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CATALYTIC HYDROGENATION OF FURFURAL.
INFLUENCE OF THE CATALYST COMPOSITION

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Catalytic hydrogenation of furfural. Influence of the catalyst composition.

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Abstract

Nickel catalysts supported on K-10 and Al-pillared montmorillonites, clays with mesoporosity and acid properties, have been prepared and characterized to be used in the hydrogenation of furfural to tetrahydrofurfuryl alcohol (THFA) in order to obtain products of interest. Clays have been modified by introducing basicity – magnesium oxide impregnation-. Catalytic activity has been tested and the effect of acidity and basicity have been also evaluated. Samples were characterized by N₂ physisorption, UV-Visible spectroscopy,

thermogravimetric analysis, temperature programmed reduction, X-Ray diffraction and transmission electron microscopy. Catalyst formed by MK-10 clay covered by magnesium oxide and 40 wt.% of nickel showed the highest conversion, higher than 99%, and 100% of THFA selectivity. The activity was maintained for several reuses. Additionally, we also studied the viability of THFA hydrogenolysis, with the ring-opening towards diols, using some catalysts containing copper or iridium with rhenium as modifier.

1. Introduction

The production of fuels and chemicals from biomass is important due to changes made in the production of oil which can affect current obtain of propellants and synthetics. One of the challenges of biomass conversion is to obtain target molecules used mainly in petrochemical industries for reducing time and costs for their synthesis. However, nowadays production of compounds from biomass is challenging due to the low conversions, which makes it difficult to obtain a big source of products. Furfural is one of these basic compounds extracted from biomass used to form other fine chemicals. It is obtained by the catalysed dehydration of sugars from xylose, extracted from hemicellulose, which is obtained from agriculture remainders, like corn cobs, oat's shells, almond shells and hazelnut peels¹.

Furfural is also an organic molecule with high oxidation powerfulness if compared with the average petrochemical products. Besides, furans are known to be toxic for the majority of microorganisms. Thus, furfural is usually converted with a catalytic hydrogenation¹ to products such as furfuryl alcohol (FOL), cyclopentanone (CPO) or tetrahydrofurfuryl alcohol (THFA), but also to other very interesting products as diols, monomers for polymers, such as polyesters and polyurethanes.

THFA is the main product of furfural's hydrogenation reaction and is used mainly as solvent, even though it's harmful for natural environment². Traditional way of tetrahydrofurfuryl

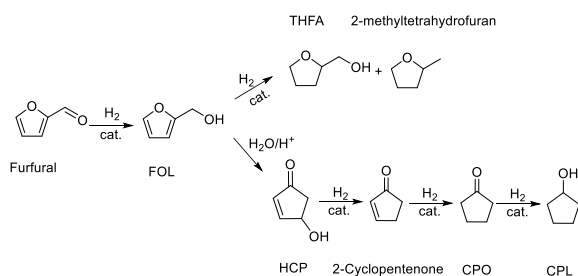
alcohol synthesis is in two steps from furfural with furfuryl alcohol (FOL) as intermediate, and this reaction can be produced in liquid or gas phase³.

First catalysts used copper as active site for the hydrogenation of furfural to THFA in gas phase. Copper chromite has been used widely in the industry for this reaction, although it is highly toxic⁴. Wu and co-authors⁵ achieved high selectivities (over 99%) of THFA and 99.5% of furfural conversion at 403 K by using a Cu-Ca catalyst supported on silica. Later on, Nakagawa *et al.*² developed a nickel catalyst supported on silica and achieved values of selectivity to THFA of 100% and a 94% yield at 403 K also in gas phase. Alternatives, such as the dehydration-hydration-hydrogenation⁶ process, are quite expensive and non-efficient. In overall, developing this reaction in gas phase requires more energy than in liquid phase. Thus, the reaction usually undergoes in liquid phase. In these conditions, the main catalysts are usually made up of iridium, rhodium or nickel supported on silica with furfural conversions of 99% and yields of THFA up to 96%⁷.

However, rearrangements are some important side-reactions to remark. This kind of reactions is typically for furanic compounds. The most important one is the formation of cyclopentanone (CPO) and cyclopentanol (CPL), which are formed in slightly acidic aqueous conditions (Scheme 1).

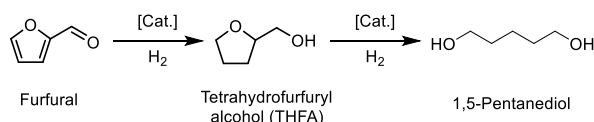
Brönsted acidity has also an important role in this reaction for the formation of humins, another by-product which can affect the active phase's activity. To avoid side reactions and achieve

high conversions the acidity should be controlled. Y. Yang *et al.*³ reported the satisfactory results in this reaction modifying the support with basic oxides of alkaline metals (Mg, Ca, Sr, or Ba). Thus, changing to basic conditions with a Ni/Ba-Al₂O₃ catalyst they obtained >99% of furfural conversion and 99% of THFA selectivity.



Scheme 1. Stages for the formation of products and by-products in the first reaction step⁸

In order to obtain diols from furfural (for example, 1,5-pentanediol), it's been described that requires two steps with a reaction intermediate, the tetrahydrofurfuryl alcohol^{9–11} (Sch.2).



Scheme 2. Scheme of synthesis of 1,5-pentanediol.

