Abstract: 5-hydroxymethylfurfural (5-HMF) is an important platform molecule for the synthesis of high-added value products. Several synthesized clay materials, such as mesoporous hectorite and fluorohectorite, in addition to commercial montmorillonite K-10, have been acid modified by different methodologies to be applied as catalysts for the obtention of 5-HMF from glucose. The effects of the Brønsted and/or Lewis acidity, the reaction temperature and time, and the catalyst/glucose ratio on the conversion but especially on the selectivity to 5-HMF have been studied. By comparing the synthesized clays, the best selectivity to 5-HMF (36%) was obtained at 140 °C for 4 h with H-fluorohectorite because of the presence of strong Brønsted acid sites, although its conversion was the lowest (33%) due to its low amounts of Lewis acid sites. Different strategies, such as physical mixtures of montmorillonite K10, which contains high amounts of Lewis acid centers, with Amberlyst-15, which has high amounts of Brønsted acid sites, or the incorporation of rhenium compounds, were carried out. The best selectivity to 5-HMF (62%) was achieved with a mixture of 44 wt % Amberlyst-15 and 56 wt % of montmorillonite K10 for a 56% of conversion at 140 °C for 4 h. This proportion optimized the amount of Brønsted and Lewis acid sites in the catalyst under these reaction conditions.

Keywords: 5-hydroxymethylfurfural; clays; glucose; acidity; Brønsted; Lewis

1. Introduction

The development of technologies to produce energy and chemicals from renewable resources, as an alternative to petroleum-derived products, has prompted biomass valorization [1–3]. Lignocellulose, the most abundant renewable biomass, is considered the main raw material in a biorefinery concept. Lignocellulose consists of three types of polymers: cellulose (40–50%), hemicellulose (25–35%) and lignin (15–20%). The conversion of biomass by fractionation into functionalized platform molecules, which includes sugars (glucose, xylose), polyols, furans (furfural, 5-hydroxymethylfurfural) and acids (levulinic) allows the production of a wide range of biofuels and chemicals [1].

Among the different platform molecules that can be obtained from biomass, 5-hydroxymethylfurfural (5-HMF) is one of the most versatile due to the presence in the same molecule of an aromatic aldehyde group, an alcohol and a furan ring that can be converted to high-added value products, such as bioplastics, biofuels or other chemicals [4]. 5-HMF is usually synthesized from glucose through two consecutive acid catalyzed reactions: isomerization of glucose to fructose catalyzed by Lewis acid sites and dehydration of fructose to 5-HMF catalyzed by Bronsted acid sites (Scheme 1) [5,6].

For the first isomerization step, which is the most difficult due to the stability of the six-carbon glucose ring, enzymatic, basic and Lewis acid catalysts have been tested [7]. Regarding basic catalysts, the use of as-synthesized, calcined and rehydrated Mg/Al-hydrotalcites led to high conversion values of glucose (73%) [8]. However, these catalytic systems required low glucose concentration and a long time of reaction. With respect to Lewis acid
catalysts, CrCl₂ in a liquid ionic solvent resulted in 68% of yield at 100 °C after 3 h, while other Cu(II) or Fe(II) salts presented worse results [9].

![Scheme 1. Mechanism for the catalytic obtention of 5-HMF from glucose.](image)

Heterogeneous catalysts have been also applied as an alternative to homogeneous catalysts due to their reusability. Sn-Beta zeolite presented interesting results related to the presence of SnO₂ as extra-framework species [10]. Davis et al. found that Sn-beta could efficiently catalyze the isomerization of glucose to fructose and then convert fast the generated fructose to 5-HMF with HCl at low pH [10,11]. The authors concluded that Sn⁴⁺ ions were active as Lewis acid centers for the glucose isomerization to fructose, while the partially hydrolyzed Sn–OH groups acted as Brønsted acid sites for the dehydration of fructose. A total amount of 5% Sn/SAPO-34 zeolite prepared by impregnation showed 98.5% of glucose conversion with a 64.4% of 5-HMF yield at 150 °C after 1.5 h of reaction [12]. Nb₂O₅:nH₂O catalysts led to 49% yield of 5-HMF at 160 °C after 110 min of reaction time when H₃PO₄ was added to the catalytic system because of the presence of Brønsted acid sites [13]. In this way, the 76.3% yield of 5-HMF obtained by using Ag₃PW₁₂O₄₀ at 130 °C after 1.5 h of reaction was attributed to the synergistic effect between the Lewis and Brønsted acid sites present in the catalyst [14,15]. A carbon-based solid catalyst prepared from crystalline cellulose by carbonization and later sulfonation has been tested, achieving good catalytic results (73% of glucose conversion and 65% of selectivity to 5-HMF) [16]. Moreover, one sulfonated carbon obtained from an active carbon resulted in total glucose conversion and 93% of selectivity to 5-HMF at 160 °C after 3 h of reaction [17].

