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**OBTAINING HIGH-VALUE ADDED PRODUCTS FROM CELLULOSE:
IMPACT OF CELLULOSE TREATMENT WITH HYDROTALCITES IN HYDROTHERMAL CATALYTIC
CONVERSION.**

MASTER'S DEGREE FINAL PROJECT

Supervised by Dr. Francesc Medina and Dr. Magda Constantí

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**Obtaining high-value added products from cellulose:
Impact of cellulose treatment with hydrotalcites in hydrothermal catalytic conversion.**

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ABSTRACT

The development of platform chemicals from biomass arises as an alternative for the sustainable progress of the chemical industry. With this in mind, the conversion of cellulose to value added products such as lactic acid using hydrotalcites (HT) as catalyst was investigated. Mg-Al hydrotalcites were used as catalyst for the hydrolysis of cellulose into lactic, acetic, formic and glycolic acids. Catalysts were characterized by XRD, FTIR, ESEM and BET surface area analysis. The best conversion yield of up to 30% with selectivity was obtained over calcined hydrotalcites at 400°C after being synthesized in aqueous medium at pH 10. Finally, a reaction route is proposed to illustrate the cellulose transformation.

1. INTRODUCTION

Our planet is currently concerned about a systematic energy and environmental problem of increased CO₂ emissions, depletion of oil reserves, and global-climate change. To confront the massive global energy and environmental sustainability problem, the planet requires several R&D efforts involving different energy technologies.

Biomass transformation is an outstanding R&D area that has potential to provide a renewable carbon source. Biomass comprises mainly cellulose (40-50%), hemicellulose (25-35%) and lignin (15-35%).^{1,2} Among these constituents, cellulose and hemicellulose can both be hydrolyzed to fermentable sugars and represent an attractive alternative replacing petroleum by biofuels, and producing a wide range of biomaterials or value-added chemicals.

Specifically, cellulose is a polymer of glucose and its general molecular formula is (C₆H₁₀O₅)_n. Cellulose has a high molecular weight (between 300,000 and 500,000 grams per mol) and consists of long chains formed by glucose units linked by glycosidic bonds³. 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 that makes cellulose

recalcitrant to hydrolysis and insoluble in most solvents, even water.⁴

Due to the high crystallinity matrix presented by cellulose, different researches selected microcrystalline cellulose (MCC) as a feedstock to mimic the recalcitrant nature of cellulose.⁴⁻⁷ With MCC, depolymerization of cellulose 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 furane derivatives, among other water-soluble and insoluble materials.⁴ Thus, a depolymerization process at milder conditions is required.

Attempts to enhance the MCC reactivity include some activation treatments before the catalytic hydrolysis known as pre-treatments. These pre-treatments should not only produce higher sugar yields and limited amounts of degradation byproducts but also cost less in terms of equipment, energy and catalyst.⁸ Until now, different pre-treatment methodologies are available, based principally on physical pretreatment, solvent fractionation and chemical pretreatment.⁴

In physical pretreatment, ball-milling is used to disrupt the crystalline network³ formed by intermolecular hydrogen bonds having readily accessible fibrils for cellulose hydrolysis⁹; and non-thermal atmospheric plasma (NTAP) has great interest in industry for surface treatments of biomass enhancing the reactivity of resistant cellulose towards hydrolysis.¹⁰ However, physical pretreatments require high energy input increasing production costs. In solvent fractionation, ionic liquids (ILs) and phosphoric acid facilitate cellulose dissolution by disrupting the hydrogen bonding between molecules¹¹, but their application on a large scale is still limited by high cost and toxicity problems. Finally, in chemical pretreatment, acids, alkalis, and oxidizing agents are used as catalysts and represent an efficient and cost effective solution for transforming the cellulose with a feasible application in industry.¹ One of these is ozone, an attractive powerful oxidizing agent that has been used as delignificant with different types of biomass, such as cereal straw, wood pulp or sugarcane bagasse; and to increase the digestibility of other biomass such as macroalgae or solid waste.²

Once cellulose is activated, it is exposed to a hydrolysis treatment 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 treatments, but it has some drawbacks like high cost and strict control of temperature and pH, which results a burden when scaling-up the process. As an alternative, catalytic hydrolysis by microwave treatment of cellulose is becoming one of the most promising techniques.¹²

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.

The catalytic hydrolysis of cellulose under acidic conditions involves the use of different acids such as sulfuric acid, oxalic acid, peracetic acid, among others. Concentrated acids are less used due to corrosion problems, toxicity and formation of inhibitory compounds as furfurals that can hinder the subsequent fermentation processes or humins that decrease the yield of desirable reaction products.¹³ On the other hand, dilute acid treatments are considered as a cheap and effective method due to low cost and easy

availability of acids.¹ However, due to its homogeneous nature reusability is not possible, sacrificing sustainability and increasing downstream wastes.