The aperture of the ring to obtain 1,5-pentanediol is difficult and needs harder and special³ conditions, over Rh or Ir catalysts combined with another metal oxide such as ReO_x or MoO_x¹¹. These combination of metal and metal oxides show good effectiveness towards the C-O bond hydrogenolysis of THFA^{6,9,18,10–17}. The ring aperture of this molecule might occur in different positions depending on the catalyst selectivity, which might lead to other by-products such as 1,2-pentanediol, 1-pentanol or 2-pentanol¹⁹. Copper is also an interesting metal since it performs the hydrogenation preferentially on the C-O bonds and decreasing the hydrogenation products of the furan ring, obtaining selective hydrogenolysis products^{20,21,22,23}. Very good results have been published about the hydrogenolysis of glycerol towards 1,2-propanediol^{6,9,20,21,24}.

In this work, we proposed to study the effect of the acid and basic sites by using nickel supported catalysts in the formation of THFA from furfural. Several catalytic tests, in aqueous solution, were performed with catalysts with different acid-basic properties. Commercial acid montmorillonite clays (K-10 and Al-Pillared) directly and modified with different amounts of magnesium oxide were used as supports. Because they have

interesting properties, such as surface area, porosity and prize, they have a potential use in this reaction. Additionally, we proposed a study of viability of the ring aperture of the THFA into diols (hydrogenolysis reaction) by using different catalysts that contain noble metals such as iridium and rhenium oxide as modifiers. Also, the effect of copper in both hydrogenation/hydrogenolysis reactions was tested in order to compare both Ni and Cu catalysts. Finally, we also did the complete catalysts characterization of the catalysts by using nitrogen physisorption, thermogravimetric analysis, cation exchange capacity, X-ray diffraction, electronic transmission microscopy and UV-Vis spectroscopy. The modification of clays with alkaline metals contributed to increase the selectivity of THFA in optimum water conditions, up to 100%.

2. Experimental

2.1. Reagents and commercial materials

Furfural was distilled under reduced pressure before used. Tetrahydrofurfuryl alcohol, montmorillonite K-10 clay, aluminium pillared montmorillonite, copper (II) chloride dihydrate, nickel (II) nitrate hexahydrate, magnesium nitrate hexahydrate and ammonium nitrate were of analytic grade and purchased in Sigma-Aldrich. Organic reagents as ethylenediamine, cyclohexylamine and 1-butanol were also purchased in Sigma-Aldrich. Furfuryl alcohol was purchased in Acros Organics and cyclopentanol, cyclopentanone, ammonia perrhenate and dihydrogen hexachloroiridate (IV) in Alfa Aesar.

2.2. Supports. Modification of commercial clays

Basic modification was made through impregnation. First, an ethanolic solution 100 mL Mg(NO₃)₂ 1 M was prepared to impregnate 1 g of the desired clay with 23 mL and 4.6 mL of the Mg(NO₃)₂ solution to prepare catalysts with 30 wt% and 10 wt.%, respectively. Then, the solvent was evaporated using a rotary evaporator, dried at 353 K and calcinated at 623 K for 5 hours in order to obtain a supported magnesium oxide. The supports were named as MgO/MK-10 (10), MgO/MK-10 (30) and MgO/MAIPillared (30).

2.3. Preparation of catalysts

Catalysts were prepared by impregnation. In the first place, an ethanolic solution Ni(NO₃)₂ 0.5 M was prepared. In second place, 6 and 25 mL of nickel (II) nitrate solution were added to 1 g of the support in order to achieve 15 wt.% and 40 wt.% of

nickel, respectively. Then, the solvent was rotary-evaporated and the solid was heated at 353 K overnight. The last step was to calcinate the sample at 723 K for 5 hours in order to obtain nickel oxide. The reduction of the precursors was carried out in a fluidized bed tubular reactor at 1.25 ml/s of H₂ flow at 723 K for 6h.

Catalyst containing iridium and rhenium, Ir-ReOx/MK-10, was prepared as following. First, an aqueous solution H₂IrCl₆ 0.1 M was prepared to impregnate 0.6 g of the desired clay. After drying and calcining at 573 K for 3 hours, the sample was impregnated with 8 ml of NH₄ReO₄ 0.05 M and later on calcined at the same previous conditions. The reduction of the precursor was carried out in a fluidized bed tubular reactor at 1.25 ml/s of H₂ flow at 573 K for 3 hours.

In the case of Cu catalysts, such as Cu/MK-10 (40), they were prepared by impregnating the clay with an aqueous solution of 6.3 ml Cu(NO₃)₂ 1 M, drying and calcining at 723 K for 5 hours. The reduction of the precursors was carried out in the same tubular reactor at 1.25 ml/s H₂ flow at 623 K for 6 hours.

2.4. Characterization techniques

Cation-exchange capacity was determined following the Bergaya and Vayer method²⁵. The samples were exchanged with a 1 M solution of [Cu(en)₂]²⁺ complex, and the exchanged amount was calculated by spectroscopic UV-Visible absorption at $\lambda=546$ nm using a calibration curve at different concentrations. All measurements were done with a Shimadzu spectrometer following the Lamber-Beer's law.

Thermogravimetric analysis (TGA) for determining acidity was carried out in a Setaram Labsys TG by leaving the samples in touch with liquid cyclohexylamine (CHA) at r.t overnight. Then, the samples were heated at 353 K for 4 h in order to eliminate the excess of cyclohexylamine and two more hours at 523 K to remove the physisorbed CHA. Finally, the samples were analysed through TGA under N₂ and a loss of weight between 523 K and 790 K was observed²⁶. Surface area was calculated by nitrogen physisorption at liquid nitrogen temperature using Quadrasorb Surface Analyzer instrument. Water and other physically adsorbed species were removed by pre-degassing the sample at 358 K for 12h. The BET surface area was calculated using the Brunauer-Emmett-Teller equation. The pore size distribution was calculated employing the Barrett-Joyner-Halenda (BJH) model.

The morphologies and particle sizes were determined by transmission electron spectroscopy (TEM) on a JEOL JSM1011 electron microscopy operating at 80 kV.

