15	1.080132	1520.81	400.29	-5.0893	284.90	1.103792	1654.59	330.93	-5.6334
314.90	1.080328	1521.72	399.74	-5.0917	284.65	1.103997	1655.98	330.31	-5.6399
314.65	1.080524	1522.64	399.18	-5.0942	284.40	1.104199	1657.39	329.69	-5.6465
314.40	1.080720	1523.56	398.63	-5.0968	284.15	1.104402	1658.82	329.06	-5.6531
314.15	1.080915	1524.48	398.08	-5.0994	283.90	1.104605	1660.28	328.42	-5.6598
313.90	1.081109	1525.43	397.51	-5.1020	283.65	1.104803	1661.78	327.77	-5.6665
313.65	1.081304	1526.33	396.97	-5.1046	283.40	1.105010	1663.27	327.12	-5.6732
313.40	1.081499	1527.27	396.41	-5.1073	283.15	1.105210	1664.72	326.49	-5.6800
313.15	1.081694	1528.20	395.85	-5.1100	282.90	1.105411	1666.23	325.84	-5.6868
312.90	1.081890	1529.13	395.30	-5.1127	282.65	1.105611	1667.75	325.19	-5.6936
312.65	1.082084	1530.06	394.75	-5.1155	282.40	1.105815	1669.23	324.55	-5.7004
312.40	1.082278	1530.99	394.20	-5.1183	282.15	1.106009	1670.77	323.90	-5.7073
312.15	1.082473	1531.95	393.64	-5.1212	281.90	1.106211	1672.29	323.25	-5.7143
311.90	1.082667	1532.85	393.10	-5.1240	281.65	1.106411	1673.87	322.58	-5.7212
311.65	1.082862	1533.78	392.56	-5.1269	281.40	1.106609	1675.44	321.92	-5.7282
311.40	1.083057	1534.75	391.99	-5.1299	281.15	1.106808	1676.99	321.27	-5.7352
311.15	1.083251	1535.67	391.45	-5.1329	280.90	1.107004	1678.63	320.58	-5.7423
310.90	1.083446	1536.62	390.89	-5.1359	280.65	1.107204	1680.19	319.93	-5.7494
310.65	1.083641	1537.55	390.35	-5.1389	280.40	1.107398	1681.78	319.27	-5.7565
310.40	1.083834	1538.49	389.81	-5.1420	280.15	1.107595	1683.55	318.54	-5.7637
310.15	1.084029	1539.44	389.25	-5.1451	279.90	1.107793	1685.08	317.91	-5.7709
309.90	1.084222	1540.39	388.71	-5.1483	279.65	1.107991	1686.81	317.20	-5.7781
309.65	1.084417	1541.34	388.16	-5.1514	279.40	1.108189	1688.46	316.52	-5.7854
309.40	1.084610	1542.30	387.60	-5.1547	279.15	1.108380	1690.11	315.85	-5.7927
309.15	1.084804	1543.24	387.06	-5.1579	278.90	1.108579	1691.83	315.15	-5.8000
308.90	1.084998	1544.20	386.51	-5.1612	278.65	1.108774	1693.58	314.45	-5.8074
308.65	1.085191	1545.14	385.97	-5.1645	278.40	1.108969	1695.33	313.74	-5.8148
308.40	1.085386	1546.11	385.42	-5.1679	278.15	1.109162	1697.09	313.04	-5.8222
308.15	1.085579	1547.07	384.87	-5.1712					

Table S2 *Values of ionic conductivity (μS·cm^{-1}) for the studied ILs in the temperature range 278.15 – 338.15 K*

Temperature	2-HEAPE	2-HDEAPE	2-HTEAPE
278.15	83.6	73.1	53.2
288.15	143.3	132.7	95.9
298.15	239.6	218.8	160.1
308.15	453.4	394.0	284.1
318.15	632.6	559.4	413.8
328.15	910.8	821.7	576.2
338.15	1202.9	1089.0	781.11

Table S3 *Values of refractive index for the studied ILs in the temperature range 288.15 – 323.15 K*