As an alternative, a catalytic treatment involving the use of hydrotalcites (HT) or layered double hydroxides (LDH), which are reusable heterogeneous catalysts, permit reducing waste stream processing and corrosive problems; easy separation and reuse; low cost and high efficiency.^{14,15} HTs consist of positively charged layers with anionic species in the interlayer, forming neutral clay materials.¹⁵ HTs are an important group of solid alkali catalysts with strong basic properties, which can be controlled by varying their composition¹⁶, and present high catalytic activity for cellulose hydrolysis. Cellulose is pretreated by synthesizing HTs over the cellulose, or mixing it previously with hydrotalcites or calcined hydrotalcites in order to enhance further hydrolysis treatment.

Regarding value-added chemicals production, one of the most important derivatives from cellulose is lactic acid.¹⁷ Highly demanded nowadays for biopolymer polylactic acid (PLA) production, a biodegradable, biocompatible, and environmentally friendly alternative to plastics derived from petrochemicals.

Lactic acid can be produced either by chemical synthesis from petrochemical resources or by microbial fermentation. Currently, fermentation is the most common process applied in industry.¹⁷ However, biotechnological processes present several drawbacks such as limited space-time yield, waste processing and demanding reactor control parameters (temperature, pH, microorganism population). These problems could be solved by chemical processes with heterogeneous catalysts as a highly effective and simpler process with low impact to the environment.¹⁸

Our study includes MCC pretreated by impregnation with hydrotalcites. We propose the catalytic conversion of pretreated cellulose by microwave conversion technology to hydrolyze cellulose, in order to determine an efficient, selective and cost effective path to transform biomass to different value-added products.

2. EXPERIMENTAL

2.1. Materials

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

purified water from a Milli-Q system with a resistivity of 18.2 MΩ·cm at 25 °C.

Aluminium 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 hydrotalcites

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 HT 4:1) was prepared by dissolution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (8.448 mmol for HT 2:1 and 10.288 mmol for HT 4:1) and the respective amount of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (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 Na_2CO_3 (0.94 M) in water.

Additionally, HTs were synthesized in two different mediums, one containing dispersed cellulose and other in aqueous media, as detailed below.

Preparation of cellulose dispersion for HT21-10, HT41-10 and HT41-40 synthesis

Dispersed cellulose was prepared with 10 grams of microcrystalline cellulose in 200 ml of water. The sample was sonicated in order to homogenize the sample, selecting a 30% power for 3 lapses of 10 minutes, stopping between every lapse to avoid over heating the sample. HT21-10 and HT41-10 contains a 10% w/w of HT over the cellulose, while HT41-40 contains a 40% w/w.

Preparation of media for HT21 and HT41 synthesis

HT21 and HT41 hydrotalcites were prepared separately from cellulose, in a beaker containing 200 ml of water.

Co-precipitation synthesis of the full range of HTs

In co-precipitation synthesis, the salts from first solution were added dropwise to a beaker containing dispersed cellulose or water, adjusting the decreasing pH with drops of the basic solution and keeping it constant in a range of 9.8-10.0. The addition was performed under constant stirring in an IKA magnetic stirrer hotplate. The HT solution was reserved for 24

hours 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 hours at 80°C.

Once the samples composed by HTs or cellulose with HTs were dried, they were grinded homogenizing the sample.

Preparation of calcined HTC21 and HTC41

Portions of the synthesized HT21 and HT41 samples were calcined separately in a preheated oven at 400°C during 3 h under air stream to obtain the calcine Mg/Al HT HTC21 and HTC41 respectively.

Preparation of HT21-10F, HT41-10F and HT41-40F

HT21-10F, HT41-10F and HT41-40F correspond to samples prepared with HT21 and HT41 respectively, mixed externally with MCC.

2.3. Hydrolysis experiments

0.5 g of MCC with the respective amount of HT was added to a Teflon vessel and 20ml of water. The reaction was carried out at 180°C in a START E Milestone microwave during 1 hour at 300W, with an additional heating time of 15 minutes.

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

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), diluting the sample 1:20 and using a 1000 ppm calibration curve. The inorganic carbon concentration was analyzed with the same equipment in order to determine the possible apparition of residual carbonates in the sample.

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 H_2SO_4 . Reaction products were identified by comparing the retention times with commercial

standards. The concentrations in the samples were determined using calibration curves obtained by injecting standard solutions of known concentrations.

