

Impact of cellulose treatment with hydrotalcites in hydrothermal catalytic conversion

Carlos [Guarín](#)

karlosguarinv@gmail.com

Llorenç [Gavilá](#)

lloren.gavila@urv.cat

Magda [Constanti*](#)

magda.constanti@urv.cat

Francesc [Medina](#)

francesc.medina@urv.cat

Department of Chemical Engineering, University Rovira i Virgili, Av. Països Catalans 26, 43007 Tarragona, Spain

*Corresponding author.

Abstract

The depletion of oil reserves pushes the development of platform chemicals from biomass, as an alternative for the sustainable progress of the chemical industry. Cellulose, which is the main component of biomass, is widely studied for its conversion into value-added chemicals. However, due to its recalcitrant nature, hydrolysis of cellulose with solid alkali catalysts still remains a challenge. Thus, the conversion of cellulose using hydrotalcites as catalyst was investigated. For this purpose, hydrotalcites were deposited on cellulose fibers and their catalytic behavior was tested at 180 °C, for 1 h, using microwave reactor (300 W). Hydrotalcites proved to efficiently convert cellulose into value-added products such as lactic, acetic, formic and glycolic acids. Catalysts were characterized by X-Ray diffraction, Fourier transform infrared spectroscopy, environmental scanning electron microscopy and BET surface area analysis. The best conversion yield of up to 30% was obtained over calcined hydrotalcites at 400 °C. The basic properties of the hydrotalcite materials have an important effect on the activity. Hence, in this study hydrotalcites are presented as a promising catalyst for cellulose hydrolysis.

Keywords: Cellulose; Hydrotalcites; Microwave; Lactic acid

1 Introduction

Depletion of oil reserves is leading many researchers to find a feasible alternative to petrochemical feedstock. According to FAOSTAT, 2800 MT/year of agricultural residues remain unexploited. Hence, agricultural residues, so called biomass, arise as an appealing alternative to petrochemical feedstock.

Biomass transformation is an outstanding R&D area with a great potential to provide a renewable carbon source. Biomass comprises mainly cellulose (40–50%), hemicellulose (25–35%) and lignin (15–35%) ([Chaturvedi and Verma, 2013](#); [Travaini et al., 2016](#)). Cellulose, consisting of long chains formed by glucose units linked by glycosidic bonds, has a high molecular weight (between 300,000 and 500,000 g per mol) ([Klemm et al., 2005](#)). Cellulose does not form any side branch; instead, cellulose fibrils are attached to each other by a strong hydrogen bond network. This hydrogen bond matrix defines a microcrystalline structure, making cellulose recalcitrant to hydrolysis and insoluble in most solvents, even water ([Zhang et al., 2013](#)).

Due to the high crystallinity matrix presented by cellulose, different researchers selected microcrystalline cellulose (MCC) as a feedstock to mimic the recalcitrant nature of cellulose ([Ni et al., 2013](#); [Peng et al., 2014](#); [Yang et al., 2014](#); [Zhang et al., 2013](#)). MCC depolymerization is more challenging; therefore, the results can be used to define a technology able to process diverse cellulose sources in order to recover water-soluble compounds such as sugars and acids. However, MCC conversion to sugars and acids demands severe conditions, and the reaction selectivity under such conditions is low due to the wide production of different compounds like furan derivatives, among other water-soluble and insoluble materials ([Zhang et al., 2013](#)). Therefore, much effort is being done in order to depolymerize cellulose under mild conditions.

Cellulose can be exposed to hydrolysis treatments in order to breakdown its polymeric structure. Such cleavage can be done by several technologies such as catalytic hydrolysis, thermal degradation or enzymatic treatment. Enzymatic is among them the most popular hydrolysis treatment, but it has some drawbacks like high cost and strict control of temperature and pH, which results a burden when scaling-up the process (Zhou et al., 2011). As an alternative, catalytic hydrolysis by microwave treatment of cellulose is becoming one of the most promising techniques (Gavilán et al., 2015).

Microwave-assisted reactions have great impact in organic synthesis and in emerging technologies for greener chemical recycling of polymers and biomass. Microwave heating is attractive for cellulose hydrolysis due to the formation of hot spots, which reduce the crystalline order and increase the cellulose degradation under mild reaction conditions (Buranov and Mazza, 2010; Liu et al., 2018; Palm and Zacchi, 2003).

Mineral acids, such HCl or H₂SO₄, have traditionally been used for cellulose hydrolysis. However, their application suffers of corrosion of the reactors, high toxicity and high by-products formation (Gitifar et al., 2013). Furthermore, due to its homogeneous nature reusability is not possible, sacrificing sustainability and increasing downstream wastes. Alternatively, solid catalysts can be easily isolated and reused, hence reducing downstream processing (Fang et al., 2011; Xu et al., 2015). Despite solid acid catalysts have received great attention (Huang and Fu, 2013), basic catalysts are rarely used for cellulose depolymerization. Hydrotalcites (HTs) or layered double hydroxides consist of positively charged layers with anionic species in the interlayer, forming neutral clay materials (Xu et al., 2015). HTs alkali properties can be controlled by tuning their composition (Sharma et al., 2011). The thermal decomposition of hydrotalcites leads to mixed metal oxides, which are characterized by high specific surface areas, homogeneous dispersion of metals and strong Lewis base sites (Corma et al., 2005). The basic properties of these sites depend on the Mg

Al ratio in the precursor hydrotalcite (Di Cosimo et al., 1998). Interestingly, these mixed oxides are able to recover the original layered structure by treatment with water. The reconstruction of decomposed Mg

Al hydrotalcite by rehydration at room temperature has been reported to enhance the catalytic activity due to the presence of strong Brønsted basic sites (Abelló et al., 2005). Hence, HT arises as an interesting thermal stable catalyst for alkali hydrolysis of cellulose. In this study, three different approaches are used: (i) hydrolysis of cellulose with HTs, (ii) hydrolysis of cellulose with in-situ synthesized HTs and (iii) hydrolysis of cellulose with calcined HTs. In order to increase their basicity. In contact with water, HT's form meixnerite, a very stable mineral (Abelló et al., 2005). The aim and novelty of this work was to evaluate the effect of different basicity of hydrotalcite materials during the hydrolysis of cellulose, when hydrotalcites were synthesized in situ with cellulose, and the influence on the basicity in the final obtained products. Furthermore, we propose the catalytic conversion of cellulose by microwave technology to hydrolyze cellulose, in order to determine an efficient and cost effective path to transform biomass to different value-added products.

