



Flow Semi-continuous Mechanochemistry as a Versatile and Efficient Tool for the Synthesis of Hydrocalumite and the Isomerization of Glucose to Fructose

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Abstract

In this work, hydrocalumite, a layered double hydroxide with formula $\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl}\cdot 2\text{H}_2\text{O}$, has been prepared for the first time using flow semi-continuous mechanochemistry with a DYNO®-MILL RESEARCH LAB (Willy A. Bachofen AG, Switzerland), with stoichiometric amount of reactants in water, after only 5 min at 25 °C. Hydrocalumite, before and after thermal treatment, was characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TG–DTA) and N_2 sorption at – 196 °C. Moreover, calcined hydrocalumite has been evaluated as catalyst for the isomerization of glucose to fructose, a catalytic process which has also been performed in the same flow semi-continuous mechanochemical reactor. This mechanochemical system, unlike conventional ball milling, allows working in semi-continuous and/or continuous mode, using solvents and allowing heating control up to temperatures of 80 °C. The isomerization of glucose to fructose was successfully carried out in this reactor, demonstrating that hydrocalumite prepared by mechanochemistry is more active than that prepared by co-precipitation. The optimization of several experimental variables (reaction temperature and time, glucose/catalyst weight ratio and concentration of glucose in water) has resulted in a 23.5% fructose yield, with a glucose conversion of 38.1%, after 1 h of reaction, at 50 °C, with a 17 wt% glucose and a glucose/catalyst weight ratio of 6. However, the highest fructose productivity was reached under similar experimental conditions, but after only 5 min, with a value of $0.50 \text{ kg}_{\text{fructose}} \text{ L}_{\text{H}_2\text{O}}^{-1} \text{ h}^{-1}$ (equivalent to $15 \text{ kg}_{\text{fructose}} \text{ Kg}_{\text{cat}}^{-1} \text{ h}^{-1}$), which is susceptible to be improved by implementing a continuous mode, assisted with a liquid pump, in the mechanochemical reactor. Therefore, this work has evidenced the versatility and potential of this new flow semi-continuous mechanochemical reactor for the synthesis of crystalline layered double hydroxides, under sustainable experimental conditions, and to perform catalytic processes with high performance, using water as solvent and atmospheric conditions.

Keywords Glucose · Fructose · Isomerization · Hydrocalumite · Mechanochemistry

1 Introduction

Lignocellulosic biomass is an attractive and sustainable resource for obtaining biofuels and high value-added chemicals, reducing our dependence on fossil-based feedstocks and moderating greenhouse gas emissions [1]. Recent

advances in biomass valorization have enabled the efficient transformation of carbohydrates to a platform of chemicals with potential applications in many industrial sectors. Mono-saccharides, present in most inedible biomass derived from waste cellulosic materials, have received special attention, in particular glucose, because of its versatility and the possibility of obtaining fructose through its isomerization. Fructose, beyond being widely used as sweetener in food industry, is becoming the main reagent to produce numerous chemicals, that could be a sustainable alternative to many of those synthesized from fossil fuels, such as 5-hydroxymethylfurfural and levulinic acid. These two platform molecules are considered valuable chemicals derived from biomass. In this context, the development of fast, inexpensive and sustainable

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processes capable of performing selective glucose isomerization is essential to advance in biomass conversion [2, 3].

This process of isomerization of glucose to fructose is carried out, at industrial level, with glucose syrups which are transformed into high fructose syrups to be used as feedstock to other industrial processes, or for the food industry [4, 5]. These fructose syrups are produced by enzymatic catalysis using glucose isomerase, or mannose isomerase, and the necessary conditions are strict due to the different pH ranges required to an efficient work of enzymes. In addition, the subsequent steps for the removal of these enzymes, such as separation and purification, are costly processes. The reaction equilibrium limits the production of fructose to 42%, although higher values can be achieved by chromatographic separation or nanofiltration [6]. Therefore, numerous studies aim at the development of acid and basic catalysts for the isomerization of glucose to fructose, many of them focusing on the search of heterogeneous catalysts, which exhibit low cost and high stability compared to enzymes [7, 8].

Among heterogeneous catalysts, several works have reported the use of zeolites, as a source of Lewis acid centers to catalyze the isomerization process. In particular, zeolites with low Sn content are selective to fructose and mannose at low temperatures, since otherwise they would favor the formation of secondary products derived from glucose [9–12].

However, most of works deal with the base-catalyzed isomerization of glucose, which was recently reviewed [13]. In this sense, hydrotalcites (mainly in calcined form), zeolites with alkali and alkaline-earth metals, alkaline-earth metal oxides, transition metal oxides, soluble amines and nitrogen-containing materials have been reported as catalysts for this process. Regarding the experimental conditions, mostly water was used as solvent, at reaction temperatures ranging between 70 and 200 °C (preferably at 80–100 °C). On the other hand, metal oxides, such as MgO, Al₂O₃, SiO₂, TiO₂, ZrO₂ and Nb₂O₅, treated with ammonia, have achieved fructose yields of 34–54 with conversions of 45%, in water at 80 °C, being the selectivity of the reactions relatively high [14]. Other inorganic solids that have been widely studied in the field of glucose isomerization to fructose are hydrotalcites. Hydrotalcite is layered double hydroxide (LDH) of general formula Mg₆Al₂CO₃(OH)₁₆·4H₂O, where anions like CO₃²⁻ compensate the positive charge created by the isomorphic substitution of Mg²⁺ by Al³⁺ in a Mg(OH)₂ structure. After calcination, a mixture of MgO and Al₂O₃ is formed. Using calcined hydrotalcites, fructose yields up to 56% with glucose conversions of 70% can be achieved [15–18].

When Ca²⁺ and Al³⁺ ions exist in the hydroxide structure, and the interlaminar anion is Cl⁻, hydrocalumite is formed,

although other anions such as CO₃²⁻ or NO₃⁻ can be hosted in the interlayer region [12, 19, 20]. Therefore, hydrocalumite is another family of layered double hydroxides, where the total charge is also compensated by anions A^{m-}, with a general formula of [M_{1-x}²⁺M_x³⁺(OH)₂]^{x+}A_{x/m}^{m-} · nH₂O. However, other divalent and trivalent cations can be incorporated into LDH structures besides Ca²⁺ and Mg²⁺, such as Co²⁺, Ni²⁺, Zn²⁺, Mn²⁺, Cd²⁺ and the trivalent cation can also be Fe³⁺, Cr³⁺, Ga³⁺ [7, 20–22].

The syntheses of hydrotalcites and hydrocalumites are generally performed by co-precipitation and ageing of the corresponding metal hydroxides, but these processes are time-demanding and, depending on the solubility constant, a fraction of reactants remains in solution in equilibrium with the solid. Thus, new synthesis methodologies have been developed for the manufacture of these families of metal hydroxides, meeting the principles of Green Chemistry [23]. In this context, mechanochemistry, a part of chemistry that uses mechanical energy to carry out chemical processes, such as solid-state reactions, preparation of materials and treatment of biomass, among many others, arises as a sustainable alternative to conventional processes [23–26]. In addition to being a mostly green method due to the absence of harmful solvents, it stands out for the high loading of reagents that can be introduced in order to increase productivity.

Mechanochemistry processes are mainly based on ball milling, and they have already been applied for the synthesis of layered Mg–Al double hydroxides. Thus, for instance, Fahami et al. prepared at high purity Mg_{0.8}Al_{0.2}(OH)₂Cl_{0.2} by mixing Mg(OH)₂, AlCl₃, NaOH and Na₂CO₃ in a high energy ball mill, with a milling time of 5 h [27]. However, a lower crystallinity was observed compared to a hydrothermal method [28]. Even manually grinding in a mortar of Mg and Al nitrates, an NaOH pellets was employed for the synthesis of a Mg–Al–NO₃ LDH [29]. Manually grinding is far away for any industrial purpose, so new technologies using mechanochemistry are envisaged. The intercalation of species, like salicylate, in a Mg:Al LDH was successfully carried out during the solvent-free deposition of this LDH on halloysite nanotubes, being a sustainable alternative to conventional methods based on solution chemistry [30].

In the present work, a mechanochemical equipment, allowing to work in a continuous or semi-continuous flow mode (depending if using a loop connection in the outlet to the inlet to increase residence times) has been used for both the preparation of catalyst precursors (hydrocalumite) and the isomerization of glucose to fructose, with the aim of improving productivity of the catalytic process, and facilitating the industrial scale-up.

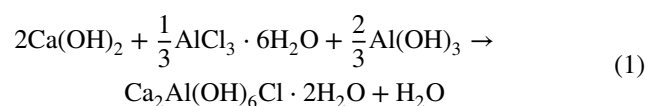
2 Materials and Methods

2.1 Reactants

Ca(OH)₂, Al(OH)₃ and AlCl₃·6H₂O (>99%) were supplied by VWR, Sigma-Aldrich and Alfa Aesar, respectively. Glucose, fructose and mannose were also obtained from Sigma-Aldrich (>99%).

2.2 Material Preparation

The synthesis of hydrocalumite was carried out according to the Reaction 1:



The stoichiometric amounts of reactants to prepare 20 g of hydrocalumite were dispersed in 200 mL of deionized water.

Two different methods were used for the synthesis of hydrocalumite:

- (1) Conventional: co-precipitation carried out at 25 °C for 1 h, where the reagents were mixed in water, maintaining a magnetic stirring of 500 rpm. Next, centrifugation at 7500 rpm for 10 min allowed to separate the solid, which was washed with deionized water and dried at 70 °C for 24 h. The sample was labelled as HC_conv
- (2) By mechanochemistry in a semi-continuous flow reactor (loop mode by leaving the machine at the outlet and feeding again to the inlet of the machine), DYNOMILL RESEARCH LAB (Willy A. Bachofen AG, Switzerland), with a tip speed of 8.5 m s⁻¹, using 1 mm beads (ZrO₂ doped with Y₂O₃) at 25 °C (measured in the outlet of the machine) for 5, 15 and 60 min. After synthesis, the suspension was centrifuged at 7500 rpm for 10 min, and the solid was washed with deionized water and dried, being labelled as HC_xmin_RL, where *x* is the time that suspension was passing through the mechanochemical reactor.