X-Ray diffraction was used to determine the crystalline phases and estimate their crystallite size using the Sherrer equation. The experiments were carried out with a Siemens D-500 instrument by using CuK α radition with a Ni filter and detecting values 2 θ between 0 and 70°.

Temperature Programmed Reduction (TPR) was carried out with a mixture of Ar/H₂ (95:5) until 1173 K at 5 K/min in the same Setaram Labsys TG.

2.5. Catalytic test

Catalytic hydrogenation of furfural was performed in a 50 mL stainless steel autoclave equipped with a stirrer, a pressure valve and automatic temperature control apparatus. The reactor was connected to hydrogen flow. 30 mL aqueous solution was loaded into the reactor (1.5 g furfural) with 600 mg of catalyst. Then, the reactor was sealed and purged three times with H₂ for air removal. Afterwards, H₂ was fully charged into the reactor until 40 bar pressure, temperature programmed to 413 K and 600 rpm. The reaction lasted 4 hours. The resulting solution was analysed by gas chromatography (GC) after adding the internal standard.

Catalytic hydrogenolysis of tetrahydrofurfuryl alcohol was performed in the same autoclave. The loading solution was 30 mL aqueous solution (1.5 g THFA) and 300 mg of catalyst. After charging H₂ into the reactor, the pressure was set to 60 bar or 80 bar, 373 K and 600 rpm. The reaction lasted 2 hours. After, the liquid phase was washed, diluted and analysed by gas chromatography.

2.6. Product analysis

GC measurements were performed on Shimadzu GC-2010A series equipped with AOC-20i Series autoinjector and FID. The column was a Suprawax-280 (60 m x 0.25 μ m x 0.50 μ m). 1-Butanol was the internal standard. The quantification of products was determined based on GC data using internal standard method, which allowed to determine the conversion and selectivity of main products calculated as below.

$$\text{Conversion (\%)} = \frac{\text{Initial furf. concentr.} - \text{Final furf. concentr.}}{\text{Initial furf. concentr.}}$$

Table 1. Characterization values of the supports.

Support	Surface BET area (m ² /g)	Pore radius value (BJH) (Å)	Acidity (meq CHA/g)	C.E.C (meq/g)
MK-10	220	18	0.5	0.56
MAIPillared	250	20 and 30	0.6	0.17
MgO/MK-10 (10)	67	17	0.21	-
MgO/MK-10 (30)	-	-	0	-
MgO/MAIPillared (30)	-	-	0	-

$$\text{Selectivity (\%)} = \frac{\frac{\text{Product area}}{\text{Internal standard area}}}{\frac{\text{Initial furfural area} - \text{Final furfural area}}{\text{Internal standard area}}}$$

3. Results and Discussion

3.1. Supports characterization

X-Ray diffraction was used to identify the composition of the commercial montmorillonite and observe the changes in composition of the modified ones. Figure 1 shows the MK-10 diffractogram and it is possible to identify quartz, kaolinite, muscovite and clay smectites with disordered stacking of the layers. This mixture of components is because the samples are originally minerals. Quartz and muscovite are crystalline. However, there are characteristics diffraction peaks at low 2θ angles and at $2\theta = 62^\circ$, that can be assigned to the reflections [001] and [060] of dioctahedral smectites $M_{x/n}^{n+} \cdot yH_2O[Al_{4.0-x}Mg_x](Si_{8.0})O_{20}(OH)_4$ as montmorillonite. The fact that the [001] peak presented low intensity could be related with the amorphous structure of the MK-10 sample as a consequence of an acid treatment of the original mineral that induced delamination. In the case of pillared clays, two planes [001] can be assigned due to a non-homogeneous pillars distribution. The plane [001]* that appears at lower angles is the one to identify the presence of pillars.

With transmission electron microscopy it was possible to observe the presence of disordered layers in the MK-10 sample, which corresponds to the results obtained with X-Ray diffraction. On the other hand, in MAIPillared images it was possible to observe little black dots (darker regions), related to the pillars (see Figure 4).

Physisorption analysis of MK-10 showed the capillarity effect in the adsorption-desorption curve at high relative pressures. The sample was classified as mesoporous solid with a surface area of 220 m²/g. The porous size distribution was unimodal with an approximate radius of 18 Å. For pillared

montmorillonite the isotherm was the same as MK-10 and the area was 250 m²/g, but the porous size distribution was in this case bimodal, with an approximate pore radius of 20 and 30 Å. In both cases the surface BET area was similar, slightly higher for MAIPillared. These area values were expected, because both disorder in the laminar structure for MK-10 due to acid pre-treatment, and the presence of pillars involves surface area increase. For modified supports with magnesium oxide, surface BET area decreased significantly for MgO/MK-10 (10) (Table 1), obtaining a value of 67 m²/g, due to the partial coverage of the surface by MgO. This fact also caused the displacement of the initial pore radius value to lower values. However, in the case of MgO/MK-10 (30) and MgO/MAIPillared (30), the isotherms were of type III, showing a N₂ interaction with the adsorbent lower than adsorbate-adsorbate. Thus, the determination of the area was not possible.

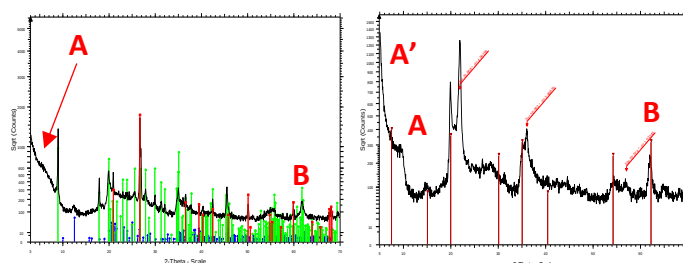


Figure 1. (Left) Diffractogram of commercial MK-10 clay. Red: quartz, Blue: kaolinite, Green: muscovite. Characteristic peaks correspond to quartz and muscovite and A: [001], B: [060] of delaminated montmorillonite. (Right) Diffractogram of commercial MAIPillared clay. Brown: muscovite and peaks A': [001], A: [001], B: [060] of pillared montmorillonite.