More recently, Pd nanoparticles supported in a highly acidic ZrO₂ exhibited 55% of glucose conversion with 74% of selectivity to 5-HMF after 3 h of reaction at 160 °C. The high catalytic activity was related to the balance between Brønsted and Lewis acid sites, in combination with the intrinsic activity of Pd species [18]. X. Li et al. concluded that the increase in Lewis acid sites promoted glucose dehydration, while Brønsted acid sites had a detrimental effect on glucose isomerization, achieving selectivity to 5-HMF of 71% for 92.6% of conversion using silica–alumina composite catalysts at optimized conditions [19]. However, a recent review on the topic remarked that more studies are needed to analyze and understand the role of Brønsted/Lewis acid sites present in the catalytic systems on the reaction [20].

Cationic clay minerals are layered microporous materials containing negatively charged aluminosilicate sheets, which further contain cations in their interlayer space to balance the charge and water molecules. Hectorites are cationic clays of the smectite group, with formula Mⁿ⁺ₓ/n[(Mgₓ₋ₓLiₓ)Si₄O₁₀(OH)₂]. When Mⁿ⁺ is replaced by H⁺, the resulting clay has Brønsted acidity. The acidity of hectorites can be improved by delamination, which increases the accessibility to the acid sites [21], or by the substitution of the –OH groups by –F, leading to fluorohectorite [22]. There are few references about the use of clays for the obtention of 5-HMF from glucose. Sn-montmorillonite and Nb-montmorillonite led to high conversion, high yield and moderate-high selectivity values to 5-HMF (54.4% and 71.2%, respectively) [23,24]. The catalytically active sites in the Nb–OH groups favored glucose isomerization and subsequent dehydration with a 70.52% yield of 5-HMF at 170 °C for 3 h. Attapulgite modified by phosphoric acid showed 56.6% of 5-HMF yield in a 2-butanol-water biphasic system at 170 °C after 3 h of reaction. The results were again attributed to the proper amount of Brønsted and Lewis acid sites [25].

The aim of this work was to study the catalytic activity of several synthesized clay materials, such as mesoporous hectorite and fluorohectorite, in addition to commercial
montmorillonite K-10, which were acid modified by different methodologies, including the preparation of physical mixtures with commercial sulfonic macroporous resin Amberlyst-15, or the incorporation of rhenium cations, to be applied as catalysts for the catalytic obtention of 5-hydroxymethylfurfural from glucose. The effect of the Brønsted and/or Lewis acidity, the reaction temperature and time, and the ratio catalyst/glucose on the conversion and selectivity results were studied.

2. Experimental Section

2.1. Materials

MgO (97%), SiO$_2$ (99%), trimethyldecylammonium chloride (98%) NH$_4$NO$_3$ (98%) and LiOH (98%) were supplied by Sigma Aldrich, LiF (98%) by Acros Organics, MgCl$_2$ (99%), MgF$_2$ (99%) and NH$_4$ReO$_4$ (99%) by Alfa Aesar and 1-butanol (99.5%) by Scharlau. Commercial montmorillonite K10 (Si/Al = 2.7) and Amberlyst-15 were supplied by Sigma-Aldrich (St. Louis, MO, USA).

2.2. Preparation of Catalysts

Na$^+$ mesoporous hectorite was synthesized as delaminated hectorite (Na-DH) using trimethyldecylammonium chloride as template, following a method previously developed by our research group [21,26].