2.5. Characterization of solid phase and raw cellulose

X-ray diffraction (XRD)

Hydrotalcites, MCC, and MCC with HT before and after the hydrolysis reaction, were characterized by XRD analyses using a Siemens D5000 diffractometer with an angular 2θ -diffraction range between 5° and 90° .⁸ Additionally, the crystallite diameter was calculated using the Scherrer equation in the 110 plane.

Fourier transform infrared spectroscopy (FTIR)

The characterization of MCC, HT, and MCC with HT, was followed by FTIR. This technique allows obtaining information about the interaction of the HT particles with the MCC before and after the hydrolysis.

The 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.

Environmental surface electron microscopy (ESEM)

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

Surface area analysis

The specific surface area of the HTC particles 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 (0.667 Pa). The total surface area and the pore specific volume were determined according to B.E.T equation, and the pore diameter was calculated using Barrett-Joyner-Halenda (BJH) method.

3. RESULTS AND DISCUSSION

3.1. Structural analysis

3.1.1. XRD results

The crystalline structure of the prepared hydrotalcites in the presence and absence of microcrystalline cellulose was confirmed using XRD in Fig. 1. The XRD of prepared HT samples (Fig. 1.A and 1.B) exhibit typical diffraction patterns of hydrotalcite-like compounds (JCPDS card 22-0700) at 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 3h, the hydrotalcite structure disappears, resulting in formation of mixed oxides phases with typical features of a $\text{Mg}(\text{Al})\text{O}$ type.¹⁹ Two weak and broad signals at 43° and 62.4° appear consistently with the presence of a MgAlO_x mixed oxide phase with a structure like MgO (periclase) (JCPDS card 04-0829), corresponding to 400 and 440 planes (Fig. 1.C. and 1.D.); and plane 111 correspond to MgAl_2O_4 spinel phase, along with other signals at 45° and 65° .²⁰ As can be seen, hydrotalcites HT21 and HT41 have the same crystalline structure than HT synthesized over MCC (Fig. 1.E and 1.F), showing that the HT structure was truly formed on cellulose during the synthesis. The diffraction spectra of MCC can be recognized in Fig. 1.E, 1.F, 1.G and 1.H, presenting peaks at approximately 15° and 16.5° (overlapped 101 and $10\bar{1}$ peaks) and 22.5° (002). MCC

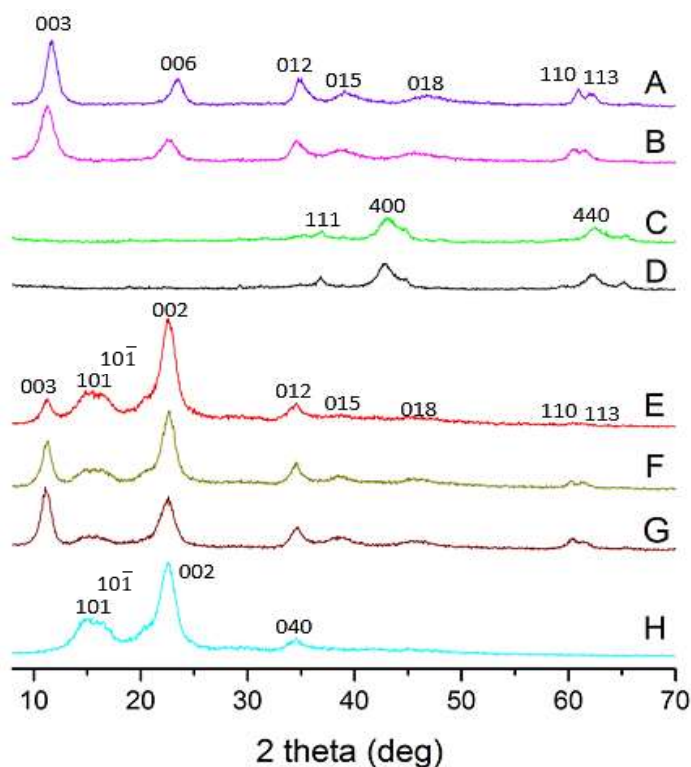


Fig. 1. XRD diffractogram of synthesized HT (A) HT21, (B) HT41, (C) HTC21, (D) HTC41, (E) HT41-10, (F) HT41-40, (G) HTC41-11 (HTC41 with cellulose after reaction), and (H) MCC.

presents a high intensity in Fig. 1.E, where the HT planes are slightly broadened maybe due to interactions between the MCC and the inorganic phase.

After reaction, the calcined HTC41 sample shows a rehydrated structure, which implies the reconstruction of the layered HT assembly (Fig. 1.G), while the remaining unreacted MCC preserves its crystalline structure.