Temperature	2-HEAPE	2-HDEAPE	2-HTEAPE
288.15	1.46744	1.47145	1.47368
293.15	1.466	1.46996	1.47175
298.15	1.4629	1.46854	1.46893
303.15	1.4602	1.46594	1.46705
308.15	1.4586	1.46372	1.46524
313.15	1.45598	1.46159	1.46353
318.15	1.4545	1.46003	1.46117
323.15	1.4525	1.45864	1.45954

Table S4 *Values of dynamic viscosity (mPa·s^{-1}) for the studied ILs in the temperature range 288.15 – 323.15 K*

Temperature	2-HEAPE	2-HDEAPE	2-HTEAPE
288.15	2763.2	1752.1	1140.9
293.15	1841.5	1160.4	722.3
298.15	1270.1	803.2	505.5
303.15	920.2	564.8	349.2
308.15	658.2	398.6	246.1
313.15	487.6	289.4	176.4
318.15	342.3	235.1	130.2
323.15	272.3	163.9	98.3

Table S5. *Values of surface tension (mN·m^{-1}) for the studied ILs in the temperature range 288.15 – 323.15 K*

Temperature	2-HEAPE	2-HDEAPE	2-HTEAPE
288.15	34.84	34.57	33.82
293.15	34.58	34.24	33.54
298.15	34.32	34.09	33.37
303.15	34.04	33.91	33.18
308.15	33.83	33.64	32.89
313.15	33.58	33.44	32.66
318.15	33.46	33.22	32.22
323.15	33.14	32.92	32.01

Scientific article (Art 9)

Alanine-supported protic ionic liquids as efficient catalysts for aldol condensation reactions

I. Cota, D. Villamayor, J. E. Sueiras, F. Medina, R. Gonzalez-Olmos, M. Iglesias

(in preparation)

Alanine-supported protic ionic liquids as efficient catalysts for aldol condensation reactions

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Abstract

A serie of novel ionic liquids were immobilized on alanine, a cheap readily available aminoacid. These short aliphatic chain ionic liquids have low cost of preparation, simple synthesis/purification and moreover very low toxicity. Their catalytic activity was tested for citral-acetone and benzaldehyde-acetone condensations, two reactions with interest for pharmacological and flavor and fragrance industry. Good results were obtained in terms of conversion and selectivity; moreover the catalysts can be recycled and reused for three consecutive cycles without significant loss of activity.

Keywords: ionic liquids, aldol condensation, catalysis, supported ionic liquids.

1. Introduction

Ionic liquids (ILs) are versatile new media for many chemical synthesis, enzymatic catalysis and green engineering processes [1]. In the last few years, room-temperature ILs have been also used as clean solvents and catalysts for green chemistry, as electrolytes for batteries, in photochemistry and electrosynthesis [2-6]. Typically, these compounds have excellent chemical and thermal stability, negligible vapour pressure and many of them are described as environmentally friendly. They also allow an easy separation of organic molecules by direct distillation without loss of the IL. In what is referred to reaction media, in the last few years, ILs have been the subject of considerable interest in the context of green synthesis because of their wide acceptability as alternative reaction media [2, 7, 8] and have been found to act as selective catalysts for different reactions [9-14].

Apart from the potential advantages, in recent years there have been reasonable doubts about the overall safety and biodegradability of ILs. The so-called protic ionic liquids (PILs) have shown a minor impact and negligible toxicity, retaining many of the features previously observed in other analogous substances. Due to this fact, the scope of this paper, and in general, our research line is focused on PILs.

The main drawback of using ILs as catalysts is their miscibility with the reaction media, since they are able to dissolve a wide range of organic, inorganic and organometallic compounds [2]. The solution to this problem is the heterogeneisation of ILs on solid supports. Immobilization and supporting of ILs can be achieved by simple impregnation, covalent linking of the cation or the anion, polymerization etc [15-17]. Compared to pure ILs, immobilized ILs facilitate the recovery and re-use of the catalyst.

Previous reports describe the immobilization of ILs by adsorption or grafting onto silica surface and their use as catalysts for reactions like Friedel-Crafts acylation [15], hydrogenation [18] and hydroformilation [19]. Organic polymers [13], natural polymers [20] and zeolites [21] have been also used as supports for ILs.