Fluorohectorite (Li-FH), with formula Li$_{0.7}$(Mg$_{5.3}$Li$_{0.7}$)Si$_8$O$_{20}$F$_4$, was synthesized by mixing sintered SiO$_2$, sintered MgO, commercial LiF and commercial MgF$_2$ in a 8:4:2:2 molar ratio, respectively [22]. The mixture was homogenized following a sequence of different methods: grounding, suspending in acetone under an ultrasounds bath (Selecta) for 20 min and finally evaporating the solvent and drying the solid in an oven at 80 °C overnight. The resulting solid was then heated in a conventional muffle furnace at 800 °C for 3 h. The product was purified by selective sedimentation in a centrifuge (Hettich Zentrifugen Rotofix 32 A). The solid was suspended in about 50 mL of water and stirred overnight at room temperature. Then, it was centrifuged at 600 rpm for 6 min, and the supernatant was centrifuged at 4000 rpm for 30 min. The settled solid was dried and stored at room temperature.

Commercial montmorillonite K10 (MK10) was also tested as a catalyst for comparison. H$^+$ delaminated hectorite (H-DH) and H$^+$ Fluorohectorite (H-FH) were prepared by the ionic exchange of previously synthesized Na-DH and Li-FH, respectively, with 1 M NH$_4$NO$_3$ aqueous solution by refluxing for 1 h. Then, the suspension was centrifuged, and the resultant solid was calcined at 540 °C for 3 h and stored at room temperature.

Several physical mixtures of montmorillonite K10 (MK10) and Amberlyst-15 (A) were prepared with different A-MK10 wt ratios: 0.4 (28 wt % A: 72 wt % MK10), 0.8 (44 wt % A: 56 wt % MK10) and 1 (50 wt % A: 50 wt % MK10).

MK10 was impregnated with an appropriate aqueous-ethanol solution of NH$_4$ReO$_4$ (with the minimum amount of water) to obtain 5 wt % of rhenium in the final sample. After rota evaporation of the solvents, the solid was calcined at 300 °C for 3 h (Re$_2$O$_7$/H-DH, Re$_2$O$_7$/MK10). The temperature of calcination of NH$_4$ReO$_4$ was chosen to prevent sublimation of NH$_4$ReO$_4$ at temperatures above 300 °C [27]. Other groups of samples were then prepared by mixing Amberlyst-15 with Re$_2$O$_7$/MK10 at the same A-Re$_2$O$_7$/MK10 ratios as those of A-MK10 mixtures. Finally, Re$_2$O$_7$, obtained by calcining NH$_4$ReO$_4$ at 300 °C for 3 h, was also tested alone for comparison.

Table 1 summarizes the different methodologies used for the acid modification of the clays.
Table 1. Methodologies for the acid modification of the clays.

| Starting Clay | Acid Modification | Sample |
|---------------|-------------------|--------|
| Na-DH         | NH$_4^+$ cation exchange +calcination | H-DH   |
| Li-FH         | NH$_4^+$ cation exchange +calcination | H-FH   |
| MK10          | Physical mixtures with Amberlyst-15 (A) | 28 wt % A: 72 wt % MK10, 44 wt % A: 56 wt % MK10, 50 wt % A: 50 wt % MK10 |
| MK10          | Impregnation with NH$_4$ReO$_4$ to obtain 5 wt % of Re + calcination | Re$_2$O$_7$/MK10 |
| H-DH          | Impregnation with NH$_4$ReO$_4$ to obtain 5 wt % of Re + calcination | Re$_2$O$_7$/H-DH |
| Re$_2$O$_7$/MK10 | Physical mixtures with Amberlyst-15 (A) | 28 wt % A: 72 wt % Re$_2$O$_7$/MK10, 44 wt % A: 56 wt % Re$_2$O$_7$/MK10, 50 wt % A: 50 wt % Re$_2$O$_7$/MK10 |

2.3. Characterization of Catalysts

X-ray diffraction was used to identify and quantify the crystalline phases present in the catalytic precursors and catalysts. The experiments were carried out with a Siemens D5000 diffractometer (Bragg–Brentano parafocusing geometry and vertical $\theta$–$\theta$ goniometer) fitted with a curved graphite diffracted-beam monochromator and diffracted-beam Soller slits, a 0.06° receiving slit and scintillation counter as a detector. The angular 2$\theta$ diffraction range was between 5° and 70°. The sample was dusted onto a low background Si (510) sample holder. The data were collected with an angular step of 0.05° at 3 s per step and sample rotation. CuK$_\alpha$ radiation was obtained from a copper X-ray tube operated at 40 kV and 30 mA. The JCPDS files used for the identification of the crystalline phases were 00-003-0168, 01-075-0909 and 01-073-5680, for hectorite, anthophyllite and fluorohectorite, respectively.