3.1.2. FTIR results

The FTIR spectra for hydrotalcite HT41, representative cellulose with HT samples (HT41-11 and HTC41-11), and MCC was depicted in Fig. 2, between a wavenumber range of 4000 cm^{-1} and 600 cm^{-1} . MCC was included for comparative purposes. MCC (Fig. 2.D) presents a broad absorption range at 3328 cm^{-1} due to the stretching of H-bonded OH groups. At 2900 cm^{-1} appears a peak associated to C-H stretching vibration. The peak at 1650 cm^{-1} is related with absorbed water in cellulose. In addition, the peak at 1429 cm^{-1} is allotted to symmetric CH_2 bending vibration, and this band is also known as the “crystallinity band”. The absorption band at 896 cm^{-1} , related to C-O-C stretching at $\beta(1,4)$ glycosidic bond, is recognized as the “amorphous” absorption region in MCC.²¹

HT41 (Fig. 2.A), HT41-11 (Fig. 2.B) and HTC41-11 (Fig. 2.C) samples presented a broad absorption band around $3336\text{--}3439\text{ cm}^{-1}$ assigned to OH stretching vibration. A sharp and intense band at 1360 cm^{-1} is recognized to the ν_3 assymetric stretching for carbonates. This shape suggests a symmetrical arrangement of the CO_3^{2-} symmetry in the interlayers.²² This band position is not affected by the presence of cellulose in the samples B and C. HT synthesized in MCC showed a small band at 2900 cm^{-1} which could correspond to the formation of intramolecular hydrogen bonds with MCC and water molecules hydrogen bonded to the carbonate ion present in the interlayer. Furthermore, these samples presented bands from MCC (1054 , 1105 and 1161 cm^{-1}) showing to have weak forces of physical interaction with HT (Fig. 2.B and Fig. 2.C).

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.²³ It can be seen in Fig. 3.A that the 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, clear to observe in Fig. 3.B.

The same behavior was observed by decreasing the size of the flat structures after calcination at 400°C (Fig.3.C and 3.D). *Xie et al* have explained this behavior by the $\text{Mg}(\text{OH})_2$ brucite sheets that compose the Mg-Al hydrotalcite, in which Al^{3+} substitutes for Mg^{2+} sites, and is transformed to periclase-like Mg-Al-O solid solutions by calcination at high temperature.¹⁹ 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.

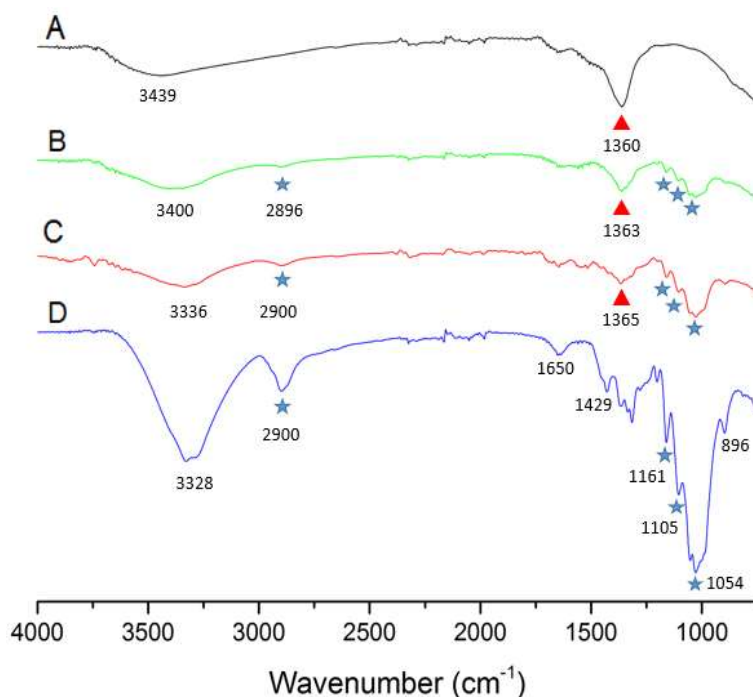


Fig. 2. FTIR spectra of synthesized HT (A) HT41, (B) HT41-11 (HT41 with cellulose after reaction), (C) HTC41-11 (HTC41 with cellulose after reaction), (D) MCC.