With this fact in mind, and as a continuation of a wider project to develop and study the applications of new ILs [22-24], in this work we describe the catalytic activity and recycling of alanine-supported ILs for a serie of aldol condensation processes. The ILs of this study consist of substituted amine cations of the form R_XNH (X is the number of alkyl substitutions) combined with organic anions of the form $R'COO^-$ (being of different nature R and R'). These short aliphatic chain ILs have low cost of preparation and simple synthesis/purification [22-24, 28]. Moreover, the very low toxicity and the degradability of this kind of ILs were verified [25]. Thus sustainable processes can be originated from their use. The immobilization on the support takes place due to the formation of covalent bonds between the IL and alanine, thus a heterogeneous catalyst which can be recycled and reused for several cycles is obtained.

On the other hand, it is a continuous challenge to find new catalysts able to perform with good activities and selectivity condensation reactions for the synthesis of pharmaceutical and fine chemicals and thus replacing the homogeneous catalysts [26, 27] used in the industrial production. In order to determine the catalytic activity of the ILs two condensation reactions of carbonyl compounds were carried out. The products obtained from these reactions are applied in pharmacological and flavor and fragrance industry.

2. Experimental

The studied ILs were 2-hydroxy ethylammonium formate (2-HEAF), 2-hydroxy ethylammonium acetate (2-HEAA), 2-hydroxy ethylammonium propionate (2-HEAPr), 2-hydroxy ethylammonium butanoate (2-HEAB), 2-hydroxy ethylammonium iso-butanoate (2-HEAiB) and 2-hydroxy ethylammonium pentanoate (2-HEAP). The synthesis of these ILs that is described elsewhere [22, 23], is a simple acid–base neutralization reaction creating the corresponding salt of ethanolamine, that in a general form should be expressed as follows:

$$(\mathrm{HOCH_2CH_2})_X\mathrm{NH}_Y + \mathrm{HOOC-R} \rightarrow (\mathrm{HOCH_2CH_2})_X\mathrm{NH}^+_{Y+1}\mathrm{R}$$

where X is the number of ethanol substitutions into the amine compound, Y the protons (X+Y=3) and R is the aliphatic end of the corresponding organic acid. For example, when X=1, Y=2, and R = CH_3, this equation shows the chemical reaction for the reactants monoethanolamine + acetic acid and 2-hydroxy ethylammonium acetate (2-HEAA) as neutralization product [22-24, 28]. The reagents, monoethanolamine (Merck Synthesis, better than 99%) and the organic acids (Merck Synthesis, better than 99%) were used without further purification.

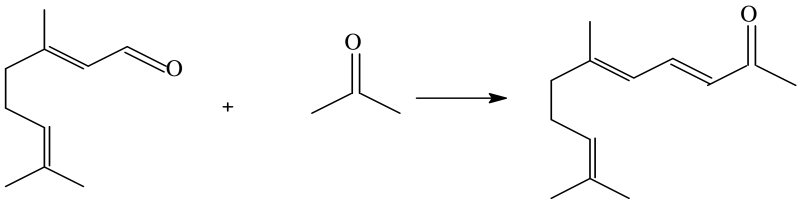
In order to obtain the supported ILs, 1 g of IL was dissolved in 7 ml of ethanol and after stirring at room temperature for 30 min, 1 g of alanine was added. The mixture was stirred for 2 h and then heated at 348 K under vacuum to remove ethanol. The supported ILs thus obtained were labelled hereafter as a-ILs.

The studied reactions were the condensation between citral and acetone and between acetone and benzaldehyde. The reactions were performed in liquid phase using a 100 mL batch reactor equipped with a condenser system. To a stirred solution of substrate and ketone (molar ratio ketone/substrate = 4.4) was added 1 g of a-IL, and the flask was maintained at 333 K using an oil bath. Samples were taken at regular time periods and analyzed by gas chromatography using a flame ionization detector and an AG Ultra 2 column (15 m x 0.32 mm x 0.25 μm). Tetradecane was used as the internal standard. Reagents (citral 95%, acetone > 99.5%, benzaldehyde > 99%, tetradecane > 99.5%) were purchase from Sigma Aldrich and used without further purification.