Acidity studies were obtained using thermogravimetric analysis and we could extract information about the acidity force. The selected range was between 523 and 790 K. The green line of Figure 2 shows the weight decrease and the blue line represents the first derivative, in which the minimum can be related to the acidity strength. These thermograms show a general tendency which is the following: first, an initial weight loss,

Table 2. Characterization values of the precursors. Crystallite size was determined by X-ray diffraction.

Precursor	Surface BET area (m ² /g)	Pore radius value (BJH) (Å)	Acidity (meq CHA/g)	Reduction temperature range (K)	Minimum of red. temp. (K)	NiO crystallite size (nm)
NiO/MK-10 (15)	186	17	0.4	616 - 883	753	7.3 ± 0.2
NiO/MK-10 (40)	106	17	0.14	611 - 874	710	18.9 ± 0.3
NiO/MAIPillared (40)	93	20	0.21	618 - 973	698	21.9 ± 0.4
NiO/MgO/MK-10 (40;10)	28	19.5 and 40	0.10	669-1010	823	-
NiO/MgO/MK-10 (40;30)	35	20	0	613-1018	873	-
NiO/MgO/MAIPillared (40;30)	11	20	0	639-1006	1002	-

corresponding to the loss of water; and second, the loss associated to CHA desorption. The results showed an acidity for the MK-10 support of 0.5 meq CHA/g of sample and the minimum loss was located at 783 K. The acidity for MAIPillared clays was 0.90 meq CHA/g and the minimum loss was located at 618 K.

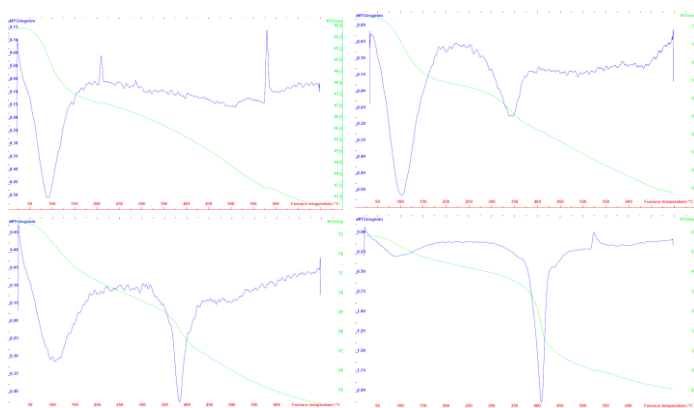


Figure 2. CHA-thermogravimetric analyses of MK-10 (top-left), MPillared (top-right), MgO/MK10 (10) (bottom-left) and MgO/MK10 (30) (bottom-right), showing the loss of cyclohexylamine in the range between 523 K and 790 K. Green line: weight loss in front of temperature. Blue line: first derivative.

Thus, we could evaluate the acidity force: the more in the left is placed the minimum of the first derivative, the easier is to lose CHA and, in consequence, the acid sites are weaker. Thus, the MAIPillared presented more but weaker acid sites than MK-10. Besides, cation exchange capacity showed a value of 0.56 for the MK-10 and 0.17 for the MAIPillared. These results showed the higher capacity of MK-10 to change cations rather than the pillared, because MAIPillared has, probably, more protons that are more difficult to exchange, according to the measured value of acidity.

When the supports were covered with a basic oxide, both area and acidity should decrease as higher the amount of MgO on the clay. Indeed, the results showed an acidity value of 0.21

meq CHA/g for MgO/MK10 (10) which was rapidly annulled as higher the amount of magnesium oxide. This loss of acidity was caused by the neutralization of the acid sites.

3.2. Characterization of the precursors

X-ray diffraction confirmed the presence of nickel oxide and the crystallite size was determined (Table 2). In all cases the crystallite size increased as the higher amount of nickel oxide (Figure 3). However, the most important case to remark is when the sample presented magnesium oxide. In principle, the peaks from MgO and NiO should appear separately, but actually it did not happen. In fact, the signal appeared between the two ones. Considering that NiO has a space group $Fm\bar{3}m$, the same as MgO, and dimensions of $a=b=c=4.1771$ Å and 4.1980 Å, respectively, it is right to say that a solid solution might be formed. This hypothesis was based on the Vegard's law, which consists of an empirical rule that establishes a lineal correlation, at constant temperature, between the cell parameters of the

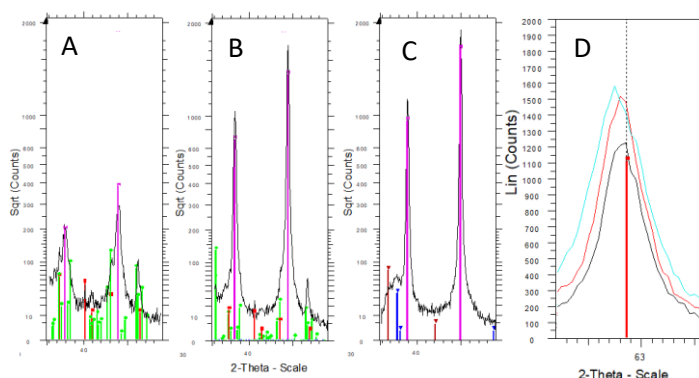


Figure 3. X-ray diffraction of NiO/MK10 (15) (A), NiO/MK10 (40) (B) and NiO/MPillared (40) (C), showing the presence of NiO in the precursor (purple peaks). Pattern D shows how it changes depending on the amount of MgO. The red line represents the NiO phase position.

crystal of an alloy and the concentration of the constituent elements²⁷. Therefore, a solid solution type $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ was formed. This fact happened in the three cases where the sample contained MgO. The more amount of MgO, the more the signal was shifted to lower angles.