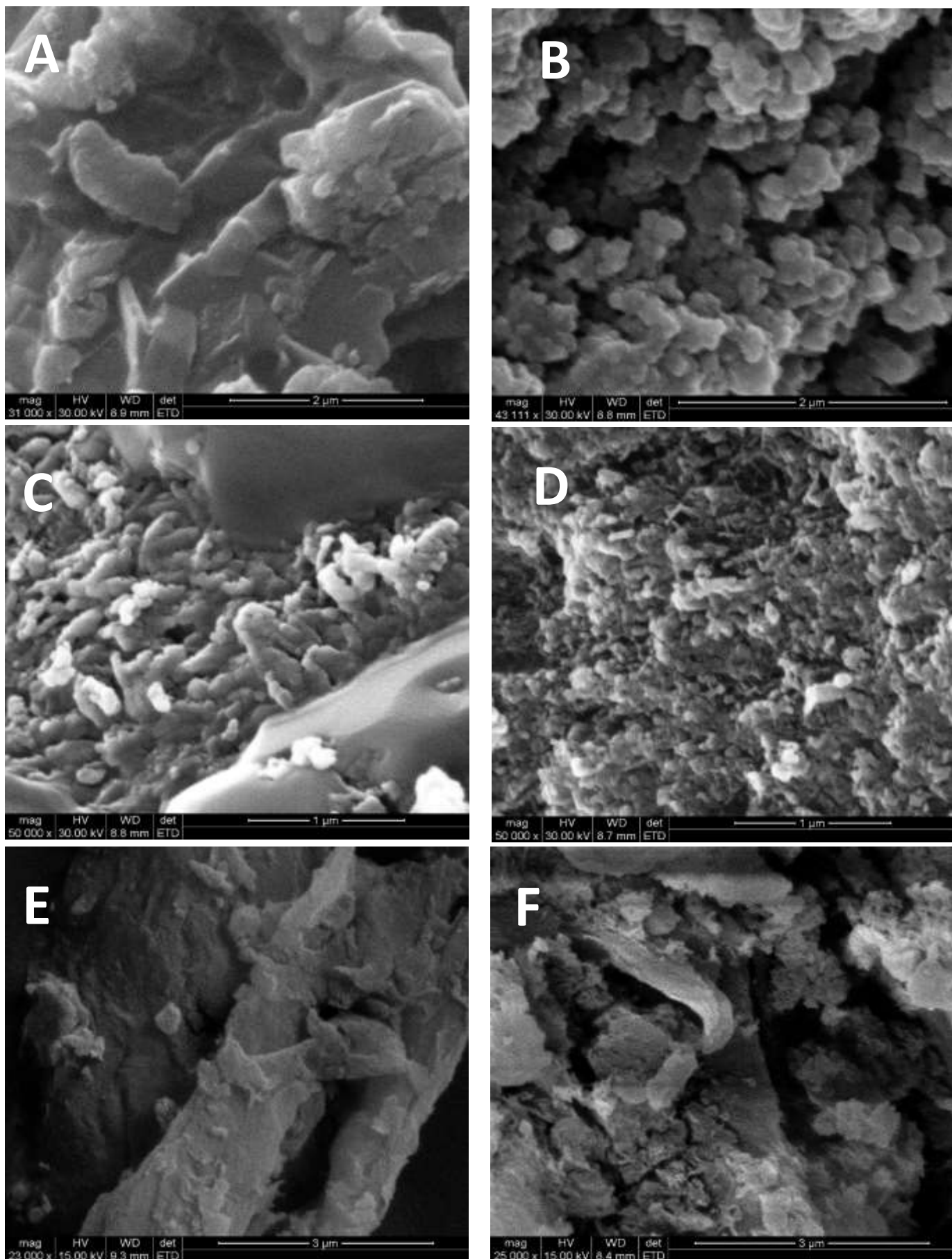


Fig. 3. ESEM images of synthesized HT (A) HT21, (B) HT41, (C) HTC21, (D) HTC41, (E) HT41-10, and (F) HT41-40.

The presence of cellulose during the HT synthesis promoted the HT particles to anchor themselves on the MCC networks. From the Fig. 3.E and 3.F, it is possible to see 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. 3.E) than in HT41-40 (Fig. 3.F). 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 HTC

The BET surface area for calcined hydrotalcites with structure $Mg_{(1-x)}Al_2O_3$ is included in table 1. The surface area and pore specific volume for HTC21 is $60.4 \text{ m}^2/\text{g}$ and $0.180 \text{ cm}^3/\text{g}$, respectively, while the surface area and pore volume for HTC41 increases to $88.3 \text{ m}^2/\text{g}$ and $0.28 \text{ cm}^3/\text{g}$, correspondingly, related with the increase in the Mg content. Furthermore, the calcination in air of the HT samples produced a mesoporous residue where the pore volume is mainly contained in pore diameters of around 7.1 nm for HTC21 and 5.3 nm for HTC41. 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 layer¹⁸.

Catalyst	BET Surface area (m^2/g)	Pore specific volumen, V_p (cm^3/g)	d_{pore} (nm)	Crystallite (nm)
HTC 21	60.4	0.18 @P/Po=0.9898	7.1	6.1
HTC 41	88.3	0.28 @P/Po=0.9961	5.3	4.3

Table 1. BET surface area, pore specific volume, average pore diameter and crystallite size (110 plane) for calcined hydrotalcites HTC21 and HTC41.