The final solids were calcined in a furnace with a heating rate of 5 °C min⁻¹ up to 650 °C and then a cooling down to 200 °C at 5 °C min⁻¹ in ramp-down. The labels of samples were: c_HC_conv and c_HC_xmin_RL.

2.3 Physico-chemical Characterization

N₂ adsorption–desorption isotherms were obtained using an automatic ASAP 2420 from Micrometrics at –196 °C. Prior analysis, the samples were evacuated at 200 °C and

10⁻⁴ bar. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method, and Barrer–Joyner–Halenda (BET) method was employed to determine average pore diameter. N₂ cross-section was considered 16.2 Å².

X-ray photoelectron spectra (XPS) were recorded in a Physical Electronics PHI 5700, with a multichannel detector and non-monochromatic Mg K_α radiation (300 W, 15 kV, 1253.6 eV). Spectra were taken in pass-energy mode at 29.35 eV and a diameter area of 720 μm and calibrated using adventitious carbon at 284.8 eV. PHI ACCESS ESCA-V6.0 F software package was employed to record and treat XPS data. Peaks were fitted using a Gaussian–Lorentzian curve, and a Shirley type background was subtracted from the signals.

Powder X-ray diffraction patterns (XRD) were enregistered on a Philips EMPYREAN automated diffractometer using Cu K_{α1,2} (15,406 Å) and a PIXcel detector. Divergence and anti-divergence slits were fixed at 1/4° and 1/2° Soler slits, respectively, for incident and refracted rays were employed at 0.04 rads. Measures were taken from 5 to 80° (2θ) for approximately 30 min with a step size of 0.0167°. The X-ray tube voltage employed was 45 kV and current of 40 mA. The sample was rotated continuously to increase particle statistics.

Thermal analysis was carried out with a TA instruments (SDT-Q600 analyzer), employing open platinum crucibles under a N₂ flow in the range of 25–1000 °C and a heating rate of 10 °C min⁻¹.

2.4 Catalytic Tests

The isomerization process was also performed in the DYNOMILL RESEARCH LAB (Willy A. Bachofen AG, Switzerland), taking advantage of semi-continuous flow, which allows recirculating the reaction medium, and the control of temperature of the reaction chamber (until 80 °C) [31]. In all cases, the reactor filling volume occupied by 1 mm size beads was 60%. Experimental variables such as the glucose/catalyst weight ratio, reaction temperature and concentration of glucose in water (wt%) were optimized. In addition, the catalysts synthesized by mechanochemistry and by conventional method were compared to observe the effect of the synthesis method on the catalytic performance.

The resulting aqueous solutions were diluted with deionized water for the analysis of the products obtained. A JASCO high performance liquid chromatography (HPLC) system was used for this purpose. An autoinjector (AS-2055) introduces 6 μL of sample from a previously prepared vial. For the aqueous mobile phase, the HPLC has a quaternary gradient pump (PU-2089) that drives the mobile phase, which is microfiltered and degassed deionized water at a flow rate of 0.40 mL min⁻¹, to a Phenomenex Rezex ROA Organic Acid (8%) column (300 mm × 7.8 mm, 5 μm). This

column is placed inside an oven (co-2065) at 70 °C during the analysis. Once the analytes have separated on the chromatographic column, they reach two detectors. A UV–Visible detector (MD-2015) that analyses the aromatic compounds and a universal refractive index detector (RI-2031 PLUS) with which the analytes are identified and quantified.

3 Results and Discussion

3.1 Material Characterization

The crystalline structure of hydrocalumite prepared by conventional and mechanochemical methods, by using the stoichiometric amount of $\text{Ca}(\text{OH})_2$, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3$, was confirmed by X-ray diffraction (Fig. 1). After only 5 min of mechanochemical treatment, the characteristic diffraction peaks of the hexagonal structure of the hydrocalumite ($\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$, with R3 rhombohedral symmetry, with Cl^- and CO_3^{2-} anions located between $[\text{Ca}(\text{OH})_6 \cdot \text{H}_2\text{O}]$ and $[\text{Al}(\text{OH})_6]$ double sheets, were observed [32]. Thus, the diffraction signals associated to the basal spacing appear at a 2θ (°) of 11.30 (003) and 22.67 (006). However, the presence of small fraction of CaCO_3 (JCPDS 05-0586) was confirmed in all cases, resulting from the reaction of $\text{Ca}(\text{OH})_2$ with atmospheric CO_2 , but its amount decreases when hydrocalumite was prepared under mechanochemical conditions at longer reaction times. Compared to the conventional method using the same reaction time, the presence of CaCO_3 is higher when this last one is employed. Thus, another advantage of this mechanochemical reactor, allowing to work in semi-continuous mode and in the presence of solvent, is the shortening of reaction times. For example,

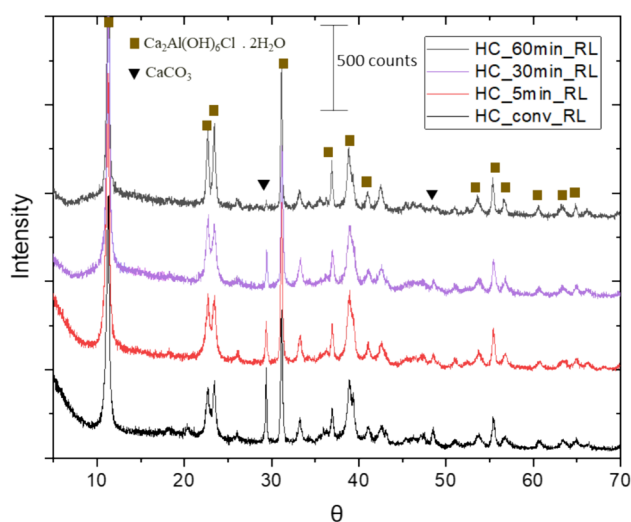


Fig. 1 XRD patterns of hydrocalumites prepared under conventional and mechanochemical treatments

the formation of a MgAl hydrotalcite with classical ball milling, besides the formation of NaCl due to the use of NaOH , brucite ($\text{Mg}(\text{OH})_2$) was detected until 5 h of milling [27]. Therefore, as observed for hydrotalcites, the synthesis of hydrocalumite can be successfully achieved in this new mechanochemical reactor, using stoichiometric amounts of reactants, without the formation of by-products, thus opening the way to the easy scale-up of the synthesis of hydrocalumite, inasmuch the capacity of the mechanochemical reactor used in the present work can be largely increased. In order to compare with previously reported syntheses, it should be mentioned that most of methods are based on co-precipitation from an aqueous solution of precursors (mainly, Ca and Al nitrates or chlorides) by addition of a basic solution (Na_2CO_3 , NaOH), requiring a very long reaction time (12 h at 80 °C) [33], or crystallization time (in water: 17 h at 80 °C [34], in water/ethanol: 18 h at 65 °C [35]). On other cases, the synthesis was assisted by microwaves, operating with a power of 1250 W and a frequency of 2450 MHz, during 2.5 min [36]. Even ball milling has been used, using a mixture of AlCl_3 , CaCl_2 and NaOH , which was treated for 30 h [37]. Therefore, the advantages of the novel methodology proposed in the present work is clear, since it uses stoichiometric amounts of AlCl_3 , $\text{Ca}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$, water as solvent, and, after only 5 min. In addition, this semi-continuous mechanochemical method is able to provide crystalline hydrocalumite, besides offering the opportunity to scale-up this sustainable process.

The calcination of hydrocalumite leads to the formation of mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, JCPDS 9-413) and calcium oxide, because the excess of Ca in hydrocalumite (Ca:Al = 2:1) respect to mayenite (Ca:Al = 6:7) (Fig. 2). Nevertheless, the presence of CaO (JCPDS 37-1497) could be beneficial for the isomerization of glucose to fructose, since basic sites catalyze this process. Moreover, diffraction peaks associated to calcium hydroxychloride were observed at 2θ (°) of 28.12, 38.22 and 47.03.

On the other hand, textural properties of hydrocalumite, before and after calcination, were determined from N_2 sorption at -196 °C. The main textural data of HC_{conv} and $\text{HC}_{5\text{min_RL}}$, before and after calcination, are gathered in Table 1, whereas the adsorption–desorption isotherms are shown in Fig. 3. In both cases, the textural properties worsen with the thermal treatment, with an important reduction of BET surface area and pore volume, although the sample prepared by co-precipitation ($c_{\text{HC}_{\text{conv}}}$) becomes more microporous than that obtained by mechanochemistry ($c_{\text{HC}_{5\text{min_RL}}}$). The average pore diameters varied between 7.9 and 12.0 nm, large enough to facilitate the access of glucose molecules to the active sites and the exist of fructose and mannose. Nevertheless, there are no important differences between both synthesis methods in terms of textural properties.