3. Results and discussion

Alanine was chosen as support because it’s a cheap, commercially available aminoacid able to form covalent bonds with the studied ILs. The catalytic activity of the alanine-supported ILs (a-ILs) was tested in the same reactions as the free ILs, results enclosed in previous works [22, 23].

The condensation reaction between citral and acetone (Scheme 1) leads to the formation of pseudoionone, an important precursor for the synthesis of vitamin A. Commercial citral consists of two isomers, neral and geranial, caused by the *cis-trans* isomerism at the C=C bond near the aldehyde group [29].



***Scheme 1** Condensation reaction between citral and acetone.*

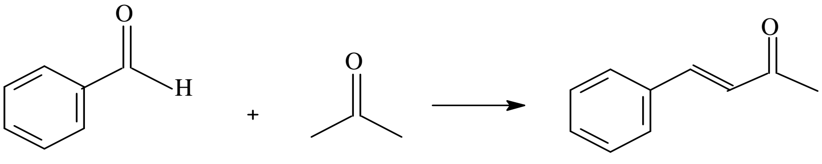
The catalytic activity results of the a-ILs for the citral-acetone condensation are presented in Table 1. After 6 h of reaction, the two isomers of citral can be converted into the corresponding pseudoionone with conversion between 30-56% except for a-HEAiB for which a conversion of 9% was obtained. The most active IL for this reaction is a-2-HEAA which gives a conversion of 56%. The selectivity obtained in this reaction ranges between 48-80%. No traces of diacetone alcohol derived from the self-condensation of acetone were found, but other secondary products coming from the self condensation of citral and oligomers derived from citral are detected in the reaction mixture. The support (entry 1) is not catalytically active.

***Table 1** Conversion at 6 h for citral-acetone condensation catalyzed by a-ILs*

Entry	Catalyst	Conversion (%)	Selectivity (%)
1	alanine	0	0
2	a-2-HEAF	30	61
3	a-2-HEAA	56	74
4	a-2-HEAPr	49	80
5	a-2-HEAB	35	63
6	a-2-HEAiB	9	52
7	a-2-HEAP	33	48

The catalytic activity of a-ILs was also tested in the production of benzylidenacetone (Scheme 2) from the condensation between benzaldehyde and acetone.

In the condensation reaction of benzaldehyde and acetone the first step is the deprotonation of an acetone molecule to give the enolate anion whose nucleophilic attack on the C=O group of benzaldehyde leads to the β-aldol. This latter is easily dehydrated on weak acid sites and benzylidenacetone is obtained.



***Scheme 2** Condensation reaction between benzaldehyde and acetone.*

In 2 hours of reaction a conversion of 98-99% is achieved for the majority of a-ILs, while a lower conversion (78%) is obtained for a-2-HEAiB (Table 2). The selectivity toward benzylidenacetone is around 80-86% due to the formation of dibenzylidenacetone as secondary product. The support, alanine (entry 1) is not active for citral acetone condensation.

***Table 2** Conversion at 2 h for benzaldehyde-acetone condensation catalyzed by a-ILs*

Entry	Catalyst	Conversion (%)	Selectivity (%)
1	alanine	0	0
2	a-2-HEAF	99	83
3	a-2-HEAA	99	82
4	a-2-HEAPr	99	85
5	a-2-HEAB	99	84
6	a-2-HEAiB	78	82
7	a-2-HEAP	98	80

It is noteworthy that, for both studied reactions, the conversions obtained with the a-ILs are in the same range as the ones obtained with free ILs [22, 23] (Figure 1 and 2).