2 Materials and methods

2.1 Materials

Commercial cellulose microcrystalline powder (MCC from Sigma-Aldrich, product number 22184) was employed in the hydrolysis reactions. All the experiments were carried out using deionized water.

Aluminum nitrate nonahydrate, magnesium nitrate hexahydrate, sodium carbonate and sodium hydroxide were purchased from Sigma-Aldrich. High purity formic acid (Fluka), acetic acid (Fluka), lactic acid (Fluka) and glycolic acid (Merck) were used for quantitative analysis.

2.2 Synthesis of HTs

The synthesis of all HTs was carried out by co-precipitation. Two solutions were used for each HT synthesis. The first solution contained nitrates of magnesium and aluminum at two different Mg/Al rates. HT (2:1 and 4:1) were prepared by dissolution of Mg(NO₃)₂·6H₂O (8.448 mmol for HT 2:1 and 10.288 mmol for HT 4:1) and the respective amount of Al(NO₃)₃·9H₂O (4.224 mmol for HT 2:1 and 2.572 mmol for HT 4:1) in 20 mL of water. The second and basic solution was prepared with NaOH (0.31 M) and Na₂CO₃ (0.94 M) in water.

HTs were synthesized by co-precipitation in aqueous medium and for the sake of comparison, in order to improve the contact between substrate and catalyst, HTs were directly prepared on the cellulose fibers.

2.2.1 Synthesis of HTs in aqueous media

The solution containing Al and Mg nitrates were added dropwise to a beaker containing 200 mL of water under constant stirring, while the pH was kept constant in a range of 9.8-10.0. The HT solution was reserved for 24 h and then it was filtered and washed with abundant water to reduce the basicity and remove the residual salts. The obtained solid was dried in oven for 24 h at 80 °C. Hydrotalcites with an Mg/Al rate of 2:1 and 4:1 were named HT21 and HT41, respectively.

2.2.2 Synthesis of HTs on cellulose fibers

Before starting HTs synthesis 10 g of MCC was dispersed, with a tip sonifier, in 200 mL of water. Afterwards the procedure was the same as described above. HTs synthesized on cellulose with a Mg/Al molar rate of 2:1 and 4:1 were named HT21-cell and HT41-cell, respectively. Two different loadings of HTs were synthesized on cellulose, 10% w/w and 40% w/w. The loading was indicated after the sample name, i.e. HT21-MCC-10% for 10% of HT with a Mg/Al molar rate of 2:1. A blank experiment

was prepared by stirring dispersed cellulose (under the above explained solutions) on a solution of NaOH with a pH of 10, and then filtered and dried as the rest of samples containing cellulose.

2.2.3 Calcination of HTs

Portions of the synthesized HT21 and HT41 samples were calcined separately in a preheated oven at 400 °C during 3 h under air stream. The calcined HTs were named HTC21 and HTC41 according to their Mg/Al molar ratio.

2.3 Hydrolysis experiments

0.5 g of MCC was hydrolyzed in 20 mL of deionized water with different amounts of the prepared HTs or calcined HTs. The amount of HTs used was expressed as weight percentage after the sample name, i.e. HT21-10% for 0.05 g of HT with a Mg/Al molar rate of 2:1. HTs synthesized on cellulose were reacted in 20 mL of water, weighting the corresponding amount of sample to have 0.5 g of MCC. The reaction was carried out at 180 °C in a START E Milestone microwave during 1 h at 300 W, with a heating time of 15 min. We just considered 1 h of reaction time in order to compare the different prepared catalysts, hence we assumed 1 h as sufficient reaction time.

Once the sample was cooled down, the liquid fraction was analyzed by TOC and HPLC. The solid fraction was dried and weighed. All the experiments were done in duplicate and the results were expressed as average with their respective standard deviation.

When the solid residues obtained after the reaction were characterized, their names were kept and the word “after” was added, i.e. HT21- 10%-after for the recovered material of 10% of HT with a Mg/Al molar rate of 2:1.

2.4 Characterization of liquid phase

The amount of carbon hydrolyzed into the liquid phase was quantified by Total Organic Carbon (TOC) Analyzer (Shimadzu, TOC-L CSN). The inorganic carbon concentration was analyzed with the same equipment in order to elucidate the potential dissolution of HTs during the reaction.

The concentration of obtained products was measured by HPLC system (HPLC Agilent tech, 1100 series) with ICsep ICE-COREGEL 87H3 (Column serial No. 12525124) as a column using DAD (measuring at 210 nm) and RID detectors. Aqueous mobile phase was prepared with filtered Milli-Q water and its pH was adjusted to 2.2 with H₂SO₄. Reaction products were identified by comparing the retention times with commercial standards. Commercial standards were used for calibration and quantification.

2.5 Characterization of solid phase and raw cellulose

2.5.1 X-ray diffraction (XRD)

HTs, MCC, and MCC with HT before and after the hydrolysis reaction, were characterized by XRD analyses using a Siemens D5000 diffractometer with an angular 2 θ -diffraction range between 5° and 90° (Chimentão et al., 2014). Additionally, the crystallite diameter was calculated using the Scherrer equation in the 110 plane (Li et al., 2006).

2.5.2 Fourier transform infrared spectroscopy (FTIR)

MCC, HTs, and MCC with HT structure, were studied by FTIR. This technique allows obtaining information about the interaction of the HT particles with the MCC before and after the hydrolysis.

FTIR spectra were recorded with a Jasco FT/IR 600 Plus equipped with a Specac's Golden Gate ATR accessory, which allows a direct measurement of the sample. The sample was recorded with 64 scans using 4 cm⁻¹ resolution, in transmittance mode.