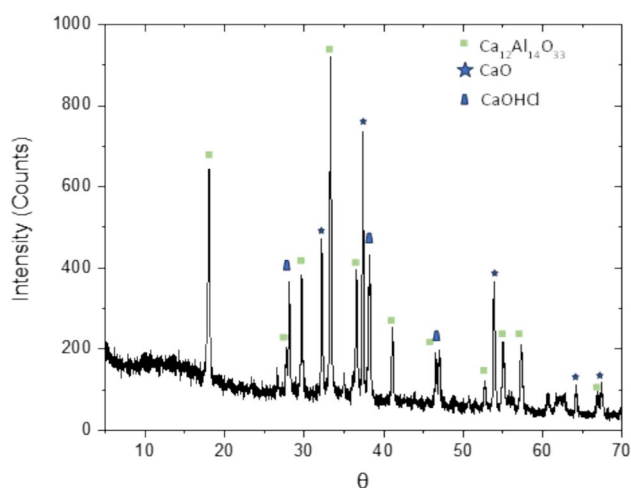


Fig. 2 XRD pattern of calcined hydrocalumite prepared in the mechanochemical reactor during 5 min (c_HC_5min_RL)

Table 1 Textural properties of fresh and calcined hydrocalumite prepared under conventional and mechanochemical methods

Sample	S_{BET} (m^2/g)	S_{micro} (m^2/g)	S_{ext} (m^2/g)	V_p^a (cm^3/g)	d_p^b (nm)
HC_conv	17.05	1.62	15.42	0.036	12.0
c_HC_conv	7.70	4.69	3.01	0.013	9.1
HC_5min_RL	23.05	1.79	21.26	0.057	10.4
c_HC_5min_RL	6.45	1.14	5.31	0.013	7.9

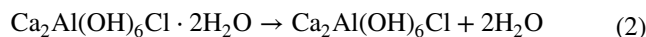
^aAt $P/P_0=0.95$

^bAverage pore width from BJH desorption

Thus, both calcined hydrocalumites prepared in the present work (c_HC_conv and c_HC_5min_RL) exhibited similar BET surface areas to those reported by Ventura et al. ($6 \text{ m}^2 \text{ g}^{-1}$ versus $7.70/6.45 \text{ m}^2 \text{ g}^{-1}$ in the present work) [38]. It is noteworthy that HC_5min_RL was synthesized in just 5 min using the mechanochemical reactor, while the HC_conv required 60 min and, and usually hydrocalumites require over 18 h, under an inert atmosphere [38]. This highlights the positive effect of mechanical energy associated to the continuous impact of beads for the synthesis of crystalline hydrocalumite.

Considering that the thermal analysis of hydrocalumite prepared with conventional methods, even from different sources of aluminum, has been previously reported [39], thermogravimetric and differential thermal analyses (TG–DTA) were only performed of the sample prepared in the mechanochemical reactor (HC_5min_RL), and results are displayed in Fig. 4. The TG curve shows four weight losses: room temperature – 100 °C, 200–400 °C, 550–700

°C and above 900 °C. The first mass loss (12.01%), below 100 °C, is associated to the removal of hydration water, since, assuming the formation of hydrocalumite (Reaction 2), the two water molecules per formula could correspond to a 12.8 wt%.



The second weight loss involves structural dehydroxylation of the CaAl layers, where hydroxyl groups seem to be bonded to Ca^{2+} weaker than to Al^{3+} , as evidenced by the FT-IR spectroscopy data with stretching vibrations at 3478 cm^{-1} (Ca–OH bonds) and 3643 cm^{-1} (AlO–H bonds) [39]. Thus, the dehydroxylation of hydrocalumite corresponds to a theoretical weight loss of 19.25%, where the sum of the second and the third weight loss in the TG curve supposes a 20.55%. This slight divergence could be explained by considering the intercalation of some carbonate ions in the interlayer region, whose interaction with calcium species gives rise to CaCO_3 , which requires high temperatures to decompose. Therefore, at 700 °C, a mixture of mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$), CaO and Ca(OH)Cl is formed. At temperatures higher than 850 °C, hydrogen chloride could evolved from Ca(OH)Cl, although, even at 1000 °C, the weight loss still continues.

X-ray photoelectron spectroscopy (XPS) has proven to be a reliable tool for the analysis of solid surfaces, giving information about the chemical composition and environment of chemical elements. In this work, the sample c_HC_5min_RL was studied by XPS (Fig. 5), because calcined hydrocalumite prepared by conventional method was reported in a previous work [40]. The O 1s core level spectrum exhibits an asymmetric band, which can be deconvoluted in two components, at 531.5 eV and 529.4 eV (shoulder), which can be assigned to oxygen in metal oxides (CaO and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$) and hydroxyl groups of Ca(OH)Cl, respectively. Regarding the Ca 2p, a doublet is observed at 347.2 and 350.7 eV, assigned to Ca $2p_{3/2}$ and Ca $2p_{1/2}$, with a typical spectral separation of 3.5 eV, characteristic values of Ca^{2+} ions in calcium oxide and hydroxide. The binding energy of Al 2p appears at 73.7 eV, while the Cl 2p core level spectrum also shows an asymmetric band, whose deconvolution gives rise to values of 198.6 and 200.2 eV, attributed to the Cl $2p_{3/2}$ and Cl $2p_{1/2}$, with a separation of 1.6 eV. These last values are characteristics of Al^{3+} in oxides, and Cl^- in metal chlorides.

The surface Ca/Al and Al/Cl atomic ratios were 1.94 and 0.99, respectively, very close to those corresponding to hydrocalumite (2 and 1, respectively), confirming that its thermal treatment gives rise to a mixture of CaO, Ca(OH)Cl and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$.

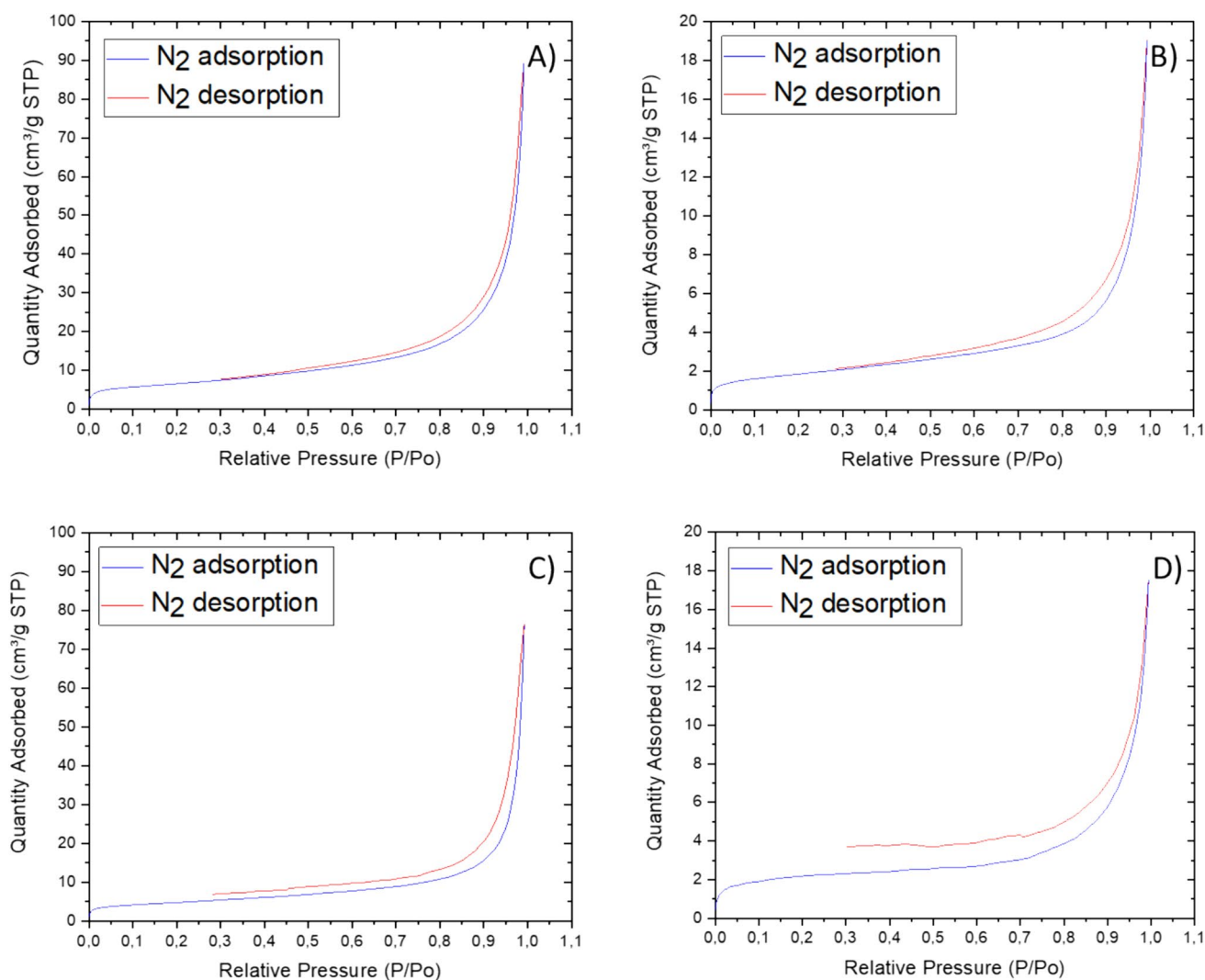


Fig. 3 N₂ adsorption-desorption isotherms at –196 °C of fresh and calcined hydrocalumite. HC_5min_RL (A), c_HC_5min_RL (B), HC_conv (C) and c_HC_conv (D)