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

Experimental results are expressed in Table 2 and figures 4 and 5.

3.2.1. Effect of Mg/Al ratio and cellulose impregnation on the product yield

The influence of different metal ratio during the synthesis of hydrotalcites over the MCC was compared

and the results are shown in Figure 4. Furthermore, it was shown the effect of synthesizing the hydrotalcites into the cellulose instead of common hydrotalcites synthesis. Using a 4:1 Mg/Al molar ratio, the conversion was higher than with a 2:1 ratio, demonstrating that synthesizing HT into cellulose improved cellulose conversion, with a maximum conversion of 9,6% with HT41-10. Besides formic acid, acetic, lactic and glycolic acids were formed during hydrolysis.

3.2.2. Effect of the amount of hydrotalcite charged into cellulose on the product yield

A higher amount of HT41 (40% instead of 10%) was synthesized over the cellulose and the hydrolysis results were compared and presented in Figure 4. The cellulose conversion increased to 16.6%, showing that a higher amount of catalyst helped in the cellulose transformation.

3.2.3. Effect of the hydrotalcite calcination on the product yield

Calcined hydrotalcites (400°C for 3 h) were investigated for cellulose hydrolysis (Fig. 5). When Mg/Al ratio increased from 2:1 to 4:1, cellulose conversion increased from 19.6 to 28.1 %. It means that catalytic activity improved with the increase in Mg content.

Catalyst	Reactants		Product selectivity (%)			
	MCC (g)	HT (g)	LA (%)	FA (%)	AA (%)	GA (%)
HT21-10F	0.5	0.05	4.6	10.6	4.7	5.2
HT21-10	0.5	0.05	10.6	14.6	3.4	10.2
HT41-10F	0.5	0.05	21.8	17.5	7.1	12.3
HT41-10	0.5	0.05	11.3	15.6	10.4	10.6
HT41-40F	0.5	0.2	10.8	13.7	6.1	7.3
HT41-40	0.5	0.2	10.5	10.3	4.6	5.3
HT21	0.5	0.5	15.3	18.3	10.3	9.2
HTC21	0.5	0.5	17.4	15.0	9.6	4.5
HT41	0.5	0.5	15.5	16.6	9.6	7.1
HTC41	0.5	0.5	20.9	17.8	8.4	5.2
BLANK	0.5	0.0	0.4	2.2	1.1	0.0

Table 2. Experimental results of MW assisted conversion of MCC with hydrotalcites at 180°C for 1 hour.