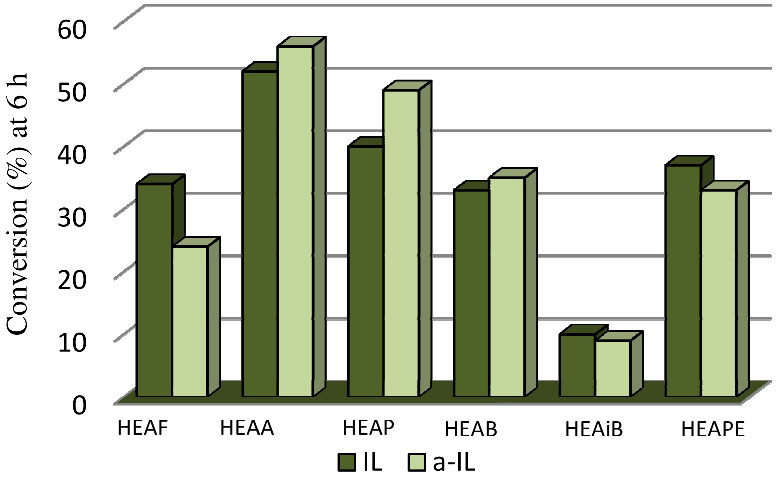


Figure 1. *Conversion at 6 h for citral-acetone condensation for free ILs and a-ILs.*

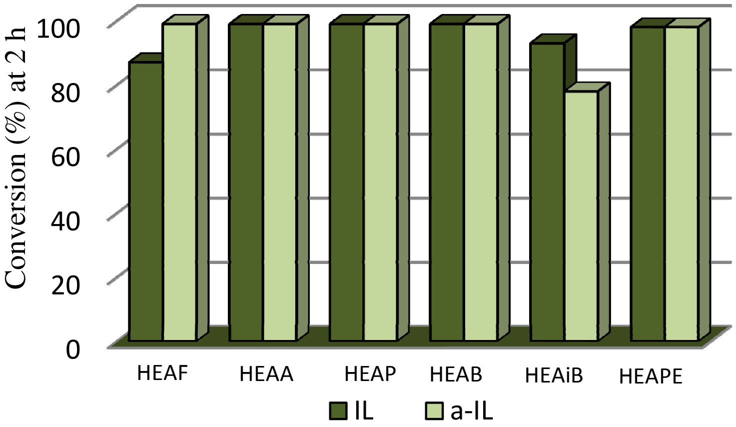


Figure 2. *Conversion at 2 h for benzaldehyde-acetone condensation for free ILs and a-ILs.*

The a-ILs are easily separated from the reaction mixture and reused. For the consecutive runs experiments we chose condensation between benzaldehyde and acetone as model reaction. The catalysts were recycled for 3 consecutive runs and in all runs a very good conversion was obtained. The results are presented in Figure 3.

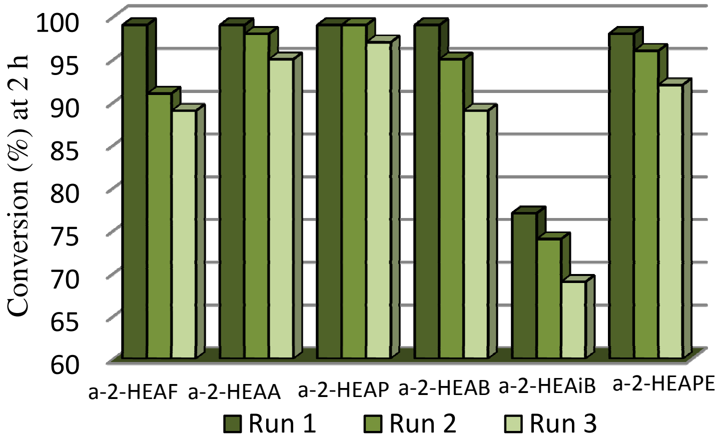


Figure 3. *Consecutive runs experiments in benzaldehyde acetone condensation.*

In the case of each IL, only a negligible loss of activity is detected in the second and third run which can be attributed to the possible adsorption of reactants or reaction products to the active sites of the catalyst.

4. Conclusions

A serie of six ILs were immobilized on alanine, a cheap readily available aminoacid. These short aliphatic chain ILs have low cost of preparation, simple synthesis/purification and moreover very low toxicity. The immobilization on the support takes place due to the formation of covalent bonds between the IL and the alanine.

Their catalytic activity was tested for citral-acetone and benzaldyde-acetone condensations, two reactions with interest for fine chemistry industry. Good results were obtained in terms of conversion and selectivity; moreover the catalysts can be recycled and reused for three consecutive cycles without significant loss of activity.