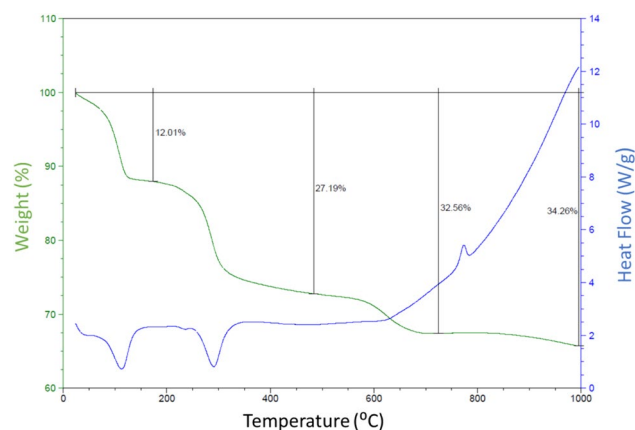
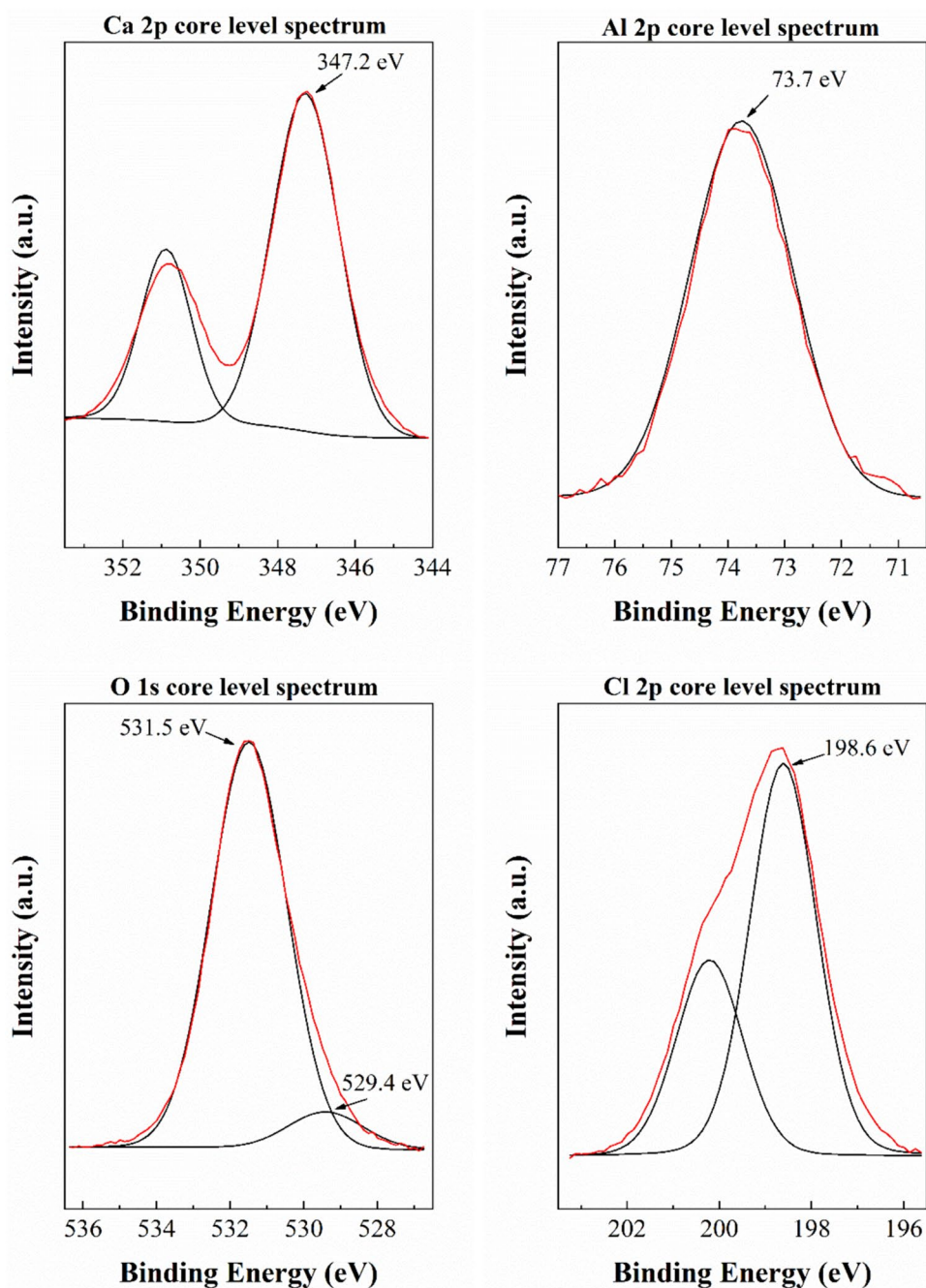


Fig. 4 ATD-TG curves of hydrocalumite prepared in the mechanochemical reactor during 5 min (HC_5min_RL)

3.2 Catalytic Tests

The first catalytic study was carried out using the mechanochemical reactor, since it has been demonstrated that chemical processes can be assisted by mechanical energy [41]. The objective was to demonstrate the versatility of this mechanochemistry approach, not only for the preparation of catalysts (as evidenced in the synthesis of hydrocalumite in the present work), but also to perform chemical processes. In this sense, the catalytic behavior of calcined hydrocalumite obtained by mechanochemistry (c_HC_5min_RL, c_HC_15min_RL, c_HC_60min_RL) was compared using 17 wt% glucose in water, a glucose/catalyst weight ratio of 12, at 50 °C (Fig. 6). Very similar fructose yields (15–16%) were obtained for the three catalysts after 60, 90 and 120 min of reaction, while glucose

Fig. 5 Core level spectra of sample c_HC_5min_RL



conversion was between 35 and 55%, giving a fructose selectivity around 30%.

There is approximately 20–30% conversion not shown in the graphs. In these cases, no products are detected by HPLC analysis. The products resulting from this conversion are derivatives of glucose and fructose degradation. These products, such as formic acid and levulinic acid, are formed under certain conditions, often leading to high conversions and low selectivities for fructose.

The maximum activity in the isomerization of glucose to fructose is attained at a reaction time of 60 min, in all cases,

so the catalyst c_HC_5min_RL, prepared at the shortest reaction time in the mechanochemical reactor was chosen to optimize different experimental variables influencing on the isomerization of glucose using the mechanochemical reactor, such as glucose/catalyst weight ratio, concentration of glucose in water and reaction temperature. In all cases, the filling volume with beads (made of Y-doped zirconia with a size of 1 mm) was 60%, so the available volume into the reactor was 40 mL, and a tip speed of 8.5 m s^{-1} was used.

On the other hand, it is worth noting the determination of the productivity of this process in the mechanochemical

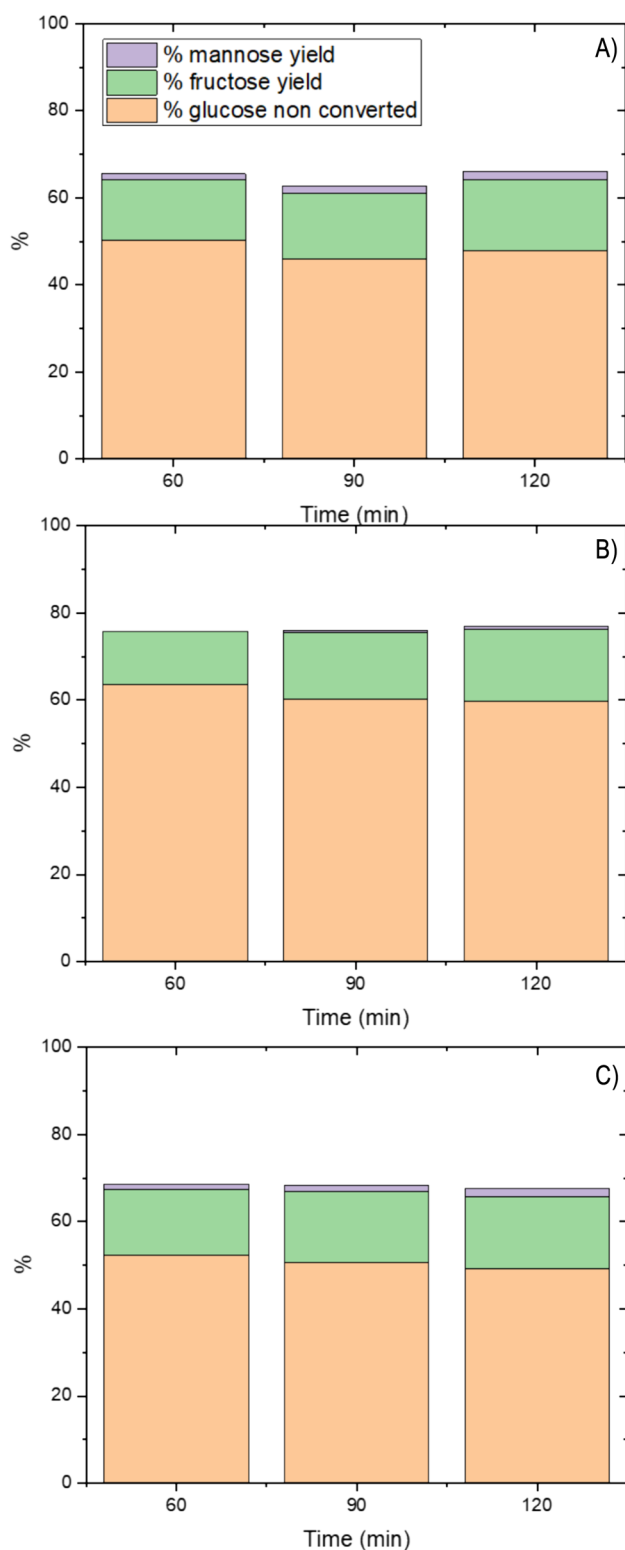


Fig. 6 Fructose yield and percentage of non-converted glucose in the isomerization of glucose in the presence of calcined hydrocalumite prepared in the mechanochemical reactor with different times: $c_HC_60min_RL$ (A), $c_HC_15min_RL$ (B) and $c_HC_5min_RL$ (C). Experimental conditions: 17 wt% glucose (20 g glucose in 100 mL H_2O); Glucose/catalyst weight ratio: 12; Temperature: 50 °C

Table 2 Catalytic data in the isomerization of glucose to fructose in the presence of $c_HC_5min_RL$