BET surface areas were calculated from the nitrogen adsorption isotherms at $-196$ °C using a Quantachrome Quadrasorb SI surface analyzer and a value of 0.164 nm$^2$ for the cross-section of the nitrogen molecule.

The Brønsted acid capacity of the physical mixtures and their starting compounds was measured through the determination of cation exchange capacities using aqueous sodium chloride (2 M) solutions as a cationic exchange agent. The released protons were then potentiometrically titrated [28].

2.4. Catalytic Activity

Catalytic isomerization of commercial glucose (Sigma-Aldrich) was tested in a 100 mL stainless-steel autoclave equipped with an electronic temperature controller and a mechanical stirrer. Several reaction parameters were studied: temperature and time of reaction and catalyst/glucose ratio. The reaction conditions tested are summarized in Table 2.

Table 2. Reaction conditions tested for the obtention of 5-HMF from glucose.

| Reaction Parameter | Reaction Conditions |
|--------------------|---------------------|
| Temperature Time   | 100, 120, 140, 160 and 180 °C 1, 4 and 24 h 0.6 g/2.4 g (0.25) 0.3 g/2.4 g (0.125) |
| Catalyst wt/glucose wt ( ratio) | 0.15 g/1.2 g (0.125) 0.3 g/0.6 g (0.5) 0.15 g/0.6 g (0.25) 0.075 g/0.6 g (0.125) |
In a typical experiment, glucose was dissolved in 50 mL of a mixture of THF:H₂O (35:15), and a fresh catalyst was transferred to the reactor. The temperature of the reaction was set with stirring of 600 rpm. At the end of the reaction, the reaction mixture was cooled, and the reaction products were separated from the catalyst by microfiltration.

Kit fructose/glucose assay, provided by Cygic Biocon SL, was used for determining the conversion of glucose and the selectivity to fructose.

\[
\text{Conversion of glucose (\%)} = \frac{\text{Number of moles of converted glucose}}{\text{Number of moles of starting glucose}}.
\]

\[
\text{Selectivity to fructose (\%)} = \frac{\text{Number of moles of glucose converted to fructose}}{\text{Number of moles of converted glucose}}.
\]

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 × 0.25 mm × 0.50 µm). 1-Butanol was the internal standard. The quantification of products was determined based on GC data using the internal standard method in order to determine the selectivity to the desired product calculated as indicated below.

\[
\text{Selectivity to 5-HMF (\%)} = \frac{\text{Number of moles of glucose converted to 5-HMF}}{\text{Number of moles of converted glucose}}.
\]

3. Results and Discussion

3.1. Characterization of Catalysts

Table 3 summarizes the main characterization results obtained for the synthesized clays and for commercial montmorillonite K10.

| Catalyst | Crystalline Phases (XRD) | BET Area \(^a\) (m\(^2\)/g) | Acidity \(^b\) (meq/g) |
|----------|--------------------------|-----------------------------|----------------------|
| MK10     | Montmorillonite          | 233                         | —                    |
| Na-DH    | Hectorite                | 327                         | 0.90                 |
| H-DH     | Hectorite                | 334                         | 0.67                 |
| Li-FH    | Fluorohectorite, anthophyllite | 17                  | 0.23                 |
| H-FH     | Fluorohectorite, anthophyllite | 21                  | 0.53                 |

\(^a\) Calculated from N\(_2\) physisorption results. \(^b\) Obtained by NH\(_3\)-TPD. Data from [22].

The XRD patterns of the mesoporous hectorites (Na-DH and H-DH) showed the presence of the peaks corresponding to the crystalline hectorite with the exception of the (0 0 1) reflection, related to layer stacking, as expected, due to delamination (e.g., Figure 1a). The high BET surface areas were similar to those obtained for delaminated hectorites previously prepared in our research group [21]. The mesopores correspond to the interparticle space of lamellar-shaped crystallites, aggregated by edge-to-face bonding.