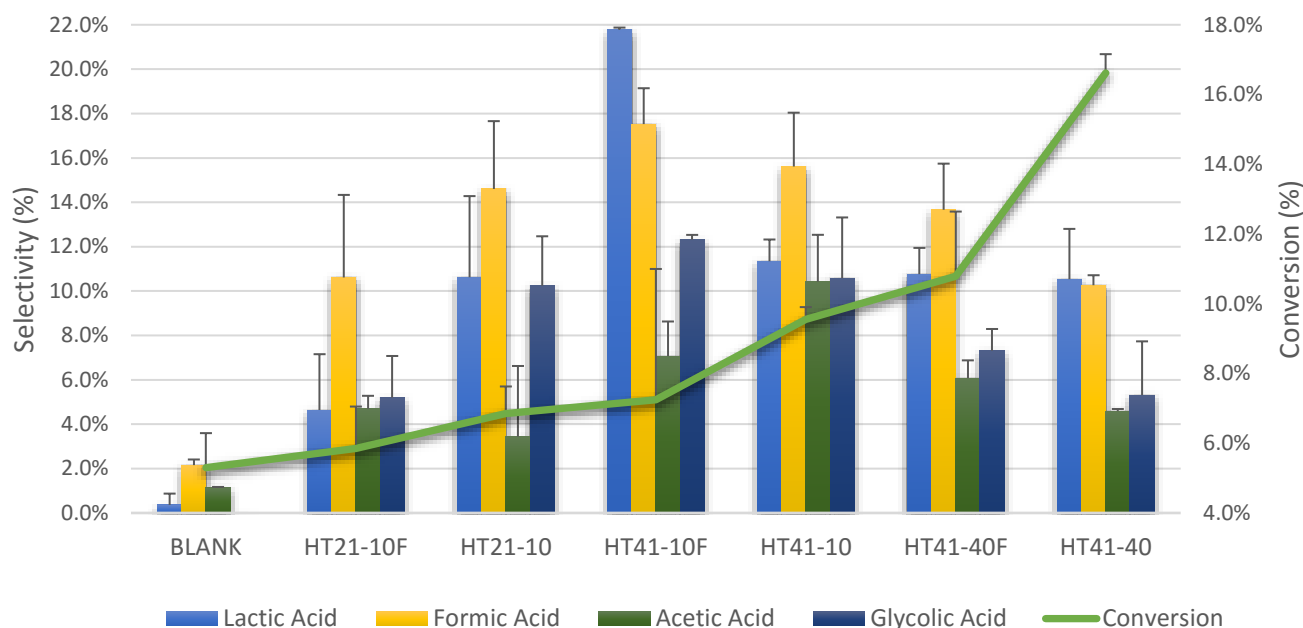


Fig. 4. Cellulose conversion and generation of compounds with different amounts of HTs.

LA and FA formation seemed to be favored when mixing the calcined and non-calcined HT with MCC, meanwhile the formation of LA, FA and GA apparently was favored when the HT was synthesized on the MCC surface.

Calcined HTs improved their catalytic activity over non-calcined HTs due to an increase in the concentration of basic sites, which is related with the accessibility of the interlayer anions, including the concentration and accessibility of edge anions explained as the dispersion of primary particles and their agglomeration. Moreover, the crystallite size might influence basicity because of the amount of defects is likely to be higher for materials with small crystallographic coherent domains.²³ The

HTC41 exhibits smaller sizes of crystallographic coherent domains in (110) direction than the sizes for HTC21 (table 1). For that reason, the probability to exhibit structural defects with increases in basicity is higher in case of HTC41.

3.2.4. Reaction pathway

As indicated above (table 2), during the hydrothermal treatment of MCC at 180°C for 1 h under alkaline conditions, the major products obtained were lactic acid (LA), acetic acid (AA), formic acid (FA) and glycolic acid (GA). Based on these results, we propose a reaction pathway as depicted in Fig. 6.

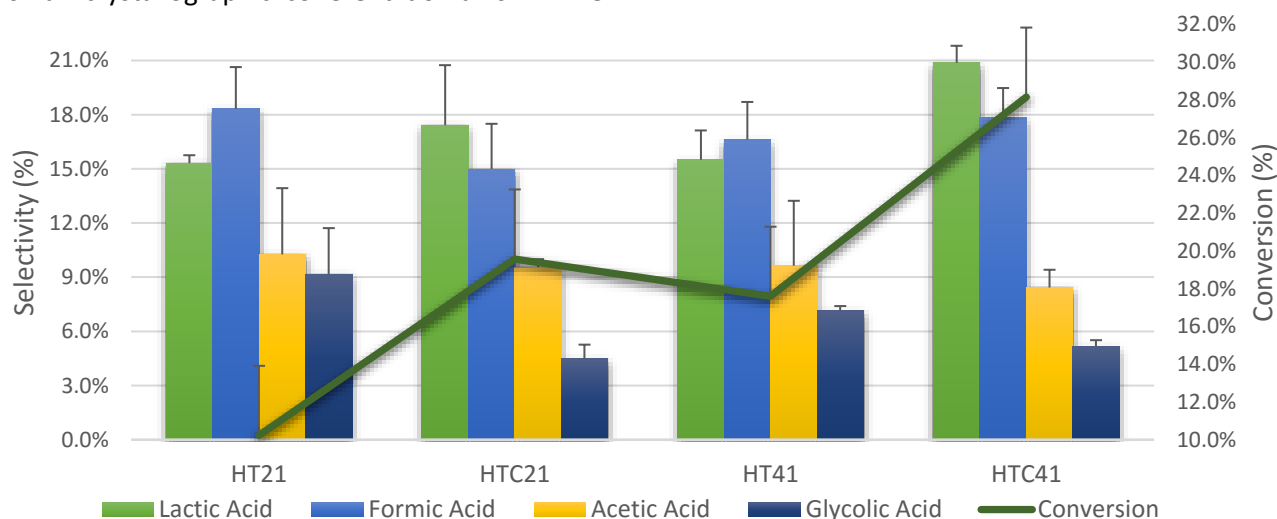


Fig. 5. Cellulose conversion and generation of compounds with no-calcined and calcined HTs.