2.5.3 Environmental surface electron microscopy (ESEM)

The morphology of MCC was analyzed by ESEM with a FEI Quanta 600 equipment. The study was performed over HT, MCC, and MCC with HT before and after the hydrolysis reaction. Samples were gold-covered by sputtering, and imaged operating at 30 kV for HTs and at 15 kV for MCC with HT samples.

2.5.4 Surface area analysis

The specific surface area of the hydrotalcites was obtained by measuring the nitrogen adsorption/ desorption isotherms at 77.35 K with a Quadrasorb SI Automated Surface Area & Pore Size Analyzer (Quantachrome Instruments). The samples were outgassed before each analysis for 5 h at 150 °C to a residual pressure below 5 mTorr. The total surface area and the pore specific volume were determined according to Brunauer-Emmett-Teller (BET) equation, and the pore diameter was calculated using Barrett-Joyner-Halenda.

2.5.5 Study of the basic properties of hydrotalcites

The basicity of the calcined hydrotalcites (400 °C), was obtained by temperature programmed desorption (TPD) of CO₂ on an Autochem II 2920 Micromeritics equipped with a TCD detector. Usually, around 0.1-0.15 g of sample is placed in a tubular quartz reactor. The sample was pretreated with Ar at 120 °C for 1 h and then cooled to room temperature and treated with a CO₂ flow (3% CO₂ in He). Then, the sample was heated from room temperature up to 800 °C at a heating rate of 10 °C/min in He flow to produce the desorption of CO₂. Magnesium perchlorate was used for trapping water. The number of basic sites was calculated from the CO₂ peaks by deconvolution using the software of the equipment, and the instrument was calibrated using a known amount of CaCO₃.

3 Results and discussion

3.1 Structural analysis

3.1.1 XRD results

The crystalline structure of the prepared HTs in the presence and absence of MCC was confirmed using XRD (Fig. 1). The XRD of prepared HT samples (Fig. 1A and 1B) exhibit typical diffraction patterns of hydrotalcite-like compounds (JCPDS card 22-0700) at 2θ angles of 11.6°, 23.5°, 35.0°, 60.9° and 62.0°, corresponding respectively to the 003, 006, 012, 110 and 113 planes. After calcination at 400 °C for 3 h, the HT structure disappears, resulting in formation of mixed oxide phase with typical features of a Mg(Al)O type (Xie et al., 2006). Two weak and broad signals at 43° and 62.4° appear consistently in the presence of a MgAlOx mixed oxide phase with a structure like MgO (periclase) (JCPDS card 04-0829), corresponding to 400 and 440 planes (Fig. 1C. and D); and plane 111 correspond to MgAl₂O₄ spinel phase, along with other signals at 45° and 65° (Constantino and Pinnavaia, 1995). As can be seen, hydrotalcites HT21 and HT41 present the same diffraction lines than HT synthesized over MCC (Fig. 1E and F), showing that the HT structure was truly formed on cellulose during the synthesis. The diffraction pattern of MCC can be recognized in Fig. 1E, F, G and H, presenting peaks at approximately 15° and 16.5° (overlapped 1 1̄ 0 and 110, respectively) and 22.5° (2 0 0). The crystallite size (Table 1) was 6.2 nm for HT21 and 4.5 nm for HT41.

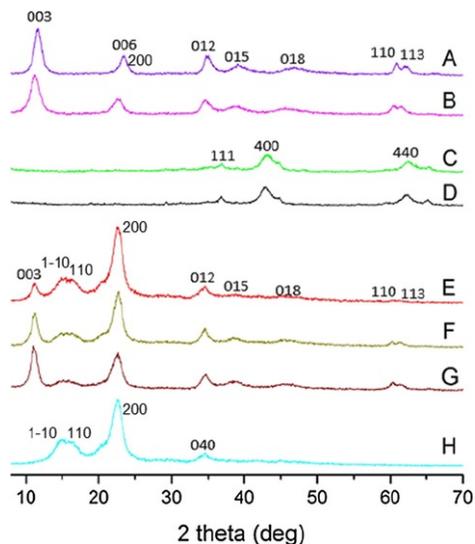


Fig. 1 XRD diffractogram of synthesized hydrotalcites (HT) and calcined hydrotalcites (HTC): (A) HT21, (B) HT41, (C) HTC21, (D) HTC41, (E) HT41-10%, (F) HT41-40%, (G) HTC41-100%-after, and (H) MCC.

Table 1 Textural properties of synthesised, calcined and rehydrated hydrotalcites.

Catalyst	BET surface area (m ² /g)	Pore volume V _p (cm ³ /g)	d _{pore} (nm)	Crystallite size (nm)
HTC 21	60.4	0.18	7.1	-
HTC 41	88.3	0.28	5.3	-
HT21	0.8	0.01	3.6	6.2

HT41	1.4	0.02	3.7	4.5
HTR21	49.3	0.15	5.1	6.9
HTR41	39.0	0.11	5.3	7.3

3.1.2 FTIR results

The FTIR spectra for hydrotalcite HT41, representative cellulose with HT samples (HT41-MCC-10%-after and HTC41-MCC-10%-after), and MCC were depicted in Fig. 2. MCC was included for comparative purposes. We followed the presence of cellulose by monitoring the characteristic bands at: 2900 cm^{-1} (CH_2 symmetric vibration), 1160 cm^{-1} (C

O asymmetric vibration), 1105 (C O and C C stretching) and 1054 (C

O valence vibration) (Schwanninger et al., 2004). HT presence was identified by a band at 1360 cm^{-1} , attributed to the ν_3 asymmetric stretching of carbonates (Sobhana et al., 2016). As can be seen in Fig. 2, after reaction the cellulose structure remained unmodified, while HT structure was also present, proving that no leaching occurred during the reaction course.

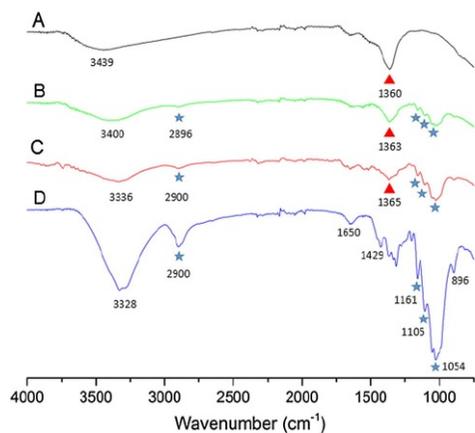


Fig. 2 FTIR spectra of synthesized hydrotalcites (HT) and calcined hydrotalcites (HTC): (A) HT41, (B) HT41-100%-after (C) HTC41-100%-after (D) ★ MCC. correspond to cellulose peaks; ▲ correspond to HT peaks.