Transmission electron microscopy showed in detail the supported particles of NiO and served as complement for the X-ray diffraction. When comparing the differences between having less or more nickel percentage, the TEM images showed these particles as darker zones (Figure 4). At 150k magnifications it was possible to observe that some NiO particles in NiO/MK-10 (40) were crystallized in the form of octahedrons and the dispersion was good enough considering that impregnation method was used to disperse the particles. Despite it was simple and rapid, it was not very efficient to achieve good dispersions. Particle size in TEM were around 20-30 nm. As the nickel percentage increased, the particles became bigger. On the other hand, when the support presented pillars (MAIPillared), there were not significant differences of particle size respect to the MK-10. In general, what it was possible to observe was that it was difficult to differentiate pillars and NiO particles, so much with 15 wt.% or 40 wt.% of nickel content. Samples containing magnesium oxide were not possible to observe or differentiate particles because the formation of the solid solution.

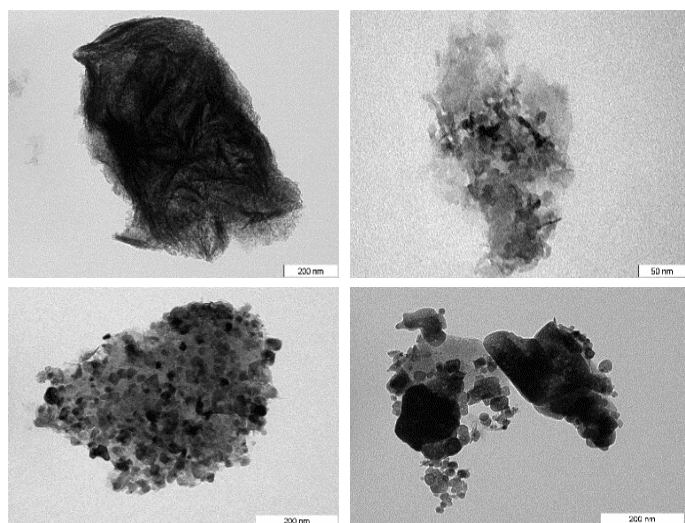


Figure 4. TEM images of (top-left) MK10 support (100k); (top-right) MPillared support (300k); (bottom-left) Ni/MK10 (40) (150k) and (bottom-right) Ni/MPillared (40) (150k).

Nitrogen physisorption analyses of the precursors without basic modification showed the area decrease as higher the amount of NiO (Table 2). The pore size, compared to the supports themselves, did not change significantly. This fact could point

that there was no priority occupation of pores of determined size. Precursors containing MgO, however, showed different values depending on its amount. In the samples containing 10 wt% of MgO, the area decrease was associated with the occupation of the support surface with particles of solid solution MgO-NiO and of NiO. Pore values also seemed to change: whether NiO/MK-10 (40) showed a value of 17 Å, in NiO/MgO/MK10 (40;10) the pore distribution was bimodal, including pore values of 19.5 and 40 Å, probably related to inter-particle space of particles with different size. On the other hand, when the sample contained 30 wt.% of MgO the surface area increased and the bimodality disappeared leaving only a single pore distribution of 20 Å. Having these results, the conclusion was that the more amount of MgO, the amount of solid solution was higher with a better dispersion of NiO and formation of smaller particles, resulting in a certain increase of the area and only a type of porosity.

Acidity studies (Table 2) were also important to understand the later catalytic activity. It was expected that these values should decrease along the higher concentration of nickel oxide. The results confirmed the hypothesis when calculating the loss of cyclohexylamine, corresponding with the acid sites, in the range between 523 K and 790 K (Figure 5). Initially, a narrow derivative peak appeared in most of the samples (NiO/MK-10 (15) and NiO/MK10 (40)) around 770 K, only slightly shifted to the left compared with the support MK-10 itself. This is a sign that no preferential acid sites were produced by NiO. Acidity in precursors that contained MgO/MK-10 shifted their loss of cyclohexylamine around 673 K, indicating that the remaining acid sites were the weaker. When the concentration of MgO was 30 wt%, both in MK-10 and MAIPillared clays, the acidity was neutralized.

Thermogravimetric reduction studies under H_2 (see Table 2) were also important to compare the NiO reducibility in the different precursors and, in consequence, to see differences in the metal phase in the catalysts that could explain their catalytic behaviour. Results for precursors without magnesium showed the easier reduction of the NiO when containing 40 wt.% of Ni. However, with the presence of solid solution the reducibility range changed: reduction started later and also finished later. The minimum, also shifted to the right, indicates that these samples were harder to reduce.

Table 3. Characterization values of the catalysts. Crystallite size was determined by X-ray diffraction.