Li-FH and its protonated form (H-FH) presented the main crystalline phase, identified as fluorohectorite, with a well-defined (001) reflection at \(2\Theta = 7^\circ\) indicating a high order of the lamellar material in the stacking direction. In addition, anthophyllite and quartz phases were detected in lower amounts. After purification, quartz was eliminated, and anthophyllite was reduced, obtaining practically pure fluorohectorite (e.g., Figure 1b). These samples had much lower surface areas (17–21 m\(^2\)/g) than delaminated hectorites due to their microporosity, high crystallinity and the sinterization suffered during calcination at high temperature. Additionally, the residual anthophyllite phase could partially block the pores of fluorohectorite samples, contributing to lowering their surface area.

For the samples prepared with rhenium, it was not possible to detect the presence of rhenium compounds by XRD, probably due to the low amount loaded (5 wt %). Considering the calcination temperature used, the presence of Re\(_2\)O\(_7\) should be expected, although according to other studies found in the literature, there could also be a mixture of Re\(^{6+}\)/Re\(^{7+}\) oxides [29].
In a previous work, we evaluated the acidity (amount and strength) of this type of clay materials by \( \text{NH}_3 \)-TPD [22]. The amount of acid sites is shown in Table 3. Na-DH had a higher amount of acid sites than H-DH because of the presence of higher amounts of Lewis acid sites (Na\(^+\)) but lower acidity strength, since the \( \text{NH}_3 \) desorption temperature was lower for Na-DH (190 °C) than for H-DH (224 °C) [22]. This confirms the higher strength of the Brønsted acid sites of the H-DH sample. The amount of acid sites of Li-FH was the lowest and can be mainly attributed to the Lewis acid sites (Li\(^+\)). H-FH showed a higher number of acid sites than Li-FH (Table 3), and, interestingly, very strong acidity, since the \( \text{NH}_3 \) desorption temperature for its main desorption peak was 721 °C [22]. The effect of the partial substitution of –OH groups by F in the hectorite structure favored an increase in the acidity of the Brønsted acid sites (H\(^+\)) of the H-FH through an inductive effect of fluorine.

Commercial montmorillonite K10 is a montmorillonite, which was submitted to an acid treatment. This involves: (a) some dealumination of the structure, and therefore, the presence of Lewis acid sites due to extra framework cations; (b) higher surface area than montmorillonite because of the generation of some mesoporosity; and (c) the presence of some amount of Bronsted acid sites due to the acidic medium used during the treatment. For the Re-containing samples, the rhenium cations act as Lewis acid centers.

The Brønsted acidity of the A-MK10 and A-Re\(_2\)O\(_7\)/MK10 physical mixtures was evaluated by titration and compared to their starting compounds alone. The results are shown in Table 4.

Amberlyst-15 showed the highest amount of Brønsted acid sites, as expected, due to the sulfonic groups present in this macroporous resin, while Re\(_2\)O\(_7\) and MK10 had the lowest, since they mainly had Lewis acidity, as commented above. The physical mixtures increased the values of Brønsted acid sites with respect to MK10 or Re\(_2\)O\(_7\)/MK10 due to the presence of Amberlyst-15. These results will be later correlated with the catalytic results.

Figure 1. XRD patterns of several synthesized clays (a) delaminated hectorite (Na-DH) and (b) Li-fluorohectorite (Li-FH). * anthophyllite.
Table 4. Characterization of the Brønsted acidity of the physical mixtures and starting compounds.

| Catalyst | Brønsted Acidity (meq H⁺/100g) |
|----------|----------------------------------|
| Re₂O₇    | 5.0                              |
| MK10     | 15.4                             |
| Re₂O₇ / MK10 | 27.2                         |
| A        | 478.8                            |
| 28 wt % A: 72 wt % MK10 | 113.6                        |
| 44 wt % A: 56 wt % MK10 | 190.4                        |
| 50 wt % A: 50 wt % MK10 | 251.6                        |
| 28 wt % A: 72 wt % Re₂O₇ / MK10 | 137.7                     |
| 44 wt % A: 56 wt % Re₂O₇ / MK10 | 229.2                     |
| 50 wt % A: 50 wt % Re₂O₇ / MK10 | 232.8                     |

3.2. Catalytic Activity

First, the effect of the reaction temperature and the catalyst/glucose weight ratio were studied with commercial montmorillonite K-10 (MK10) in order to find the optimized conditions to check the rest of the catalysts. All studies were conducted with a solvent mixture of THF:H₂O in a volume ratio of 35:15. From several preliminary experiments with different solvents and mixtures of solvents, this was found to be the best solvent to favor the obtention of 5-HMF. Figure 2 shows the effect of the reaction temperature using 2.4 g of glucose and 0.3 g of MK10 catalyst for 1 h of reaction.