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Conclusions of chapter three

In the this work, we present a new synthesis protocol for short aliphatic chain ionic liquids and experimental data for density, ultrasonic velocity, ionic conductivity, viscosity, surface tension and refractive index of these liquid salts.

We also studied the influence of chain length of the anion and the substitution into the cation (bulk degree) on the physicochemical properties of the ILs. The influence of anion residue is higher in terms of steric hindrance, due to its longer structure. This factor produces a higher disturbation on ion package. For these ions, the bulk cation develops a lower steric hindrance influence than the anion.

The catalytic activity of this new ILs was tested for several aldol condensations reactions with interest for fine chemistry industry. Good results were obtained in terms of conversion and selectivity. We also studied the optimization of the recovery process of the ILs and their reuse in repeated runs of experiments. The catalysts can be recycled and reused for three consecutive cycles without significant loss of activity.

In addition, the most active ILs were immobilized on alanine, a cheap readily available aminoacid. The immobilization on the support takes place due to the formation of covalent bonds between the IL and the alanine. The catalytic activity of the alanine supported ILs was tested for citral-acetone and benzaldyde-acetone condensations. Good results were obtained in terms of conversion and selectivity; moreover the catalysts can be recycled and reused for three consecutive cycles without significant loss of activity.

General conclusions

In the first chapter of this thesis we applied DBU (diazabicyclo[5.4.0]undec-7-ene) and TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene), two strong N-bases, as catalysts for several aldol condensation reactions with interest for fine chemistry. The reason for choosing these bases as catalysts is that they are strong bases, readily available and can be easily separated from the reaction media. Moreover they have been already applied successfully as base catalysts for several organic syntheses.

We demonstrated that DBU which possesses Lewis basic properties is inactive for aldol condensation reactions; however when it reacts with equimolar amounts of water a complex possessing Brønsted basic properties is formed. The obtained DBU-H_2O complex is highly active for several aldol condensation reactions.

TBD efficiently catalyzed the same aldol condensation reactions as DBU; yielding the corresponding products with high conversion. This methodology works under solvent-free conditions and moreover, a simple and effective protocol for the separation of the catalyst from the reaction medium was developed emphasizing the benign character of this catalyst.

DBU-H_2O complex and TBD represent a convenient and green alternative for the traditional homogeneous catalysts (NaOH or KOH) used for aldol condensation reactions.

In the second chapter, highly basic catalysts were obtained by intercalation of guest negatively charged M^{n+}-based colloids ($M^{n+} = Ca^{2+}, Sr^{2+}, Ba^{2+}, La^{3+}$) into the host Mg/Al LDHs, preparation route which takes advantage of the anionic exchange capacity and the ability to expand the interlayer space of the LDH. The nature of the intercalated cations allows to finely control the basicity of the obtained materals in order to perform reactions requiring different basic strength.

The mixed oxides obtained by thermal activation of these precursors were successfully applied as catalysts for highly demanding basic reactions with interest for fine chemistry, namely: double bond migration of olefins and synthesis of unsymmetrical organic carbonates.

For several base-catalyzed reactions that are important for the pharmaceutical and fragrance industry, the LDH containing OH^- as compensating anions in the interlayer space, which corresponds to the natural mineral meixnerite, is increasingly regarded as good alternative to the traditional homogeneous base catalysts (NaOH and KOH). A main drawback of meixnerite is that it is not easy to prepare by classical co-precipitation or anionic exchange procedures therefore; meixnerite is likely prepared by reconstruction using the memory effect, process which takes place in three steps.

In our study, a new one-step synthesis route for hydrocalumite-type materials was developed. Hydrocalumite-like compound containing mainly OH^- as compensating anions is obtained after aging the precipitate at 298 K. This layered material is particularly interesting to achieve catalytic reactions requiring Brønsted-type sites leading to 100% yield into benzylideneacetone in 2 h by condensation of benzaldehyde and acetone, behaviour which compares well with that of meixnerite considered as a highly efficient Brønsted-type catalyst. We must emphasize that the preparation procedure of the hydroxylated hydrocalumite-like compound is simpler than that of the meixnerite.