Catalysts	% Ni	% NiO	% Solid Solution	Ni crystallite size (nm)
Ni/MK-10 (15) 723 K	100	0	0	6.8 ± 0.3
Ni/MK-10 (40) 623 K	83	17	0	19.7 ± 1.6
Ni/MK-10 (40) 723 K	100	0	0	22.2 ± 0.4
Ni/MAIPillared (40) 723 K	100	0	0	23.7 ± 0.4
Ni/MgO/MK-10 (40;10) 723 K	32	0	68	12.2 ± 0.2
Ni/MgO/MK-10 (40;30) 723 K	22	0	78	12.7 ± 0.2
Ni/MgO/MAIPillared (40;30)	21	0	79	6.2 ± 0.2

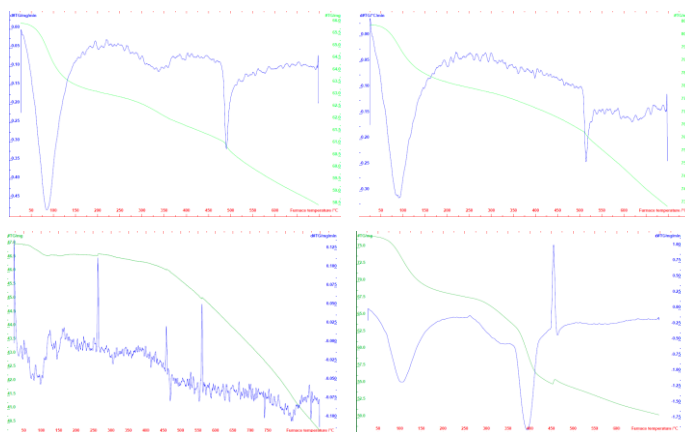


Figure 5. TGA-thermogravimetric analyses of (top-left) NiO/MK10 (15); (top-right) NiO/MMK-10 (40); (bottom-left) NiO/MgO/MK10 (40;10) and (bottom-right) NiO/MgO/MK10 (40;30). Green line: weight loss. Blue line: first derivative.

3.3. Catalysts characterization

Reduced precursors were characterized by X-ray diffraction (Figure 6) to check the metallic, crystalline nickel phase and their crystallite size. Results for catalysts that contained only nickel showed total reduction of nickel oxide when reduced at temperatures of 723 K, both for 15 wt.% and 40 wt.% of nickel content. The crystallite size of Ni is higher for the catalysts with the 40 wt.% of the metal. Interestingly, when the samples were reduced at 623 K, the reduction was not complete (83%) and the crystallite size of Ni was smaller. This should suppose lower metal area and lower capacity of hydrogenation. In catalysts containing MgO the presence of metallic nickel was much lower than the ones without magnesium and the presence of oxide solid solution was also detected. The amount of acidity, that can be considered similar to that in the precursor and the amount of metal phase, should be correlated with the catalytic behaviour.

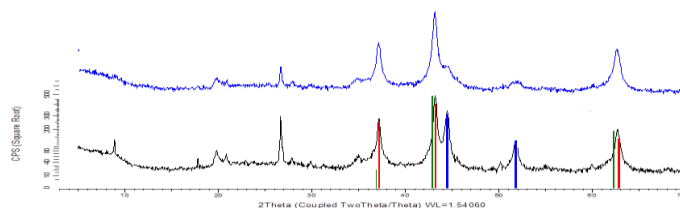


Figure 6. XRD pattern of Ni/MgO/MK10 (40;10) (blue) and Ni/MgO/MK10 (40;30) (black) showing the presence of solid solution at $2\theta=43^\circ$, according to table 3.

4. Catalytic activity

4.1. Hydrogenation of furfural a THFA

The catalytic tests realized for the hydrogenation of furfural can lead several products. The results are shown based on the conversion of furfural and the selectivity to THFA, FOL, CPO and CPL that were obtained from the data from gas chromatography.

4.1.1. Effect of the amount of nickel and the support

The general tendency was that the catalysts supported on MK-10 clay and reduced at 723 K showed better results in regard to the clay with pillars as to the conversion of furfural (Figure 7). For commercial supports, the selectivity to THFA was slightly higher in MAIPillared. Higher quantities of CPO and CPL were obtained when Ni/MK10 (15) and Ni/MK10 (40) were used as catalysts due to their strength and amount of acidity (see Table 2). However, FOL was mainly present in Ni/MAIPillared (40). Although this catalyst has a total formation of metallic Ni, the higher concentrations of FOL in Ni/MAIPillared (40) at 723 K could be explained by the formation of resinification products due to its amount of acidity of less strength. These condensation products deactivated the catalyst.

On the other hand, the introduction of basic sites favoured notably the selectivity to tetrahydrofurfuryl alcohol (100%)

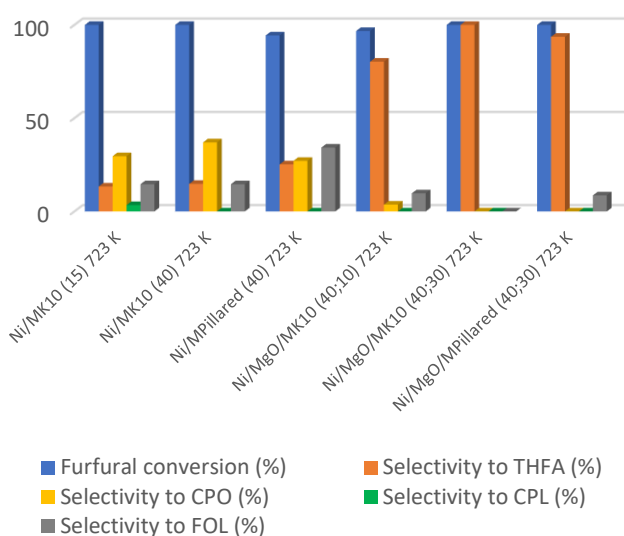


Figure 5. Catalytic results.

when the catalysts contained 40 wt.% of nickel and 30 wt.% of magnesium, in the form of MgO. The least quantity of THFA was obtained when it contained only 10 wt.% of magnesium. In this case, the formation of solid solution, the low amount of metallic Ni, and as well as the acidity that was not fully neutralized due to the low amount of magnesium oxide, favoured the competition between both metallic and acid sites, which led into the formation of FOL and CPO as by-products.