Figure 2. Effect of the reaction temperature on the catalytic activity of the catalyst MK10. Reaction conditions: 2.4 g of glucose, 0.3 g of catalyst, catalyst/glucose wt ratio = 0.125, solvent volume ratio (THF:H₂O) = 35:15 and reaction time = 1 h.

The results showed an increase in the conversion values with the temperature, as expected, and the formation of the desired product, 5-hydroxymethylfurfural (5-HMF), from 160 °C. No other reaction products, such as levulinic acid or formic acid, were detected by gas chromatography. Therefore, the other reaction products should be related to the polymerization of glucose, fructose and 5-HMF that result in the formation of condensation products. These undesired products easily formed from 100 °C, while isomerization reaction was slower and needed higher temperatures or, as concluded below, longer times.

The effects of using different catalyst/glucose weight ratios on the conversion and selectivity to 5-HMF values were then studied with the MK10 catalyst at 180 °C for 1 h (Figure 3).
was the optimized ratio, and the second-best result was achieved with the same ratio using 0.6 g of catalyst and 2.4 g of glucose with a catalyst/glucose ratio of 0.25. This was the optimized ratio, and the second-best result was achieved with the same ratio using lower amounts of catalyst and glucose. One more catalytic test with catalyst MK10 was performed at the optimized catalyst/glucose ratio, decreasing the reaction temperature (140 °C) and increasing the reaction time (4 h) (Figure 3). The selectivity to 5-HMF was maintained (34%) at moderate conversion (62%).

We selected these reaction conditions—0.6 g of catalyst, 2.4 g of glucose, 140 °C and 4 h—to test catalysts with different total acidity and different presence of Brønsted and/or Lewis acid sites. The corresponding results are shown in Figure 4.

![Figure 3](image_url)

**Figure 3.** Effect of the different catalyst/glucose wt ratios on the catalytic activity of the catalyst MK10. Reaction conditions: solvent volume ratio (THF:H₂O) = 35:15, temperature = 180 °C and reaction time = 1 h. * Reaction temperature = 140 °C and Reaction time = 4 h.

On the whole, there are not significant differences between the catalytic tests. The highest selectivity to 5-HMF (38%) and the highest yield of 5-HMF (36%) were observed when using 0.6 g of catalyst and 2.4 g of glucose with a catalyst/glucose ratio of 0.25. This was the optimized ratio, and the second-best result was achieved with the same ratio using lower amounts of catalyst and glucose. One more catalytic test with catalyst MK10 was performed at the optimized catalyst/glucose ratio, decreasing the reaction temperature (140 °C) and increasing the reaction time (4 h) (Figure 3). The selectivity to 5-HMF was maintained (34%) at moderate conversion (62%).

The catalysts with higher amounts of acid centers, especially Lewis acid centers, and higher surface areas (MK10 and Na-DH) (Table 3) showed higher conversion values, as
expected, due to the importance of Lewis centers for the first isomerization step from glucose to fructose (Scheme 1). By comparing the selectivity to 5-HMF and to fructose obtained for these two catalysts, the lower amount of Brønsted acid sites of Na-DH justifies its lower selectivity to 5-HMF but higher selectivity to fructose, while the Brønsted acid sites remaining in the K10 montmorillonite, after the acid treatment to which it was submitted to obtain it, favored the transformation of fructose to 5-HMF, the second step of the reaction (Scheme 1).