Time (min)	% Yield (fructose)	% Selec (fructose)	% Conv (glucose)	Fructose productivity ($kg_{fructose} L_{H_2O}^{-1} h^{-1}$)
5	5.0	12.2	40.9	0.12
15	6.9	17.2	40.1	0.06
30	11.7	24.5	40.1	0.05
60	15.0	31.5	47.7	0.03
90	16.2	32.9	47.8	0.02
120	16.5	32.6	49.4	0.02

Experimental conditions: Glucose/catalyst weight ratio: 12; wt% glucose: 17 (20 g glucose in 100 mL H_2O); Temperature: 50 °C

reactor at different reaction times. Table 2 shows the catalytic results together with the productivity at each reaction time obtained with $c_HC_5min_RL$ at 50 °C, using a 17 wt% glucose in water, with a glucose/catalyst weight ratio of 12. The fructose yield increases from 5.0 to 16.5% when the reaction is extended from 5 to 120 min, with glucose conversion ranging between 40 and 50%, but, in all cases, the selectivity toward fructose was lower than 33%. Regarding productivity, an industrially important parameter in catalysis, it decreases from 0.12 until 0.02 $kg_{fructose} L_{H_2O}^{-1} h^{-1}$, from 5 to 90 min. However, the yield is similar to that obtained by Ventura et al., but they achieve a productivity of 0.108 $kg_{fructose} L^{-1} h^{-1}$, after 4 h [38]. Even with high fructose yields and selectivity values, as those obtained by Zhang et al. with 40.7 and 99.9%, respectively, a productivity of only 0.004 $kg_{fructose} L^{-1} h^{-1}$ was attained [42].

The influence of the glucose/catalyst weight ratio was studied by using values of 3, 6 and 12 (Fig. 7). The best catalytic results, as inferred from a fructose yield of 24.5%, after 60 min, and a carbon balance higher than 90%, were achieved with a ratio of 6. In all cases, mannose was detected, resulting from the epimerization of glucose, but its yield was always lower than 10%. With a glucose/catalyst weight ratio of 3, corresponding to the highest catalyst loading, fructose yield remained nearly constant from 15 to 60 min, with a carbon balance close to 60%. It is well-known that the isomerization of glucose to fructose tends to thermodynamic equilibrium, with a $K_{eq} = 1.45$ at 110 °C, although some catalysts have reached up to 40% fructose yield in water. However, with most of inorganic solids, such as hydrotalcites or similar families, this yield does not exceed 35%, at reaction temperatures of 80–120 °C, in water [13]. Ventura et al. obtained a fructose yield of 21% with a carbon balance of 85%, at 45 °C, with a glucose/catalyst weight ratio of 1, after 4 h of reaction [38].

However, the productivity was much better for a glucose/catalyst weight ratio of 6, reaching a value of 0.50 $kg_{fructose} L_{H_2O}^{-1} h^{-1}$ after 5 min (Table 3), equivalent to 15 $kg_{fructose} Kg_{cat}^{-1} h^{-1}$, but decreases for longer reaction

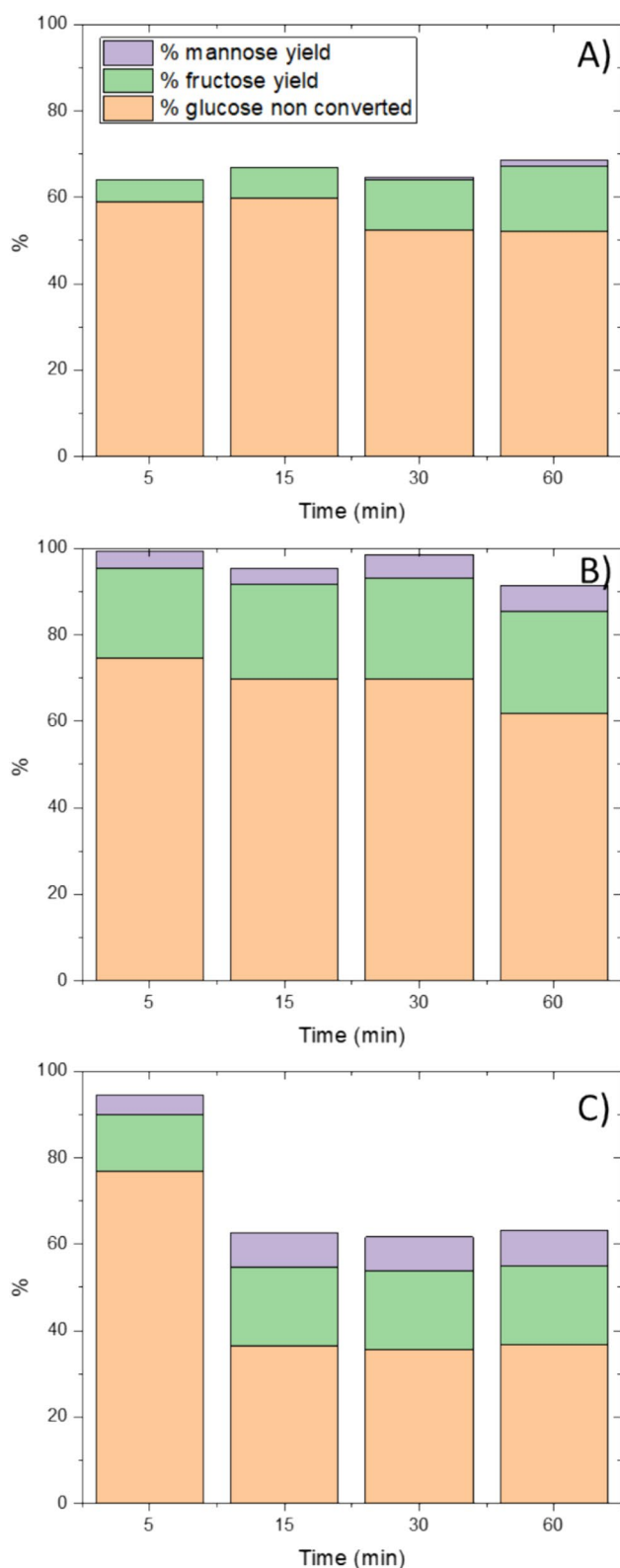


Fig. 7 Influence of the glucose/catalyst weight ratio (R) on fructose and mannose yields and percentage of non-converted glucose in the isomerization of glucose in the presence of $c_HC_5min_RL$: $R=12$ (A), $R=6$ (B) and $R=3$ (C). Experimental conditions: 17 wt% glucose (20 g glucose in 100 mL H_2O); Temperature: 50 °C

Table 3 Catalytic activity in the isomerization of glucose with $c_HC_5min_RL$

Time (min)	% Yield (fructose)	% Selec (fructose)	% Conv (glucose)	Fructose productivity ($kg_{fructose} L_{H_2O}^{-1} h^{-1}$)
5	20.8	82.3	25.3	0.50
15	22.0	72.4	30.3	0.18
30	23.5	77.4	30.3	0.09
60	23.5	61.7	38.1	0.05
90	23.7	58.0	40.9	0.03
120	24.5	62.4	39.3	0.03

Experimental conditions: Glucose/catalyst weight ratio: 6; wt% glucose: 17 (20 g glucose in 100 mL H_2O); Temperature: 50 °C

times. This value holds considerable significance, as after just 5 min of reaction with a 17 wt% glucose concentration, the mentioned productivity values tripled compared to those previously reported, but working in a flow semi-continuous mode, in water, at 50 °C.

Next, the effect of the reaction temperature was studied at temperatures of 50, 70 and 90 °C (Fig. 8), because most of studied carried out on the isomerization of glucose to fructose use higher temperatures. Fructose yield decreases with increasing temperature, as expected, which can be attributed to the degradation of glucose and fructose into other products, such as levulinic acid or other acids derived from sugars by cleavage of C–C bonds. The presence of these acids can catalyze other secondary processes leading to a decrease in the carbon balance, selectivity and yield. In addition, the use of basic heterogeneous catalysts does not require high temperatures to shift the equilibrium of this reaction to some extent either in water or other solvents such as ethanol [16, 18]. Therefore, an increase in temperature has no beneficial effect on the isomerization process under the experimental conditions used in the present work.

Finally, the concentration of glucose in the aqueous solution was varied from 17 to 50 wt%, to evaluate the capacity of the catalyst to isomerize a higher amount of glucose (Fig. 9). The catalytic data reveal that, even with a 50 wt% glucose, maintaining a glucose/catalyst weight ratio of 6, a fructose yield of 12% can be obtained after 5 min at 50 °C, with a 19% of glucose conversion, which raises until 42% after 60 min.