Catalysts containing pillars as support with MgO highlighted the obtain of THFA to almost its totality. Nevertheless, and regarding to the same catalyst without MgO, the presence of basic sites also decreased the formation of by-products such as CPO. Although the % of metallic phase was not high in this catalyst, the conversion of furfural was favoured by the low competition of acid sites. In general, for catalysts containing 40 wt.% of Ni and 30 wt.% of Mg, the furfural conversion and the selectivity towards THFA were total. This fact could be explained not only by the amount of metallic Ni, which was much lower compared to its homologue Ni/MK10 (40) or Ni/MAlPillared (40), but, instead, for its lack of acid sites: no acid-catalysed products were formed. In fact, these good results could agree with the experimental results of Y. Yang *et al*³. In detail, the magnesium coordinates with the oxygen from FOL, gets closer into the metallic surface and improves the hydrogenation of the furanic ring to continue with the catalytic reduction.

4.1.2. Effect of the temperature of reduction

To evaluate the contribution of the metal phase we prepared the catalysts at lower reduction temperature (623 K – Figure 8). In overall, the selectivity to THFA kept constant for catalysts without MgO (around 10%). However, the most important fact when the temperature of reduction was lower is that the number of by-products, such as CPO and FOL, were higher. XRD studies of catalysts Ni/MK10 (40) (see Table 3) confirmed that at 623 K the amount of metallic Ni is much lower than at 723 K, which resulted in the decrease of the metallic surface area, and Ni could not compete enough with the acid sites, so acid catalysis was more important. The presence of MgO improved the THFA production. In Ni/MgO/MK-10 (40;30) catalyst the differences by reduction temperature were not very important; only the presence of a certain amount of FOL, when the reduction was at 623 K, was observed. In Ni/MgO/MAlPillared (40;30) the differences were more important and at lower temperature of reduction, FOL was the main product.

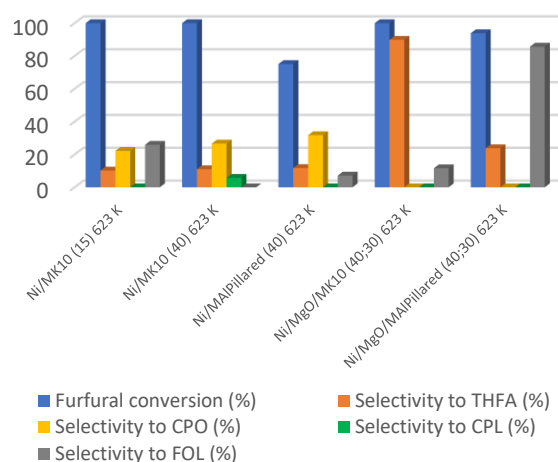


Figure 6. Catalytic results for nickel catalysts reduced at 623 K.

4.1.3. Study on the reusability of the catalysts

In heterogeneous catalysts, their capacity of a catalyst to be reused is an important characteristic to be studied. In this case, we proposed to test the sample that got us the best results, Ni/MgO/MK10 (40;30), thrice, and each time by using the same sample as before (Figure 9).

Results showed good stability of the catalyst. The loss of catalytic activity, including conversion and selectivity of THFA, was, in average, 5%. The test showed the production of FOL. This fact supposed the contamination of some residual products on the surface of the catalyst that deactivated the catalyst in the first use. An efficient wash of the catalyst is a crucial factor in

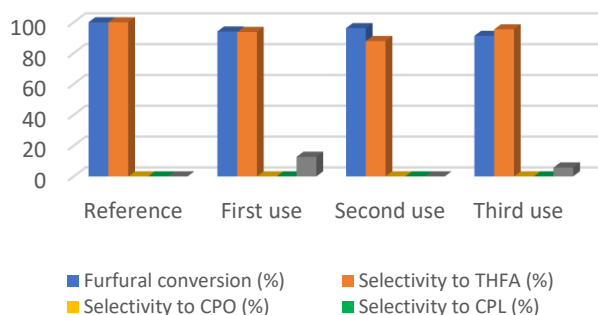


Figure 7. Reutilisation tests.

order to obtain good values of conversion and selectivity in later tests.

4.2. Hydrogenation of furfural and THFA into diols

4.2.1. Hydrogenolysis of THFA to 1,5-pentanediol

The reference study was performed by Nakagawa, Tomishige *et al*¹⁴ following its method to prepare the reaction. Initial conditions for this study were 3 g of THFA, 3 g of H₂O, 300 mg of catalyst, 60 bar H₂, 2 h. Results showed 64% of conversion of furfural and 93% of 1,5-pentanediol selectivity over Ir-ReO_x/SiO₂ catalyst with a relation Re/Ir = 2. In base all these premises, we also proceeded to do an intensive study for the viability of this reaction, since the low volume used was an important restriction. Therefore, we performed our analyses scaling the volume to 30 mL and reducing the initial concentration of THFA. Catalysts contained a 4% Ir and 7.8% of Re. Reaction conditions were kept to compare the results. Therefore, we studied, in fifteen tests, the possible problems that could explain the lack of activity. ReO_x was maintained in all catalysts due to its ability to hold the C-O bond from the THFA, favouring the other metal to the later hydrogenolysis. We modified conditions such as the reduction of the precursors, solvent, percentages of Ir and Re, the amount of catalyst or the support¹¹ (S.I. Table 1). However, none of these changes improved the catalytic activity, obtaining no conversion of

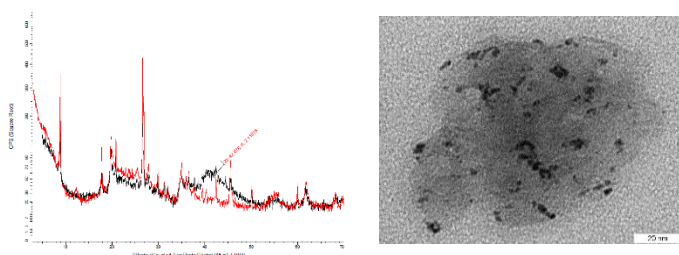


Figure 8. (Left) XRD pattern of Ir/ReO_x/MK10 catalyst showing no identification of Re or Ir particles. Characteristic peaks are from the support. (Right) TEM image of an Ir-ReO_x catalyst at 800k.