H-DH had lower amounts of Lewis acid sites and higher amounts of Brønsted acid sites than Na-DH, and consequently, lower conversion but higher selectivity to 5-HMF was obtained when compared to Na-DH. For the fluorohectorite (Li-DH), the conversion was lower, and the selectivity to 5-HMF was higher than for the Na-DH catalyst. The lower amount of acid centers of Li-DH (Table 3) justifies its lower conversion, although it was higher than for H-DH, probably because of the higher amounts of Lewis acid centers due to cations Li⁺. The higher selectivity to 5-HMF compared to Na-DH should be related to the presence of some amounts of Brønsted acid sites due to the hydrolysis of the Li⁺ cations. Interestingly, the highest selectivity to 5-HMF for this group of catalysts was achieved with the protonated fluorohectorite (H-FH) due to its stronger Brønsted acid sites, as commented above, although its conversion was the lowest due to the low amounts of Lewis acid sites of this catalyst.

Taking into account that the montmorillonite K10 showed the best yield of 5-HMF and one of the best selectivity values to 5-HMF, in order to improve these results, we planned to modify its acidity by preparing several physical mixtures of MK10 with sulfonic macroporous resin Amberlyst-15 (A), which had higher amounts and stronger Brønsted acidity, in order to favor the second step of the reaction, the formation of 5-HMF from fructose (Scheme 1). Figure 5 shows the catalytic activity results obtained for these A-MK10 mixtures with different wt % ratios compared to the catalytic results of A and MK10 catalysts. The amount of Brønsted acid sites (meq H⁺/100 g), determined by titration, is also indicated in the figure.

The catalytic activity of Amberlyst-15 (A) showed lower conversion but higher selectivity to 5-HMF and lower selectivity to fructose than that of catalyst MK10. This confirms again that Lewis acid sites are more active for the overall transformation of glucose, and
Brønsted acid sites are responsible for the selective conversion of fructose to 5-HMF. By mixing physically both catalysts in different wt % proportions, a synergetic effect was clearly observed. Thus, the presence of 28 wt % of Amberlyst-15 favored both an increase in conversion and selectivity to 5-HMF due to the stronger Brønsted acid sites provided by Amberlyst-15 (Table 4) but with a still significant contribution of the Lewis acid centers of MK10. On the other hand, the mixed catalyst with 50 wt % of A led to lower conversion than those of MK10 and the mixed catalyst with 28 wt % of A, and a slight increase in selectivity to 5-HMF with respect to MK10 but lower than for the mixed catalyst with 28 wt % of A (Figure 5). These results can be explained because of the covering of part of the Lewis acid sites of MK10 by the Brønsted acid sites of A. Then, an optimized A-MK10 ratio was searched, and it was found at the proportion 44 wt % of A and 56 wt % of MK10, obtaining a moderate glucose conversion of 56% and the highest selectivity to 5-HMF of 62%.

Another way to modify the acidity of the clay MK10 was to load a 5 wt % of rhenium to increase Lewis acidity and then to prepare mixtures with Amberlyst-15, with high amounts of strong Brønsted acidity. The catalytic results are shown in Figure 6.

![Figure 6](image-url)

**Figure 6.** Catalytic activity of physical mixtures A-Re2O7/MK10 in different wt % proportions compared to A, MK10, Re2O7 and Re2O7/MK10 catalysts. Reaction conditions: 2.4 g of glucose, 0.6 g of catalyst mixture, catalyst/glucose wt ratio = 0.25, solvent volume ratio (THF:H2O) = 35:15, temperature = 140 °C and reaction time = 4 h.

The incorporation of rhenium in MK10 increased the selectivity to fructose, with respect to the MK10 or Re2O7 alone, as expected due to its higher amount of Lewis acid sites, and it led to higher selectivity to 5-HMF (51%) than MK10 (34%) and Re2O7 (29%). This can be explained by the higher amount of Brønsted acidity of catalyst Re2O7/MK10, as determined by titration (Table 4, Figure 6), which could be related to some hydrolysis of the rhenium cations during the reaction. Finally, the decrease in conversion can be attributed to a decrease in the surface area of the catalyst because of the impregnation-calcination procedure employed.

From these results, the following attempt to improve the selectivity to 5-HMF was to mix this Re2O7/MK10 catalyst in different proportions with Amberlyst-15. Independently of the proportions used, the selectivity to 5-HMF did not improve the value obtained for catalyst Re2O7/MK10 (Figure 6). The mixture with the highest selectivity to 5-HMF (45%) was 44 wt % of Re2O7/MK10 and 56 wt % of Amberlyst-15. A possible explanation for this catalytic behavior is that the acid properties of Re2O7 were modified when mixed with Amberlyst-15. It is well known that rhenium cations can be protonated. This should decrease the amount and strength of Lewis acid sites of the mixtures.