3.1.3 ESEM morphological analysis

The morphology of the samples was evaluated by ESEM analysis and is presented in Fig. 3. HTs are composed of platelet-like particles that are agglomerated with each other in different ways depending on the preparation conditions (Delidovich and Palkovits, 2015). Fig. 3A shows that HT21 is composed of an agglomeration of sheets, irregular in size and shape. In contrast, the HT41 is composed by regular size grains and presents flake-like conglomerates (Fig. 3B).

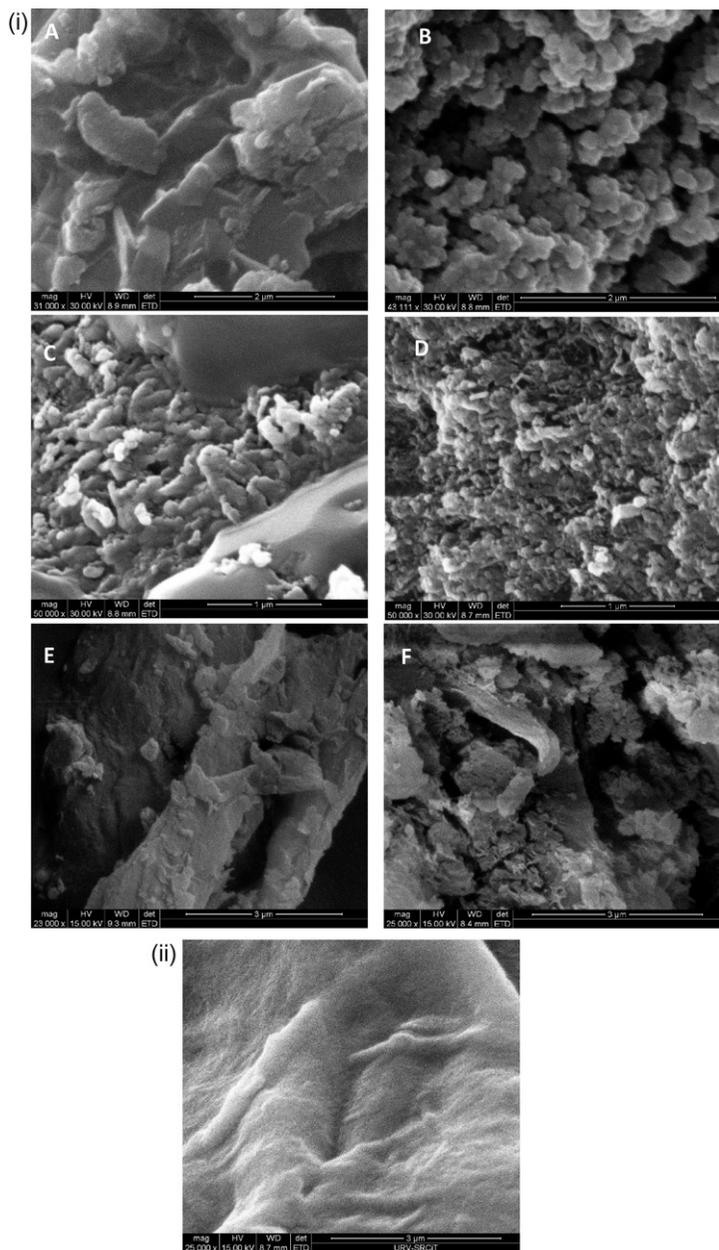


Fig. 3 (i) ESEM images of synthesized hydrotalcites (HT) and calcined hydrotalcites (HTC): (A) HT21, (B) HT41, (C) HTC21, (D) HTC41, (E) HT41-10%, and (F) HT41-40%. (ii) ESEM image of cellulose.

The same behavior was observed by decreasing the size of the flat structures after calcination at 400 °C (Fig. 3C and D). Xie et al (2006) have explained this behavior by the $\text{Mg}(\text{OH})_2$ brucite sheets that compose the Mg-Al HT, in which Al^{3+} substitutes for Mg^{2+} sites, and is transformed to periclase-like Mg

O solid solutions by calcination at high temperature. Therefore, the morphology was kept after calcination and remained in the resulting periclase-like Mg

Al

O structure. Such activation of HTs via thermal treatment is considered to involve the replacement of interlayer carbonate by hydroxyl groups without a drastic effect on the original ordered stacked structure of the aggregates.

The presence of cellulose during the HT synthesis promoted the HT particles to anchor themselves on the MCC networks. From [the Fig. 3E and F](#), it is possible to observe how the HTs have grown one upon the other over the MCC forming interconnected networks. The particles are more densely packed in HT41-10 ([Fig. 3E](#)) than in HT41-40 ([Fig. 3F](#)). This may be due to the increase in HT concentration, which provided a more homogeneous distribution of the inorganic particles formed on MCC.

3.1.4 Structural characterization of hydrotalcites

The BET surface area of HTs, calcined HTs, and rehydrated HTs (HTR) are shown in [table 1](#). The surface area and pore specific volume for HTs were fairly small, 0.8 m²/g and 0.01 cm³/g for HT21 and 1.4 m²/g and 0.02 cm³/g for HT42. While the surface area and pore specific volume for calcined HTs increased, HTC21 is 60.4 m²/g and 0.180 cm³/g and HTC41 increases to 88.3 m²/g and 0.28 cm³/g. The higher surface area and larger pore volume of HTC41 can be referred to the release of interlayer water molecules and carbon dioxide from carbonate anions present in the brucite layer ([Onda et al., 2008](#)). After the rehydration process in the water solution, the mixed oxides phase is reconstructed obtaining the meixnerite phase. [Table 1](#) shows that the surface areas of the rehydrated samples decreased with respect to the calcined ones. A surface area of 49.3 and 39.0 m²/g were obtained for HTR21 and HTR41, respectively. Furthermore, a decrease of the pore volume and a slight increase in the particle size of the rehydrated materials were also observed.