THFA but consuming some H₂ during the process that was attributed to a partial reduction of ReO_x.

XRD characterization of the catalysts was unable to identify any of the species of Ir and Re due to the low amount of these elements. TEM images of catalysts were also not helpful to differentiate between Ir particles and Re particles, as they all appear as dark spots. Their average size was 2 nm (Figure 10).

4.2.2. Hydrogenation/Hydrogenolysis of furfural to diols

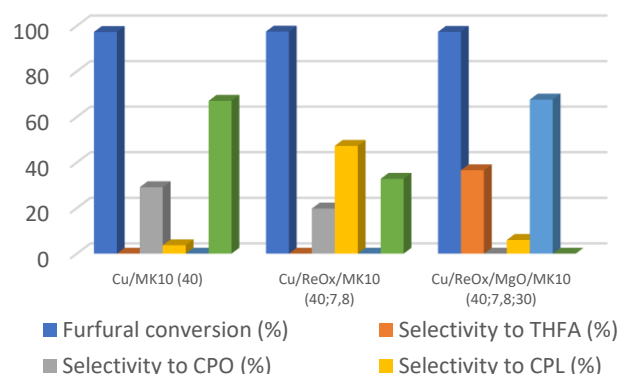


Figure 9. Catalytic activity of Cu catalysts.

Preliminary characterization of the precursors showed different behaviour from the precursors with Ni (Table 4). Acidity for Cu/MK10 (40) presented a slightly greater acidity value (0.55 meq CHA/g) than the support itself (0,5 meq CHA/g). When Re was introduced, the acidity value turned to 4.67 meq CHA/g, which is greater than the expected. The hypothesis was that some weight loss associated to the complexation of CHA with Cu²⁺ cations, along with the extra acidity that provides from rhenium oxide. Catalytic activity was expected according to the acidity of the precursors (Figure 11). Because these high values, acid catalysis was present in all tests. Thus, there was no production of 1,5-pentanediol or even 1,2-pentanediol.

Table 4. Characterization values of Cu catalysts. Acidity values in meq CHA/g and crystallite size determined by XRD.

Catalyst	Acid. prec.	% Cu	% CuO	Cu Cryst. size
Cu/MK10 (40)	0.55	100	0	71 ± 3
Cu/ReO _x /MK10 (7;40)	4.67	100	0	-
Cu/ReO _x /MgO/MK10 (40;7;30)	1.14	100	0	21.6 ± 0.6

Results showed a major production of others and cyclopentanone when the catalyst contained only copper and mainly cyclopentanol when the catalyst contained rhenium. However, when the catalyst contained magnesium oxide, there

was production of THFA and the acid-catalysed products decreased significantly due to the partial neutralisation of the acid sites, although there was mainly production of FOL. Other products could not be identified. Even though the percentage of metal Cu was total, the metallic sites could not compete with the acid-sites.

5. Conclusions

The hydrogenation of furfural is highly dependent on the amount of metallic nickel but also on the acidity of the catalysts. Higher values of acidity involve catalyst deactivation due to resinification products or selectivity to acid-catalysed products. Therefore, the yield to THFA can be improved by decreasing the acidity of the support whilst maintaining a good reduction degree of the metallic nickel phase. The best montmorillonite catalyst (Ni/MgO/MK-10 (40;30)) showed 100% of selectivity to THFA and total conversion of furfural. The aperture of the ring to diols was unviable to achieve. In this context, this reaction presented many problems that we tried to solve. In fact, there was no conversion of furfural or THFA into diols and selectivities turned towards acid-catalysed products, although hydrogenation and hydrogenolysis reactions were carried out with noble metals and copper modified with rhenium oxide. Further studies are needed to understand the behaviour of this reaction.

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SUPPLEMENTARY INFORMATION

CATALYTIC HYDROGENATION OF FURFURAL. INFLUENCE OF THE CATALYST COMPOSITION

CARLES SUNYOL OCÓN
MASTER'S DEGREE THESIS
2018

Table 1. Problems faced during the hydrogenolysis over Ir/ReOx/Support catalysts.

Problem	Solution	Reaction conditions
Accessibility issues	Reduction in situ instead of in a tubular reactor	1) 373 K, 60 bar, 2 h; then, 2) 393 K, 60 bar until 24 h
Competition between water, furfural and Re	Replaced most solvent with sulpholane Decreased the amount of water	1) 393 K, 50 bar, 4 h; then, 2) 60 bar until 72 h
Ratio Re/Ir not optimized	Changed to ratio Re/Ir = 1,5	100 °C, 60 bar, 4 h
Not enough catalyst	Increased the amount of catalyst to 400 mg	1) 373 K, 60 bar, 2 h; then, 2) 373 K, 80 bar, 1 h; then, 3) 423 K, 80 bar, 1h
Precursor preparation	Calcination after introducing Ir and the other one after introducing Re	100 °C, 60 bar, 4 h
Support issues	Used Na-Saponite and SiO ₂	Na-S: 373 K, 60 bar, 4 h SiO ₂ : 373 K, 60 bar, 4 h
Inactivity of THFA	THFA obtained from the hydrogenation of furfural	423 K, 60 bar, 2 h