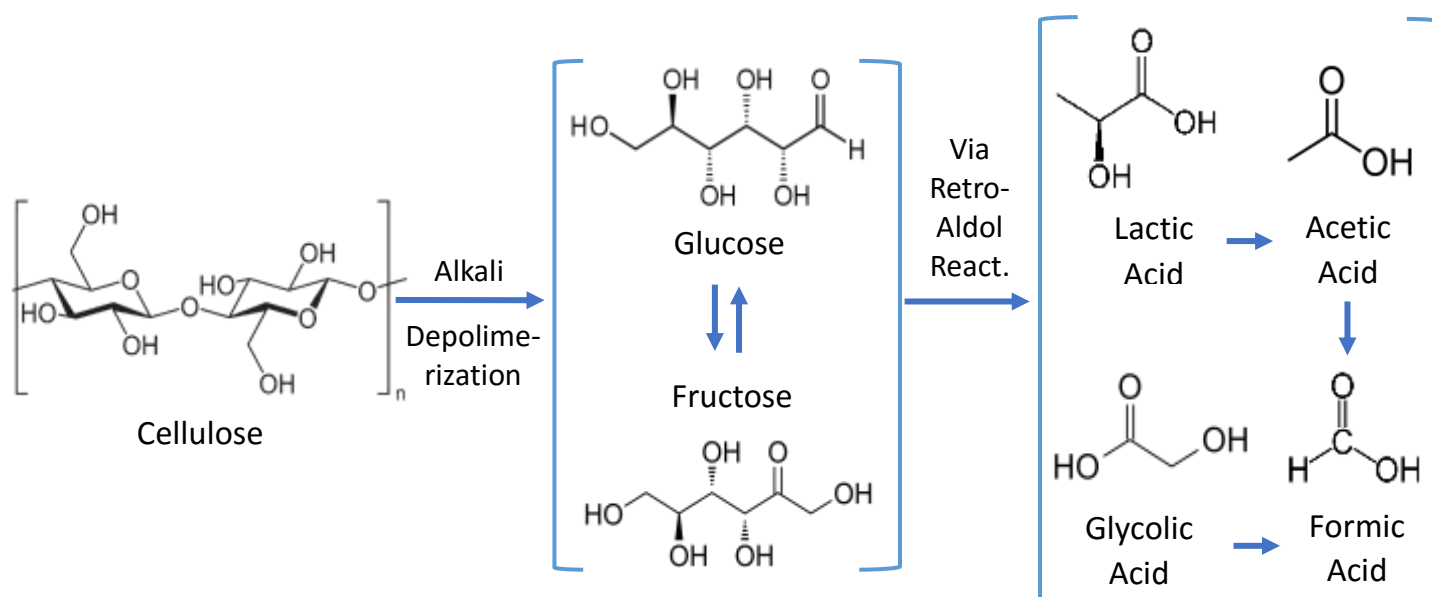


Fig. 6. Reaction pathway of cellulose over base catalyst with hydrotalcites

Cellulose is firstly hydrolyzed to glucose, which through a dynamic equilibrium might isomerize into fructose. Then, C_6 sugars break by retro-aldol splitting into two C_3 fragments, forming dihydroxyacetone or glyceraldehyde. The dehydration of these fragments affords pyruvaldehyde, which is converted to LA via a 1,2-hydride shift as proposed by D. Esposito and M. Antonietti (2015).²⁴ Other feasible route for breaking C_6 sugars undergo also a retro-aldol condensation forming glycolaldehyde (C_2) and erythrose (C_4) molecules, intermediates in the production of GA.^{25–27} Once the carboxylic acids are obtained, GA and LA can be further degraded into FA or AA respectively.²⁸

It is worth noting that retro-aldol appears to be a very interesting reaction as it occurs with 100% atom efficiency, and it is a valuable pathway to increase functionality of the biomass feedstock without the use of sacrificial reagents or oxidants, due to its capacity to transform a sugar into value-added compounds.²⁹

CONCLUSIONS

Microcrystalline cellulose was selected as a recalcitrant model for biomass transformation and its catalytic hydrolysis in basic conditions was demonstrated. MCC was depolymerized in a single step with HT treatment assisted by microwave irradiation, this fact has a great importance for the production of different value-added products such lactic, formic or glycolic acids. Which could be obtained from different cellulosic sources.

The synthesized materials were characterized by different physico-chemical analysis. The increase in the crystallite diameter with a higher Mg content in HTC41 was proved by XRD results. FTIR confirmed the presence of HTs and MCC in the residual solid after hydrolysis. ESEM images supported the particle size decrease in HTs after calcination, and also verified the presence of HTs resting on the MCC after synthesis in HT41-10 and HT41-40 samples. BET measurements showed that HTC41 had the highest surface area with $88 \text{ m}^2/\text{g}$. This fact was in consonance with higher catalytic performance, converting up to 28% of MCC in valuable products, principally lactic, formic, acetic, and glycolic acids.

According to proposed reaction pathway, HTs were able to produce LA, FA, AC and GA from cellulose. In conclusion, Mg/Al hydrotalcites present good yields for cellulose transformation via retro-aldol mechanism, presenting an outstanding alternative for the current processes being able to produce wide variety of high-value added products.

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