3.1.5 Characterization of the basic sites of hydrotalcites

The TPD-CO₂ profiles of the calcined and rehydrated materials are presented in [Fig. 7 Fig. 6](#). The basic strength can be assigned according to the temperature at which the CO₂ is desorbed. Besides, the number of basic sites can be determined by the integration of these desorption peaks. The samples showed the presence of CO₂ desorption at temperatures between 100 and 200 °C (weak basic sites), 350–450 °C (medium basic sites) and between 450 and 650 °C (strong basic sites). [Table 2](#) also summarizes the amount of basic sites of the samples. The HTC21 sample showed mainly weak basic sites (450 μmol/g) and a little amount of strong basic sites (44 μmol/g) and a total amount of basic sites of (494 μmol/g). The HTC41 sample showed weak basic sites (175 μmol/g), medium basic sites (78 μmol/g) and strong basic sites (150 μmol/g) and a total amount of basic sites of (403 μmol/g). After sample rehydration, a decrease of the number of basic sites was observed for both samples. HTR21 and HTR41 showed a total amount of CO₂ of 290 and 274 μmol/g, respectively. However, there is an important increase in the presence of medium and strong basic sites compared with the calcined samples. These medium and strong basic sites can be assigned to the decomposition of bicarbonate and carbonate species, formed by the adsorption of CO₂ on the Brønsted basic sites (hydroxyl groups). [Table 2](#) also reports the basicity of the samples with respect to the surface area of the samples, but only considering the medium and strong basic sites and expressed in μmolCO₂/m². The rehydrated samples showed similar values, 5.9 and 6.3 μmolCO₂/m² for HTR21 and HTR41, respectively, that are higher than for the calcined ones. This indicates an important increase in the presence of stronger basic sites after the rehydration process. Furthermore, the sample HTR41 showed a shift to higher desorption temperatures of the CO₂ peak compared to the sample HTR21, 565 and 495 °C, respectively. This indicates a stronger basicity for the HTR41 sample with respect to the HTR21.

Table 2 Basic properties of the calcined and rehydrated hydrotalcites.

Sample	TPD analysis of adsorbed CO ₂			Total amount of CO ₂ (μmol/g)	Evolved CO ₂ (II + III) ^a (μmol m ⁻²)
	Desorption peaks				
	I (100–200 °C)	II (350–450 °C)	III (450–650 °C)		
HTC21	450 (107 °C)	–	44 (535 °C)	494	0.73
HTC41	175 (184 °C)	78 (482 °C)	150 (587 °C)	403	2.6
HTR21	–	165(433 °C)	125(495 °C)	290	5.9
HTR41	25(170 °C)	135(430 °C)	114(565 °C)	274	6.3

The maxima temperatures of the desorbed CO₂ peaks are given in brackets (°C).

^a Evolved CO₂ from medium (II) and strong-strength (III) basic sites of catalysts.

3.2 Production of value-added products: lactic, formic, acetic and glycolic acids

We started testing the reaction with 10% w/w loading of HT21 as catalyst (Fig. 4). A slight increase in the conversion was observed when the catalyst was synthesized directly on cellulose fibers (supported HTs, thereafter), 6.9%, while, only 5.9% of conversion was achieved when the HTs were synthesized externally and added afterwards (bulk HTs, thereafter). Both, bulk and supported HT41 with 10% loading, were tested, observing that an increase in the Mg/Al molar ratio improved HTs activity for cellulose hydrolysis, 7.2% and 9.6% conversion for the bulk and supported HTs, respectively. This effect indicates that the increase of the Mg/Al ratios that produces an increase in the basicity of the material is beneficial for the hydrolysis of cellulose. Since higher performance was achieved using HT41 we chose this Mg/Al ratio for further experiments.

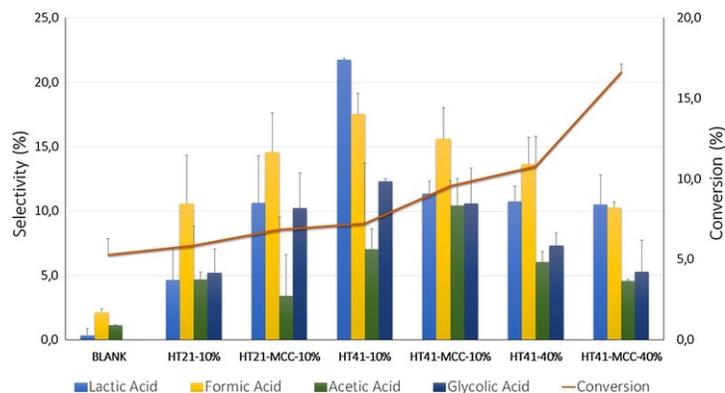


Fig. 4 Cellulose conversion and generation of products with different amounts of hydrotalcites.

The catalyst loading was increased to 40% using HTs with Mg/Al of 4. By increasing the catalyst loading the reaction was favored, in this case is more noteworthy the increase in the performance for supported HTs, which converted 16.6% of cellulose, while bulk HTs just converted 10.7% of cellulose. Our assumption is that by directly preparing HTs on the cellulose fibers a better contact between the substrate and the catalyst is achieved, minimizing the mass transfer problems of such a heterogeneous reaction.

Due to our previous experience, we assumed that loadings higher than 40% would not be possible for supported HTs, since HTs would no longer be able to crystallize on cellulose fibers, rather they would crystallize on the solution. Even though, we tested 100% w/w loadings for bulk HTs in order to better understand the catalyst role for cellulose hydrolysis. As can be seen in Fig. 5, HT21 converted 10.2%, whereas HT41 converted 17.6% of cellulose. As previously commented HTs with Mg/Al ratio of 4 showed higher performance, hence, presumably, the stronger basic properties the better activity of HTs for cellulose hydrolysis. At this point is worth comparing the results of HT41-MCC-40% and HT-100% (Figs. 4 and 5, respectively), we observe that the conversion is comparable for 40% supported HTs and 100% bulk HTs, showing conversions of 16.6 and 17.6%, respectively. This fact has a great importance because by directly preparing the catalyst on the cellulose fibers, the catalyst loading can be reduced by 60% showing similar performance on cellulose conversion.