In the third chapter a new synthesis protocol for short aliphatic chain ionic liquids and an extensive study of their physico-chemical properties is presented. The catalytic potential of this new ILs was tested for several aldol condensations reactions with interest for fine chemistry industry. Good results were obtained in terms of conversion and selectivity; moreover an efficient recovery process was developed. The catalysts can be recycled and reused for three consecutive cycles without significant loss of activity.

In addition, the most active ionic liquids belonging to this family were immobilized on alanine, a cheap readily available aminoacid. The catalytic activity of the alanine supported ionic liquids was tested for citral-acetone and benzaldyde-acetone condensations. Good results were obtained in terms of conversion and selectivity; moreover the catalysts can be recycled and reused for three consecutive cycles without significant loss of activity.

In this work several new protocols for synthesis of different types of base catalysts were developed. Applying these catalysts in base-catalyzed reactions with interest for fine chemistry, good results were obtained in terms of conversion and selectivity, in some cases better than the results existing in the literature. Moreover the catalysts can be easily recovered and re-used for several consecutive runs.

The work done in this thesis can be regarded as a progress in the design of new catalytic systems, more active and efficient for use in fine chemical processes.

List of Publications and Communications

Articles

Directly related with the thesis:

Authors: Cota, I., Ramírez, E., Medina, F., Sueiras, J.E., Layrac, G., Tichit, D.
Title: *Highly basic catalysts obtained by intercalation of La-containing anionic complexes in layered double hydroxides*
Journal: Applied Catalysis A: General
Volume: in press **Year:** 2010
Impact index: 3.19
ISI category: Physical; Chemistry; Environmental Sciences
AIF (AIF)**:** 2.228
Position in the category: 29; 29; 21

Authors: Cota, I., Ramirez, E., Medina, F., Layrac, G., Chebout, R., Tichit, D
Title: *Alkaline-earth-doped mixed oxides obtained from LDH nanocomposites as highly basic catalysts*
Journal : Catalysis Today
Volume: DOI: 10.1016/j.cattod.2009.08.004 **Year:** 2009
Impact index: 3.004
ISI category: Chemistry, Applied; Chemistry, Physical; Engineering, Chemical
AIF: 1.947; 2.828; 1.583
Position in the category: 3; 31; 5

Authors: Cota, I., Chimentao, R., Sueiras, J.E, Medina, F.
Title: *The DBU-H_2O complex as a new catalyst for aldol condensation reactions*
Journal: Catalysis Communications
Volume: 9 **Pages:** 2090-2094 **Year:** 2008
Impact index: 2.791
ISI category: Chemical, Physical
AIF: 2.828
Position in the category: 36

Authors: Cota, I., Gonzales-Olmos, R., Iglesias, M., Medina, F.
Title: *New short aliphatic chain ionic liquids: synthesis, physical properties and catalytic activity in aldol condensations*
Journal: Journal of Physical Chemistry B
Volume: 111 **Pages:** 12468-12477 **Year:** 2007
Impact index: 4.189
ISI category: Chemical, Physical
AIF (AIF)**:** 2.828
Position in the category: 22

Derived from other research lines different of the thesis:

Authors: Chebout, R., Tichit, D., Layrac, G., Barama, A., Coq, B., Cota, I., Ramirez, E., Medina, F
Title: New basic catalysts obtained from layered double hydroxides nanocomposite
Journal: Solid State Sciences
Volume: 12 **Pages:** 1013-1017 **Year:** 2010
Impact index: 1.742
ISI category: Chemistry, Inorganic&Nuclear; Chemistry, Physical; Physics, Condensed Matter
AIF: 2.247; 2.828; 2.089
Position in the category: 20; 60; 21

Authors: Chimentao, R., Cota, I., Dafinov, A., Medina, F., Gomez de la Fuente, J.L., Fierro, J.L.G., Sueiras, J.E., Cesteros, Y., Salagre, P
Title: *Synthesis of silver-gold alloy nanoparticles by a phase-transfer system*
Journal: Journal of Materials Research
Volume: 21 **Pages:** 105-111 **Year:** 2006
Impact index: 1.743
ISI category: Materials Science; Multidisciplinary
AIF (AIF)**:** 2.206
Position in the category: 36