There is a decrease in the carbon balance but not to a large extent, reaching in most cases more than 80%. In addition, the fructose yields decrease with increasing glucose concentration due to the kinetics of the glucose to fructose isomerization reactions, but eventually tending to equilibrium [11, 43]. The increase of glucose in solution increases the productivity values in large ranges. The highest fructose productivity obtained was $0.50 kg_{fructose} L_{H_2O}^{-1} h^{-1}$. This productivity result indicates the great potential that this type

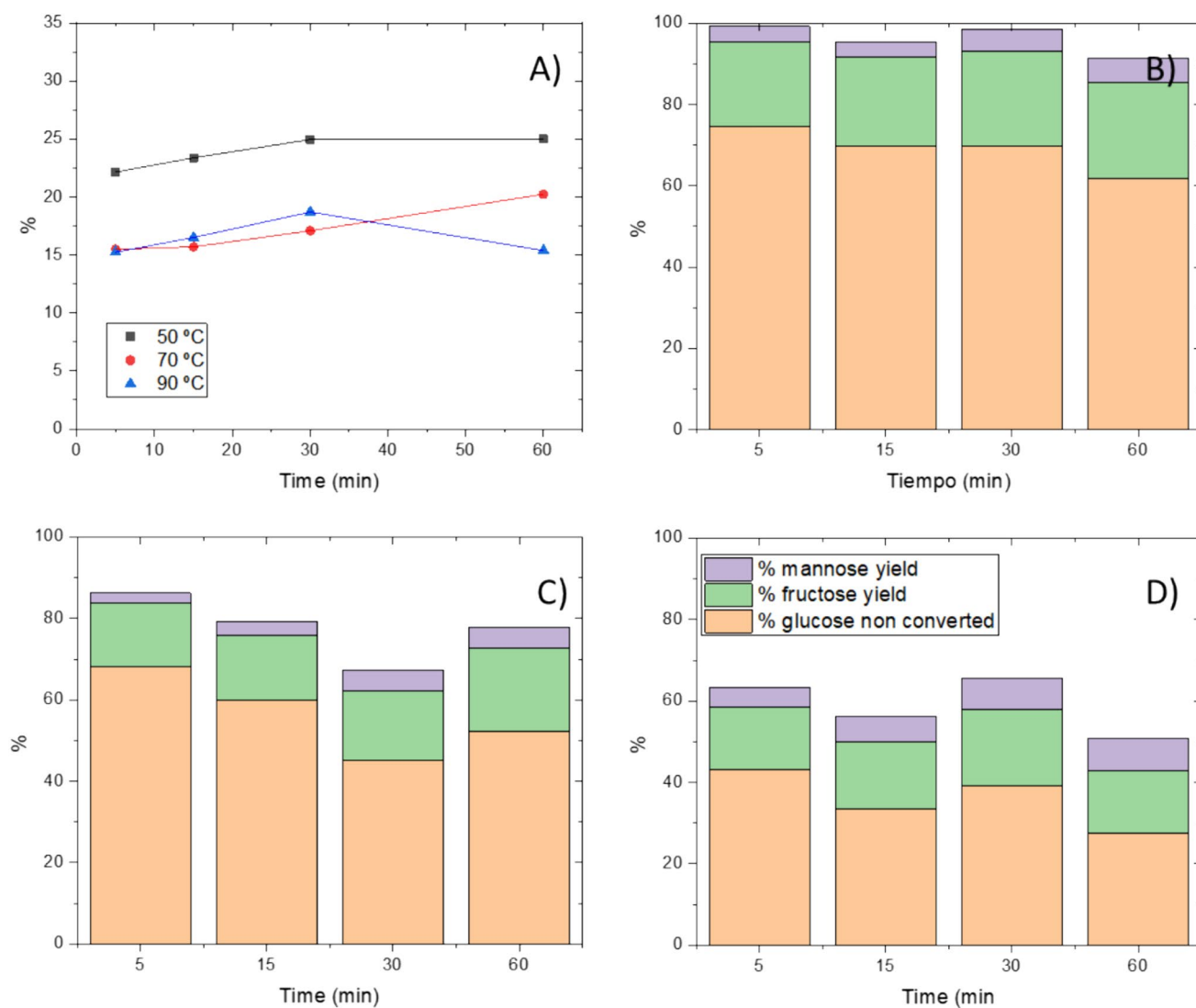


Fig. 8 Fructose yields at different reaction temperatures (A), fructose and mannose yields and percentage of non-converted glucose in the isomerization of glucose with *c*_{HC}5min_{RL} at 50 °C (B), 70 °C

(C) and 90 °C (D). Experimental conditions: 17 wt% glucose (20 g glucose in 100 mL H₂O); glucose/catalyst weight ratio: 6

of reactor has for working with high reagent concentration loadings and thus being able to obtain high productivity values.

When the optimum reaction conditions were determined in the mechanochemical reactor for the calcined

hydrocalumite obtained by mechanochemistry, this catalytic performance was compared with the calcined hydrocalumite prepared by conventional synthesis (coprecipitation). The catalytic performance was compared at 50 °C, 17 wt% glucose in water, a glucose/catalyst weight ratio of 6 and

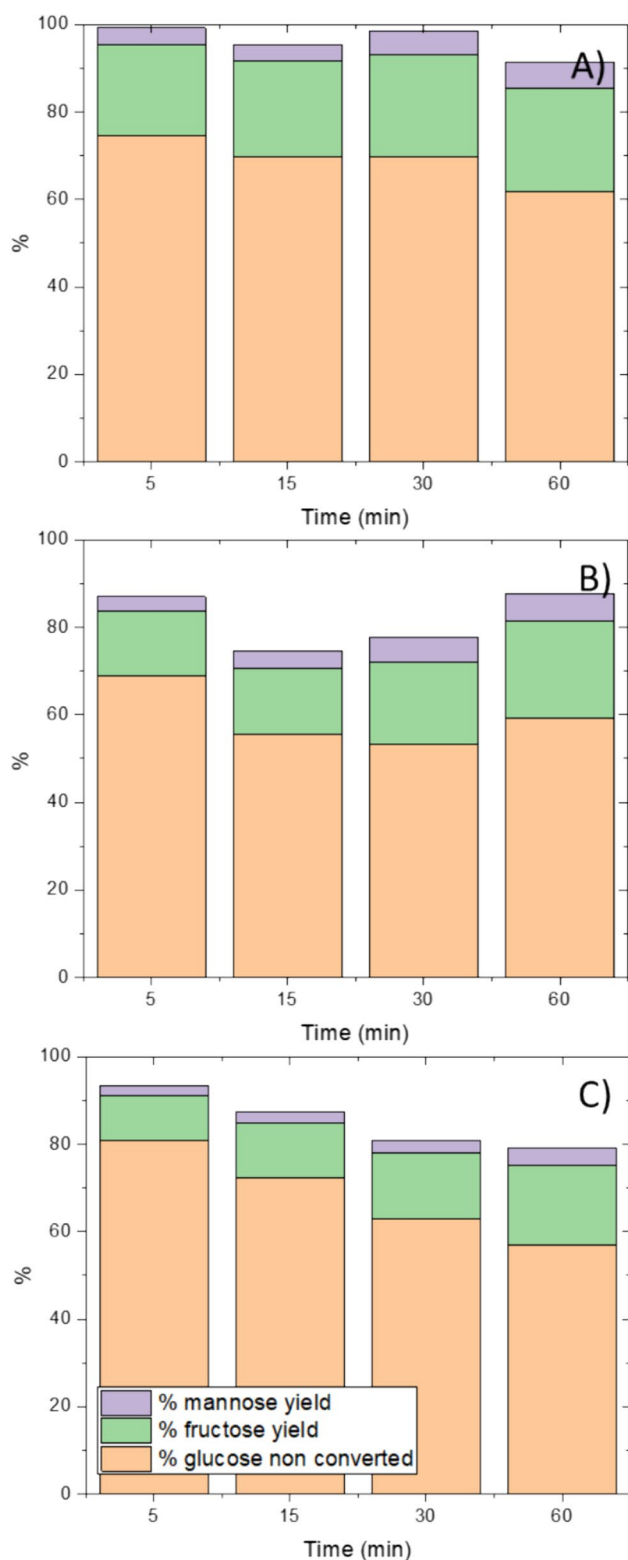


Fig. 9 Influence of the percentage of glucose in solution on fructose and mannose yields and percentage of non-converted glucose in the isomerization of glucose in the presence of $c_{HC_5min_RL}$: wt% glucose = 17 (A), 33 (B) and 50 (C). Experimental conditions: 100 g H_2O ; Glucose/catalyst weight ratio: 6; Temperature: 50 °C

different times varying from 15 to 120 min. Figure 10 shows the kinetics of both catalysts inside the mechanochemical reactor.

The reaction carried out with c_{HC_conv} is much faster, with glucose conversions close to 60%, but low fructose yields (less than 14%), providing a carbon balance lower than 60%. However, with $c_{HC_5min_RL}$, although the glucose conversion values are lower (25–38%), fructose yields rise until 23 wt%, with carbon balances higher than 95%. In addition, the maximum productivity reached with $c_{HC_5min_RL}$ is $0.50 \text{ kg}_{\text{fructose}} \text{ L}_{\text{H}_2\text{O}}^{-1} \text{ h}^{-1}$, which is twice the value obtained with c_{HC_conv} . This would demonstrate the advantage of this mechanochemical reactor for the fast and sustainable preparation of hydrocalumite.

Finally, Table 4 shows the experimental conditions and catalytic performance of a selection of basic catalysts reported in the literature, which are compared with $c_{HC_5min_RL}$ prepared in the present work. Although the fructose yield is not the highest (21 versus 54%), it presents some important advantages, such as scalability and easy synthesis, working at low temperature (50 °C) and short reaction time (5 min), with a high percentage of glucose (17 wt%) and a high selectivity towards fructose (82%), in addition to achieving high productivity compared to other continuous methods ($15.1 \text{ kg}_{\text{fructose}} \text{ L}^{-1} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$ versus $0.22 \text{ kg}_{\text{fructose}} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$). Furthermore, this novel glucose–fructose isomerization process is environmentally friendly, low-cost, and catalyst separation is feasible.