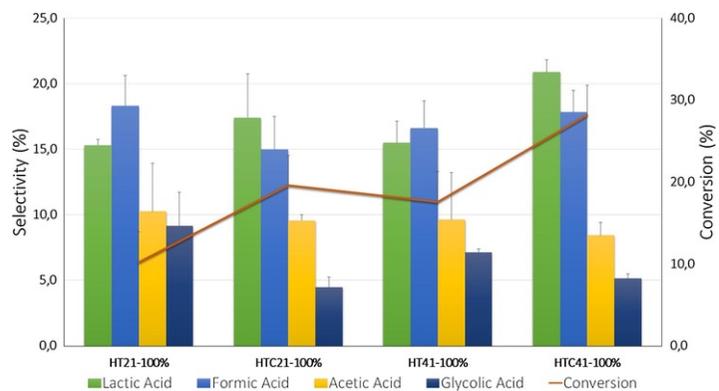


Fig. 5 Cellulose conversion and generation of products with no-calcined and calcined hydrotalcites.

To finalize, in order to study the influence of the basicity of the catalyst, calcined HTs were investigated for cellulose hydrolysis (Fig. 5). After reaction, the calcined HTC41 (Fig. 1G) shows a meixnerite-like structure, which implies the reconstruction of the calcined HT, by rehydration, in the aqueous medium of reaction. When Mg/Al ratio increased from 2:1 to 4:1, cellulose conversion increased from 19.6 to 28.1%, achieving similar conversion to that obtained by Fang et al. (2011), but with shorter reaction time. This result can be explaining considering the stronger basicity of the rehydrated HTR41 sample with respect to the HTR21 sample, observed by TPD-CO₂. The determined hydrolyzed products accounted for up to 60% of all the produced products. Lactic acid and formic acid formation seemed to be favored when mixing the calcined and non-calcined HT with MCC. Calcined HTs improved their catalytic activity over no-calcined HTs due to an increase in the strong basic sites (Chimentão et al., 2007). During the catalyst tests, no lixiviation of the catalyst was observed.

3.3 Reaction pathway

Based on the obtained products and information in literature, the hypothetical alkali-catalyzed reaction pathway would include first cellulose depolymerization into glucose, which would isomerize into fructose (Fig. 6 Fig. 7). Then, C₆ sugars would split trough a retro-aldol mechanism, either forming (i) glycolaldehyde (C₂) and erythrose (C₄), intermediates in the production of glycolic acid (Carnaroglio et al., 2015; Wang et al., 2014; Zhang et al., 2012) or (ii) two dihydroxyacetone or glyceraldehyde (both C₃) which trough a dehydration and a subsequent hydride shift may afford lactic acid (Esposito and Antonietti, 2013). Once the carboxylic acids are obtained, glycolic acid and lactic acid can be further degraded into formic acid or acetic acid respectively (Cao et al., 2015). In conclusion, when compared with acid hydrolysis under similar set-up (Gavilà et al., 2015), alkali catalyzed hydrolysis of cellulose assisted by microwave gives more moderate yields, however, the obtained products do differ. Thus, alkali hydrolysis gives directly smaller molecules (C2-C3) with higher functional group densities, then the election of the catalyst would certainly give the chance to elect the desired product.

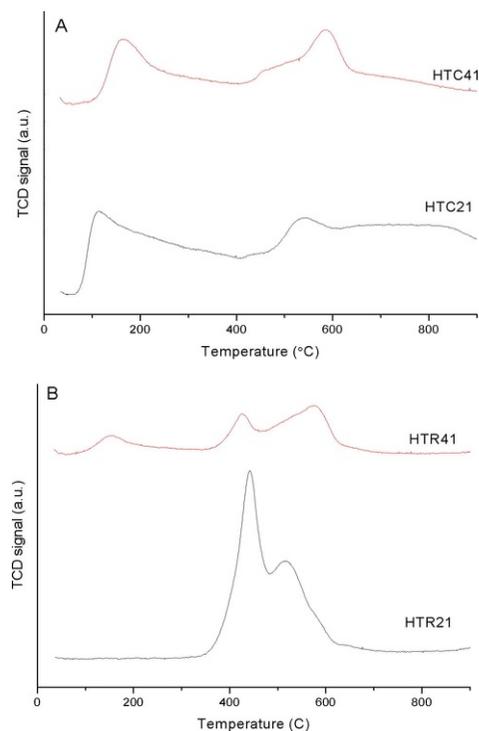


Fig. 7 TPD-CO₂ profiles of: (A) calcined (HTC21 and HTC41) and (B) rehydrated (HTR21 and HTR41) hydrotalcites.

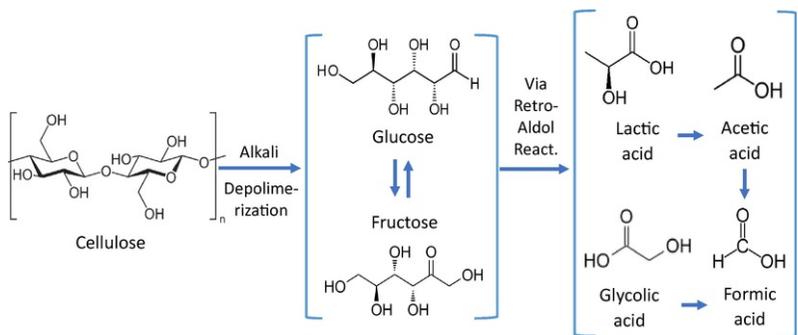


Fig. 67 Reaction pathway of cellulose over basic catalyst with hydrotalcites.

4 Conclusions

To conclude, HTs directly prepared on cellulose fibers, were presented here as a new strategy for alkali hydrolysis of cellulose. By direct preparation of the catalyst on the cellulose fibers, we improved its activity, most likely due to a better contact between substrate and catalyst. Furthermore, the basicity role of the catalyst seemed to deeply influence the reaction performance, achieving the highest cellulose conversion, 28%, for calcined HTC41.