Finally, the effect of the reaction time was studied for the best catalyst (44 wt % of A and 56 wt % of MK10) by comparing its catalytic activity at 4 and 24 h of reaction with those of its precursors, A and MK10, and also with catalyst Re2O7/MK10 (Figure 7).
Figure 7. Effect of the reaction time, 4 h and 24 h, for several catalysts. Reaction conditions: 2.4 g of glucose, 0.6 g of catalyst mixture, catalyst/glucose wt ratio = 0.25, solvent volume ratio (THF:H₂O) = 35:15, temperature = 140 °C.

All catalysts showed an increase in conversion with the reaction time but, with the exception of MK10, this increase in conversion did not involve an increase in the selectivity to 5-HMF, and in general, a decrease in fructose was also observed. This means that the increase in conversion was at the expense of the formation of other reaction products, probably polymerization products, especially more favored for the catalysts that had higher amounts of stronger Brønsted acid sites due to Amberlyst-15. Interestingly, catalyst MK10 showed an increase of 10% in the selectivity to 5-HMF with time, and for Re₂O₇/MK10, only a slight decrease was observed (Figure 7). This behavior could be explained by the low amounts of acid centers present in these catalysts, which do not favor polymerization as much, and in the case of MK10 favor the slow transformation to 5-HMF with time.

Figure 8 shows the reproducibility of the catalytic results of the best catalysts, which were checked thrice. Higher standard deviation was observed when the physical mixture of Amberlyst-15 and montmorillonite K10 was tested. This can be related to its preparation procedure.

Figure 8. Reproducibility of the catalytic results of the best catalysts. Reaction conditions: 2.4 g of glucose, 0.6 g of catalyst mixture, catalyst/glucose wt ratio = 0.25, solvent volume ratio (THF:H₂O) = 35:15, temperature = 140 °C and reaction time = 4 h.

4. Conclusions

Several synthesized clays, such as delaminated Na- Hectorite and Li-fluorohectorite, in addition to commercial montmorillonite MK-10, were acid modified by different methodologies: the incorporation of protons (H- Hectorite and H-fluorohectorite), physical mixtures of montmorillonite MK-10 with Amberlyst-15 to combine Lewis and Bronsted acidity and
the addition of rhenium compounds with Lewis acidity. The catalytic results confirmed the importance of combining Lewis and Brønsted acid centers in the appropriate amounts to favor the transformation of glucose to fructose by the Lewis acid sites and the subsequent conversion of fructose to 5-HMF by the Brønsted acid sites. The optimized reaction conditions were established in a reaction temperature of 140 °C, reaction time of 4 h, using 0.6 g of catalyst and 2.4 g of glucose, with a catalyst/glucose ratio of 0.25.

Regarding the synthesized clays, H-fluorohectorite showed the highest selectivity value to 5-HMF (36%) at 140 °C for 4 h that can be attributed to the strong Brønsted acid sites of this catalyst due to the incorporation of fluorine in the hectorite structure during fluorohectorite preparation. For the physical mixtures between Amberlyst-15, with high amounts of strong Bronsted acid sites, and montmorillonite K10, with Lewis acid centers, the best selectivity to 5-HMF (62%) was achieved with a mixture of 44 wt % Amberlyst-15 and 56 wt % of montmorillonite K10 for a 56% conversion. The incorporation of rhenium in MK10 increased the selectivity to fructose, with respect to the MK10 or Re₂O₇ alone, due to the higher amount of Lewis acid sites and led to higher selectivity to 5-HMF (51%) than MK10 (34%) and Re₂O₇ (29%). This has been related to the generation of Brønsted acidity in catalyst Re₂O₇/MK10 due to some hydrolysis of the rhenium cations during reaction. However, the physical mixtures of Re₂O₇/MK10 with Amberlyst-15 did not improve the selectivity to 5-HMF. Catalyst MK10 showed an increase of 10% in the selectivity toward 5-HMF when the reaction time was increased to 24 h. This was related to low amounts of acid centers in this catalyst, which, with time, do not favor polymerization as much and continue forming 5-HMF.

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