Congress Contributions

Authors: Cota, I., Ramirez, E., Medina, F., Layrac, G., Tichit, D.
Title: *Highly basic catalysts obtained by intercalation of La-complex in HT structures*
Congress: Europacat IX Catalysis for a Sustainable World
Format (poster or oral): poster
Dates: 30th August -4th September 2009 **Place:** Salamanca (Spain)

Authors: Cota, I., Ramirez, E., Medina, F., Layrac, G., Tichit, D.
Title: *Nuevo protocolo de síntesis de hidrocalumitas y su aplicación en la síntesis de bencilidenacetona*
Congress: SECAT 09 Nuevas Fronteras de la Catálisis
Format (poster or oral): oral
Dates (dates)**:** 29th-1st July 2009 **Place:** Ciudad Real (Spain)

Authors: Cota, I., Ramirez, E., Medina, F., Layrac, G., Tichit, D.
Title: *New basic catalysts obtained from alkaline-earth cations-containing LDH nanocomposites*
Congress: ABC-6 Catalysis by Acids and Bases
Format (poster or oral): oral
Publication: *Alkaline-earth-doped mixed oxides obtained from LDH nanocomposites as highly basic catalysts*
Dates: 10th-14th 2009 **Place:** Genova (Italy)

Authors: Tichit, D.,Garardin, C., Kostadinove, D., Chebout, R., Ramirez, E., Cota, I, Medina, F
Title: *Influence of the composition of the guest entities on the properties of LDH nanocomposites used as precursors of metal supported and basic catalysts*
Congress: First International Conference on Multifunctional, Hybrid and Nanomaterials
Format (poster or oral): poster
Dates: 15th-19th March 2009 **Place:** Tours (France)

Authors: Gonzales-Olmos, R., Cota, I., Medina, F., Iglesias, M., Gomez-Diaz, D., Navaza, J.M.
Title: *Physicochemical properties of new protic ionic liquids*
Congress: 11thMediterranean Congress of Chemical Engineering
Format (poster or oral): poster
Dates: 21st-24th October 2008 **Place:** Barcelona (Spain)

Authors: Cota, I., Gonzales-Olmos, R., Medina, F., Iglesias, M., Sueiras, J.E.
Title: *Catalytic activity and recycling of new short aliphatic chain ionic liquids in aldol condensation reaction*
Congress: ICC08 14th International Congress on Catalysis
Format (poster or oral): poster
Dates (dates)**:** 13th-18th July 2008 **Place:** Seoul (Korea)

Authors: Cota, I., Gonzales-Olmos, R., Medina, F., Iglesias, M
Title: *Catalytic activity of new short aliphatic chain ionic liquids in aldol condensation reaction*
Congress: Europacat VIII From Theory to Industrial Practice
Format (poster or oral): poster
Dates: 26th-31st August 2007 **Place:** Turku (Finland)

Authors: Cota, I., Medina, F., Sueiras, J.E., Cesteros, Y., Salagre, P
Title : *Aplicación de nuevos catalizadores básicos en reacciones de condensación aldolica*
Congress: SECAT 07"Catalysis y procesos Catalíticos: Tendencias y Perspectivas para un Desarrollo Sostenible
Format (poster or oral): poster
Dates: 26th-29th July 2007 **Place:** Bilbao (Spain)

Authors: Cota, I., Medina, F., Sueiras, J.E.
Title: *DBU-H_2O complex as a new catalyst for aldol condensation reactions*
Congress: GPE 2007 1thInternational Congress on Green Process Engineering
Format (poster or oral): poster
Dates: 24th-26th April 2007 **Place:** Toulouse (France)

Authors: Chimentao, R.J., Cota, I., Dafinov, A., Medina, F., Gomez de la Fuente, J.L., Fierro, J.L.G., Sueiras, J.E., Cesteros, Y., Salagre, P.
Title: *Synthesis of silver-gold alloy nanoparticles by a phase-transfer system*
Congress: SECAT 05"Catalysis y Materiales Mesoestructurados
Format (poster or oral): poster
Dates: 27th-29th June 2005 **Place:** Madrid (Spain)