As a result, we proved that HTs are good catalysts for the depolymerization of cellulose, which afterwards might undergo through retro-aldol mechanism to the formation of different organic acids such, formic, lactic, acetic and glycolic acids. Therefore, by taking advantage of the improved contact between catalyst and substrate HTs appear as an interesting alternative for conventional cellulose hydrolysis, even its potential is not yet fully developed.

Acknowledgements

This work was funded by the [Spanish Ministry of Economy and Competitiveness \(MINECO\)](#), project [CTM2015-69848-R](#).

Conflict of interest

None.

References

- Abelló S., Medina F., Tichit D., Pérez-Ramírez J., Cesteros Y., Salagre P. and Sueiras J.E., Nanoplatelet-based reconstructed hydrotalcites: towards more efficient solid base catalyts in aldol condensations, *Chem. Commun.* 2005, 1453-1455.
- Buranov A.U. and Mazza G., Extraction and characterization of hemicelluloses from flax shives by different methods, *Carbohydr. Polym.* **5**, 2010, 17-25.
- Cao X., Peng X., Sun S., Zhong L., Chen W., Wang S. and Sun R.-C., Hydrothermal conversion of xylose, glucose, and cellulose under the catalysis of transition metal sulfates, *Carbohydr. Polym.* **118**, 2015, 44-51, <https://doi.org/10.1016/j.carbpol.2014.10.069>.
- Carnaroglio D., Tabasso S., Kwasek B., Bogdal D., Gaudino E.C. and Cravotto G., From lignocellulosic biomass to lactic- and glycolic-acid oligomers: a gram-scale microwave-assisted protocol, *ChemSusChem* **8**, 2015, 1342-1349, <https://doi.org/10.1002/cssc.201403183>.
- Chaturvedi V. and Verma P., An overview of key pretreatment processes employed for bioconversion of lignocellulosic biomass into biofuels and value added products, *3 Biotech* **3**, 2013, 415-431, <https://doi.org/10.1007/s13205-013-0167-8>.
- Chimentão R.J., Abelló S., Medina F., Llorca J., Sueiras J.E., Cesteros Y. and Salagre P., Defect-induced strategies for the creation of highly active hydrotalcites in base-catalyzed reactions, *J. Catal.* **252**, 2007, 249-257, <https://doi.org/10.1016/j.jcat.2007.09.015>.
- Chimentão R.J., Lorente E., Gispert-Guirado F., Medina F. and López F., Hydrolysis of dilute acid-pretreated cellulose under mild hydrothermal conditions, *Carbohydr. Polym.* **111**, 2014, 116-124, <https://doi.org/10.1016/j.carbpol.2014.04.001>.

- Constantino V.R.L. and Pinnavaia T.J., Basic properties of $Mg_{2+1-x}Al_{3+x}$ layered double hydroxides intercalated by carbonate, hydroxide, chloride, and sulfate anions, *Inorg. Chem.* **34**, 1995, 883-892, <https://doi.org/10.1021/ic00108a020>.
- Corma A., Abd Hamid S.B., Iborra S. and Velty A., Lewis and Brønsted basic active sites on solid catalysts and their role in the synthesis of monoglycerides, *J. Catal.* **234**, 2005, 340-347.
- Delidovich I. and Palkovits R., Structure-performance correlations of Mg-Al hydrotalcite catalysts for the isomerization of glucose into fructose, *J. Catal.* **327**, 2015, 1-9, <https://doi.org/10.1016/j.jcat.2015.04.012>.
- Di Cosimo J.I., Diez V.K., Xu M., Iglesia E. and Apesteguía C.R., Structure and surface and catalytic properties of MgAl mixed oxides, *J. Catal.* **178**, 1998, 499-510.
- Esposito D. and Antonietti M., Chemical conversion of sugars to lactic acid by alkaline hydrothermal processes, *ChemSusChem* **6**, 2013, 989-992, <https://doi.org/10.1002/cssc.201300092>.
- Fang Z., Zhang F., Zeng H.-Y. and Guo F., Production of glucose by hydrolysis of cellulose at 423K in the presence of activated hydrotalcite nanoparticles, *Bioresour. Technol.* **102**, 2011, 8017-8021, <https://doi.org/10.1016/j.biortech.2011.06.052>.
- Gavilà L., Constanti M. and Medina F., D-lactic acid production from cellulose : dilute acid treatment of cellulose assisted by microwave followed by microbial fermentation, *Cellulose* **22**, 2015, 3089-3098, <https://doi.org/10.1007/s10570-015-0720-1>.
- Gitifar V., Eslamloueyan R. and Sarshar M., Experimental study and neural network modeling of sugarcane bagasse pretreatment with H₂SO₄ and O₃ for cellulosic material conversion to sugar, *Bioresour. Technol.* **148**, 2013, 47-52, <https://doi.org/10.1016/j.biortech.2013.08.060>.
- Huang Y.-B. and Fu Y., Hydrolysis of cellulose to glucose by solid acid catalysts, *Green Chem.* **15**, 2013, 1095-1111, <https://doi.org/10.1039/c3gc40136g>.
- Klemm D., Heublein B., Fink H.-P. and Bohn A., Cellulose: fascinating biopolymer and sustainable raw material, *Angew. Chem. Int. Ed. Engl.* **44**, 2005, 3358-3393, <https://doi.org/10.1002/anie.200460587>.
- Li B., He J., Evans D.G. and Duan X., Morphology and size control of Ni-Al layered double hydroxides using chitosan as template, *J. Phys. Chem. Solids* **67**, 2006, 1067-1070, <https://doi.org/10.1016/j.jpcs.2006.01.027>.
- Liu Y., Sun B., Zheng X., Yu L. and Li J., Integrated microwave and alkaline treatment for the separation between hemicelluloses and cellulose from cellulosic fibers, *Bioresour. Technol.* **247**, 2018, 859-863, <https://doi.org/10.1016/j.biortech.2017.08.059>.
- Ni J., Wang H., Chen Y., She Z., Na H. and Zhu J., A novel facile two-step method for producing glucose from cellulose, *Bioresour. Technol.* **137**, 2013, 106-110, <https://doi.org/10.1016/j.biortech.2013.03.104>.
- Onda A., Ochi T., Kajiyoshi K. and Yanagisawa K., Lactic acid production from glucose over activated hydrotalcites as solid base catalysts in water, *Catal. Commun.* **9**, 2008, 1050-1053, <https://doi.org/10.1016/j.catcom.2007.10.005>.
- Palm M. and Zacchi G., Extraction of hemicellulosic oligosaccharides from spruce using microwave oven or steam treatment, *Biomacromolecules* **4**, 2003, 617-623, <https://doi.org/10.1021/bm020112d>.
- Peng H., Chen H., Qu Y., Li H. and Xu J., Bioconversion of different sizes of microcrystalline cellulose pretreated by microwave irradiation with/without NaOH, *Appl. Energy* **117**, 2014, 142-148, <https://doi.org/10.1016/j.apenergy.2013.12.002>.
- Schwanninger M., Rodrigues J.C., Pereira H. and Hinterstoisser B., Effects of short-time vibratory ball milling on the shape of FT-IR spectra of wood and cellulose, *Vib. Spectrosc.* **36**, 2004, 23-40, <https://doi.org/10.1016/j.vibspec.2004.02.003>.
- Sharma Y.C., Singh B. and Korstad J., Latest developments on application of heterogenous basic catalysts for an efficient and eco friendly synthesis of biodiesel: a review, *Fuel* **90**, 2011, 1309-1324, <https://doi.org/10.1016/j.fuel.2010.10.015>.
- Sobhana S.S.L., Bogati D.R., Reza M., Gustafsson J. and Fardim P., Cellulose biotemplates for layered double hydroxides networks, *Microporous Mesoporous Mater.* **225**, 2016, 66-73, <https://doi.org/10.1016/j.micromeso.2015.12.009>.
- Travaini R., Martín-Juárez J., Lorenzo-Hernando A. and Bolado-Rodríguez S., Ozonolysis: an advantageous pretreatment for lignocellulosic biomass revisited, *Bioresour. Technol.* **199**, 2016, 2-12, <https://doi.org/10.1016/j.biortech.2015.08.143>.