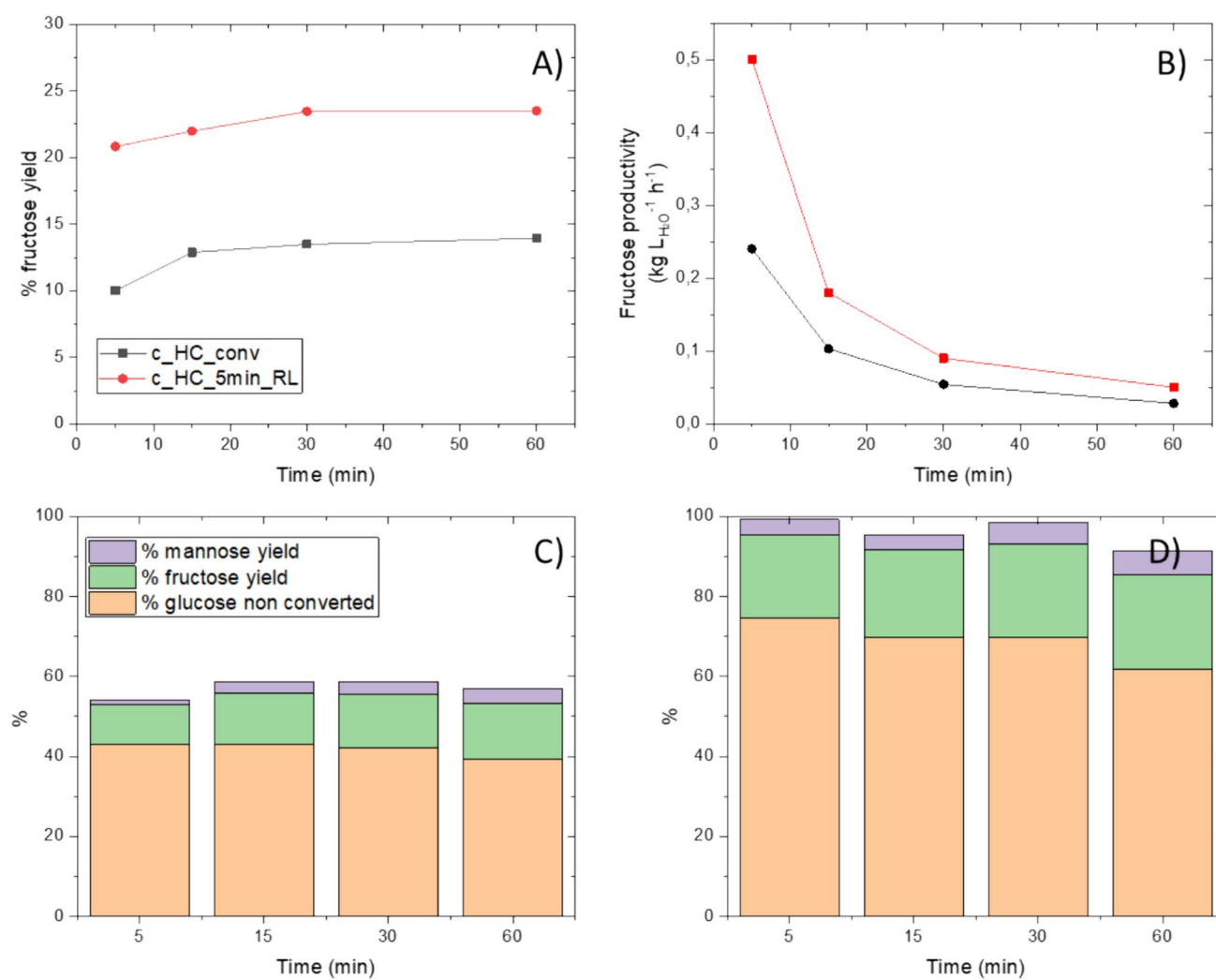


Fig. 10 Isomerization of glucose at different reaction times in the presence of calcined hydrocalumite prepared with different methods: fructose yield (**A**), productivity expressed as concentration (kg/L) of fructose formed per hour (**B**), fructose and mannose yields, and

percentage of non-converted glucose with c_HC_conv (**C**) and c_HC_5min_RL (**D**). Experimental conditions: 17 wt% glucose (20 g glucose in 100 mL H₂O); Glucose/catalyst weight ratio: 6; Temperature: 50 °C

Table 4 Data of catalytic activity in the isomerization of glucose to fructose of different basic catalysts, using water as solvent

Catalyst	Experimental conditions	% Conv (glucose)	% Sel (fructose)	% Yield (fructose)	Productivity ($\frac{\text{g}_{\text{fruct}} \text{L}_{\text{H}_2\text{O}}^{-1}}{\text{h}^{-1} \text{g}_{\text{catalyst}}^{-1}}$)	Eco-friendly ^c	Cost	Separation	References
CaO-Al ₂ O ₃ (Ca/Al=3)	Continuous, 10 wt% glucose, 0.5 g cat, Flow rate=2 mL/h, 45 °C, TOS=4 h	68	80	54	0.22 ^d	+	+	+	[38]
LDH_CO ₃	Batch, 1 wt% glucose, 0.33 wt % cat, 90 °C, 48 h	58	73	42	0.027	+	+	+	[44]
PAO ^a	Batch, 0.9 wt% glucose, 0.1 wt% cat, 85 °C, 5 h	49	99	49	0.88	+	-	+	[45]
IRA-900	Batch, 10 wt% glucose, 10 wt% cat, 80 °C, 30 min	36	75	27	0.54	+	-	+	[46]
<i>Thermus Ohsimai</i> ^b	Batch, 40 wt% glucose, 25 g/L wet cells bio-catalyst, 85 °C, 5 h	-	-	52	1.66	-	-	-	[47]
Calc_HC	Semi-continuous, 17 wt% glucosa, 2.8 wt% cat, 50 °C, 5 min	25	82	21	15.1	+	+	+	This work

^aAmidoximed polyacrylonitrile^bGlucose isomerase^cInnovative scientific solutions to environmental problems in the laboratory^d $\frac{\text{g}_{\text{fruct}} \text{h}^{-1}}{\text{g}_{\text{catalyst}}^{-1}}$

4 Conclusion

In this work, the effect of mechanochemistry on the preparation of hydrocalumite was studied. It was observed that the use of the mechanochemical reactor DYNO®-MILL RESEARCH LAB reduces the hydrocalumite preparation time to 5 min. Furthermore, the presence of calcium carbonate together hydrocalumite, as inferred from XRD, was minimized by using this new flow semi-continuous mechanochemical reactor. Physico-chemical characterization has demonstrated that sample prepared by mechanochemistry (c_HC_5min_RL) is more mesoporous than that obtained by co-precipitation (c_HC_conv), although specific surface area and pore volume are similar. The calcination of hydrocalumite (Ca₂Al(OH)₆Cl·2H₂O) leads to a mixture of mayenite (Ca₁₂Al₁₄O₃₃), CaO and Ca(OH)Cl. The isomerization of glucose to fructose was successfully carried out in the mechanochemical reactors, and the optimization of reaction temperature and time, glucose/catalyst weight ratio and concentration of glucose in water, has resulted in a 23.5% fructose yield, with a glucose conversion of 38.1%, after 1 h of reaction, at 50 °C, with a 17 wt% glucose in water and a glucose/catalyst weight ratio of 6. Nevertheless, the highest fructose productivity of 0.50 $\frac{\text{kg}_{\text{fructose}} \text{L}_{\text{H}_2\text{O}}^{-1}}{\text{h}^{-1}}$ (equivalent to 15 $\frac{\text{kg}_{\text{fructose}} \text{kg}_{\text{cat}}^{-1}}{\text{h}^{-1}}$) was achieved after only 5 min, under similar experimental conditions. Therefore, this

work has evidenced the versatility and potential of this new flow semi-continuous mechanochemical reactor for the synthesis of crystalline layered double hydroxides, under sustainable experimental conditions (water), and to perform catalytic processes with high performance, using water as solvent and no control of the atmosphere.

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Data availability Data are available upon request from the corresponding author.

References

- Nayak NS, Purohit MS, Tipre DR, Dave SR (2020) Biosurfactant production and engine oil degradation by marine halotolerant *Bacillus licheniformis* LRK1. *Biocatal Agric Biotechnol* 29:101808. <https://doi.org/10.1016/J.BCAB.2020.101808>
- Mitra J, Zhou X, Rauchfuss T (2015) Pd/C-catalyzed reactions of HMF: decarbonylation, hydrogenation, and hydrogenolysis. *Green Chem* 17:307. <https://doi.org/10.1039/c4gc01520g>
- Jakob A, Grilc M, Teržan J, Likožar B (2021) Solubility temperature dependence of bio-based levulinic acid, furfural, and hydroxymethylfurfural in water, nonpolar polar aprotic and protic solvents. *Processes* 9:924. <https://doi.org/10.3390/PR9060924>