Wang Y., Yao G. and Jin F., Hydrothermal conversion of cellulose into organic acids with a CuO oxidant, In: *Application of Hydrothermal Reactions to Biomass Conversion*, 2014, Springer-Verlag; Berlin, 31–60, <https://doi.org/10.1007/978-3-642-54458-3>.

Xie W., Peng H. and Chen L., Calcined Mg-Al hydrotalcites as solid base catalysts for methanolysis of soybean oil, *J. Mol. Catal. A Chem.* **246**, 2006, 24–32, <https://doi.org/10.1016/j.molcata.2005.10.008>.

Xu S., Liao M.C., Zeng H.Y., Chen C.R., Duan H.Z., Liu X.J. and Du J.Z., Magnetic hydrotalcites as solid basic catalysts for cellulose hydrolysis, *Appl. Clay Sci.* **115**, 2015, 124–131, <https://doi.org/10.1016/j.clay.2015.07.039>.

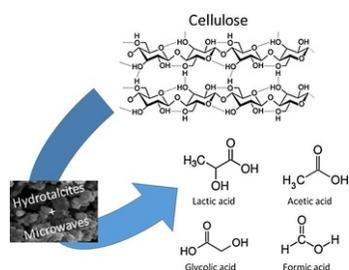
Yang H., Wang L., Jia L., Qiu C., Pang Q. and Pan X., Selective decomposition of cellulose into glucose and levulinic acid over Fe-resin catalyst in NaCl solution under hydrothermal conditions, *Ind. Eng. Chem. Res.* **53**, 2014, 6562–6568, <https://doi.org/10.1021/ie500318t>.

Zhang J., Liu X., Sun M., Ma X. and Han Y., Direct conversion of cellulose to glycolic acid with a phosphomolybdic acid catalyst in a water medium direct conversion of cellulose to glycolic acid with a phosphomolybdic acid catalyst in a water medium, *ACS Catal.* **2**, 2012, 1698–1702, <https://doi.org/10.1021/cs300342k>.

Zhang Q., Benoit M., De Oliveira Vigier K., Barrault J., Jegou G., Philippe M. and Jerome F., Pretreatment of microcrystalline cellulose by ultrasounds: effect of particle size in the heterogeneously-catalyzed hydrolysis of cellulose to glucose, *Green Chem.* **15**, 2013, 963–969, <https://doi.org/10.1039/c3gc36643j>.

Zhou C.-H., Xia X., Lin C.-X., Tong D.-S. and Beltrami J., Catalytic conversion of lignocellulosic biomass to fine chemicals and fuels, *Chem. Soc. Rev.* **40**, 2011, 5588–5617, <https://doi.org/10.1039/c1cs15124j>.

Graphical abstract



Highlights

- Hydrotalcites were successfully deposited on cellulose fibrils.
- Deposition of hydrotalcites was followed by XRD, FTIR and ESEM.
- Deposited hydrotalcites exhibited better catalytic performance.
- Hydrotalcites converted cellulose into lactic, acetic, formic and glycolic acids.
- Calcined hydrotalcites showed the best conversion yield, up to 30%.

Queries and Answers

Query: Your article is registered as a regular item and is being processed for inclusion in a regular issue of the journal. If this is NOT correct and your article belongs to a Special Issue/Collection please contact ge.krishnan@elsevier.com immediately prior to returning your corrections.

Answer: Yes

Query: Please check to replace Authors' commercial domain e-mail address with a professional e-mail address.

Answer: This is the current e-mail

Query: The author names have been tagged as given names and surnames (surnames are highlighted in teal color). Please confirm if they have been identified correctly.

Answer: Yes

Query: Ref. Gavila et al., 2015 is cited in the text but not provided in the reference list. Please provide it in the reference list or delete these citations from the text.

Answer: The surname is accentuated

Query: Please check the hierarchy of the section headings.

Answer: Yes

Query: Please check the edit(s) made in the sentence "The diffraction pattern of MCC can be and 22.5° (200)", and correct if necessary.

Answer: Yes