- Hanover LM, White JS (1993) Manufacturing, composition, and applications of fructose. *Am J Clin Nutr* 58:724S-732S. <https://doi.org/10.1093/AJCN/58.5.724S>
- Parker K, Salas M, Nwosu VC (2010) High fructose corn syrup: production, uses and public health concerns. *Biotechnol Mol Biol Rev* 5:71–78
- Putra MD, Sulieman AK, Abasaeed AE et al (2017) A green process for simultaneous production of fructose and ethanol via selective fermentation. *J Clean Prod* 162:420–426. <https://doi.org/10.1016/j.jclepro.2017.06.069>
- Li H, Yang S, Saravanamurugan S, Riisager A (2017) Glucose isomerization by enzymes and chemo-catalysts: status and current advances. *ACS Catal* 7:3010–3029. https://doi.org/10.1021/ACSCATAL.6B03625/ASSET/IMAGES/LARGE/CS-2016-03625F_0013.JPG
- Delidovich I, Palkovits R (2016) Catalytic isomerization of biomass-derived aldoses: a review. *ChemSuschem* 9:547–561. <https://doi.org/10.1002/SSC.201501577>
- Harris JW, Cordon MJ, Di Iorio JR et al (2016) Titration and quantification of open and closed Lewis acid sites in Sn-Beta zeolites that catalyze glucose isomerization. *J Catal* 335:141–154. <https://doi.org/10.1016/J.JCAT.2015.12.024>
- Bermejo-Deval R, Orazov M, Gounder R et al (2014) Active sites in Sn-beta for glucose isomerization to fructose and epimerization to mannose. *ACS Catal* 4:2288–2297. https://doi.org/10.1021/CS500466J/SUPPL_FILE/CS500466J_SI_001.PDF
- Rajabbeigi N, Torres AI, Lew CM et al (2014) On the kinetics of the isomerization of glucose to fructose using Sn-Beta. *Chem Eng Sci* 116:235–242. <https://doi.org/10.1016/j.ces.2014.04.031>
- Guo Q, Tian J (2013) Removal of fluoride and arsenate from aqueous solution by hydrocalumite via precipitation and anion exchange. *Chem Eng J* 231:121–131. <https://doi.org/10.1016/J.CEJ.2013.07.025>
- Delidovich I (2021) Recent progress in base-catalyzed isomerization of D-glucose into D-fructose. *Current Opin Green Sustain Chem* 27:100414. <https://doi.org/10.1016/j.cogsc.2020.100414>
- Otomo R, Fujimoto M, Nagao M, Kamiya Y (2019) Ammonia-treated metal oxides as base catalysts for selective isomerization of glucose in water. *Mol Catal* 475:110479. <https://doi.org/10.1016/j.mcat.2019.110479>
- Upare PP, Chamas A, Lee JH et al (2020) Highly efficient hydrocalumite/1-butanol catalytic system for the production of the high-yield fructose crystal from glucose. *ACS Catal* 10:1388–1396. <https://doi.org/10.1021/acscatal.9b01650>
- Yabushita M, Shibayama N, Nakajima K, Fukuoka A (2019) Selective glucose-to-fructose isomerization in ethanol catalyzed by hydrocalumites. *ACS Catal* 9:2101–2109. <https://doi.org/10.1021/acscatal.8b05145>
- Delidovich I, Palkovits R (2015) Structure-performance correlations of Mg–Al hydrocalumite catalysts for the isomerization of glucose into fructose. *J Catal* 327:1–9. <https://doi.org/10.1016/j.jcat.2015.04.012>
- Liu C, Carraher JM, Swedberg JL et al (2014) Selective base-catalyzed isomerization of glucose to fructose. *ACS Catal* 4:4295–4298. <https://doi.org/10.1021/cs501197w>
- Zheng L, Xia S, Lu X, Hou Z (2015) Transesterification of glycerol with dimethyl carbonate over calcined Ca–Al hydrocalumite. *Chin J Catal* 36:1759–1765. [https://doi.org/10.1016/S1872-2067\(15\)60915-9](https://doi.org/10.1016/S1872-2067(15)60915-9)
- Tóth V, Sipiczki M, Pallagi A et al (2014) Synthesis and properties of CaAl-layered double hydroxides of hydrocalumite-type. *Chem Pap* 68:633–637. <https://doi.org/10.2478/S11696-013-0500-Z/MACHINEREADABLECITATION/RIS>
- Gevers BR, Labuschagné FJWJ (2020) Green synthesis of hydrocalumite (CaAl-OH-LDH) from Ca(OH)₂ and Al(OH)₃ and the parameters that influence its formation and speciation. *Crystals* 10:672. <https://doi.org/10.3390/CRYST10080672>
- Vaccari A Preparation and catalytic properties of cationic and anionic clays
- Do JL, Friščić T (2017) Mechanochemistry: a force of synthesis. *ACS Cent Sci* 3:13–19. https://doi.org/10.1021/ACSCENTSCI.6B00277/ASSET/IMAGES/LARGE/OC-2016-002774_0003.JPG
- Fernández-Bertran JF (1999) Mechanochemistry: an overview. *Pure Appl Chem* 71:581–586. <https://doi.org/10.1351/PAC199971040581/MACHINEREADABLECITATION/RIS>
- Pérez-Merchán AM, Rodríguez-Carballo G, Torres-Olea B et al (2022) Recent advances in mechanochemical pretreatment of lignocellulosic biomass. *Energies* 15:5948. <https://doi.org/10.3390/EN15165948>
- Arfelis S, Malpartida I, Lair V et al (2023) Life cycle assessment on calcium zincate production methods for rechargeable batteries. *Sci Total Environ* 866:161094. <https://doi.org/10.1016/j.scitotenv.2022.161094>
- Fahami A, Beall GW (2016) Structural and morphological characterization of Mg_{0.8}Al_{0.2}(OH)₂Cl_{0.2} hydrocalumite produced by mechanochemistry method. *J Solid State Chem* 233:422–427. <https://doi.org/10.1016/j.jssc.2015.11.006>
- Fahami A, Al-Hazmi FS, Al-Ghamdi AA et al (2016) Structural characterization of chlorine intercalated Mg–Al layered double hydroxides: a comparative study between mechanochemistry and hydrothermal methods. *J Alloy Compd* 683:100–107. <https://doi.org/10.1016/j.jallcom.2016.05.032>
- Ay AN, Zümreoglu-Karan B, Mafra L (2009) A simple mechanochemical route to layered double hydroxides: synthesis of hydrocalumite-like Mg–Al–NO₂–LDH by Manual Grinding in a Mortar. *Z Anorg Allg Chem* 635:1470–1475. <https://doi.org/10.1002/zaac.200801287>
- Boccalon E, Viscusi G, Sorrentino A et al (2021) Solvent-free synthesis of halloysite-layered double hydroxide composites containing salicylate as novel, active fillers. *Colloids Surf A* 627:127135. <https://doi.org/10.1016/j.colsurfa.2021.127135>
- Malpartida I, Maireles-Torres P, Vereda C et al (2020) Semi-continuous mechanochemical process for biodiesel production under heterogeneous catalysis using calcium diglyceroxide. *Renewable Energy* 159:117–126. <https://doi.org/10.1016/j.renene.2020.05.020>
- Rousselot I, Taviot-Guého C, Leroux F et al (2002) Insights on the structural chemistry of hydrocalumite and hydrocalumite-like materials: Investigation of the series Ca₂M³⁺(OH)₆Cl·2H₂O (M³⁺:Al³⁺, Ga³⁺, Fe³⁺, and Sc³⁺) by X-ray powder diffraction. *J Solid State Chem* 167:137–144. <https://doi.org/10.1006/jssc.2002.9635>
- Linares CF, Ocanto F, Bretto P, Monsalve M (2014) Study of as-synthesized and calcined hydrocalumites as possible antacid agents. *Bull Mater Sci* 37:941–944
- Tang B, Peng G, Luo D, Zhou X (2021) Preparation and adsorption properties of soybean dreg/hydrocalumite composites. *ACS Omega* 6:27491–27500. <https://doi.org/10.1021/acsomega.1c04460>
- Almeida RD, Campos JC, Souza MMVM (2021) Synthesis and characterization of hydrocalumite for removal of fluoride from aqueous solutions. *Environ Sci Pollut Res* 28:22439–22457. <https://doi.org/10.1007/s11356-020-12307-5/Published>
- Linares CF, Moscoso J, Alzurutt V et al (2016) Carbonated hydrocalumite synthesized by the microwave method as a possible

- antacid. *Mater Sci Eng, C* 61:875–878. <https://doi.org/10.1016/j.msec.2016.01.007>
37. Fahami A, Beall GW, Enayatpour S et al (2017) Rapid preparation of nano hexagonal-shaped hydrocalumite via one-pot mechanochemistry method. *Appl Clay Sci* 136:90–95. <https://doi.org/10.1016/j.clay.2016.11.014>
38. Ventura M, Mazarío J, Domine ME (2022) Isomerization of glucose-to-fructose in water over a continuous flow reactor using Ca–Al mixed oxide as heterogeneous catalyst. *ChemCatChem* 14:e202101229. <https://doi.org/10.1002/cctc.202101229>
39. Jiménez A, Misol A, Morato Á et al (2021) Optimization of hydrocalumite preparation under microwave irradiation for recovering aluminium from a saline slag. *Appl Clay Sci* 212:106217. <https://doi.org/10.1016/j.clay.2021.106217>
40. Campos-Molina MJ, Santamaría-González J, Mérida-Robles J et al (2010) Base catalysts derived from hydrocalumite for the transesterification of sunflower oil. *Energy Fuels* 24:979–984. <https://doi.org/10.1021/ef9009394>
41. Andersen J, Mack J (2018) Mechanochemistry and organic synthesis: from mystical to practical. *Green Chem* 20:1435–1443. <https://doi.org/10.1039/c7gc03797j>
42. Zhang Y, Liu W, Zhao X et al (2023) Water-induced efficient isomerization of glucose into fructose over the lithium loaded silicalite-1 catalyst at 50 °C. *Green Chem* 25:3449–3452. <https://doi.org/10.1039/d3gc00638g>
43. Fischer M, Drabo P, Delidovich I (2022) Study of base-catalyzed isomerization of d-glucose with a focus on reaction kinetics. *React Kinet Mech Catal* 135:2357–2377. <https://doi.org/10.1007/s11144-022-02277-9>
44. Delidovich I, Palkovits R (2014) Catalytic activity and stability of hydrophobic Mg–Al hydrotalcites in the continuous aqueous-phase isomerization of glucose into fructose. *Catal Sci Technol* 4:4322–4329. <https://doi.org/10.1039/c4cy00776j>
45. Huang H, Meng XG, Yu WW et al (2021) High selective isomerization of glucose to fructose catalyzed by amidoximed polyacrylonitrile. *ACS Omega* 6:19860–19866. <https://doi.org/10.1021/acsomega.1c02577>
46. El Tawil-Lucas M, Montaña M, Macias-Villasevil M et al (2023) Isomerization of hemicellulose aldoses to ketoses catalyzed by basic anion resins: catalyst screening and stability studies. *Catalysts* 13:1301. <https://doi.org/10.3390/catal13091301>
47. Jia DX, Zhou L, Zheng YG (2017) Properties of a novel thermostable glucose isomerase mined from *Thermus oshimai* and its application to preparation of high fructose corn syrup. *Enzyme Microb Technol* 99:1–8. <https://doi.org/10.1016/j.enzmictec.2017.01.001>

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