

Isomerization of Glucose-to-Fructose in Water over a Continuous Flow Reactor using Ca–Al Mixed Oxide as Heterogeneous Catalyst

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This work reports the continuous isomerization of glucose to fructose in aqueous media under mild conditions using a mixed oxide hydrotalcite-derived catalyst based on Ca and Al. Different operational parameters of the continuous flow fixed-bed catalytic reactor system were studied. At the optimal conditions, the Ca–Al-based catalyst achieved a very high conversion and

almost quantitative selectivity towards fructose, this being one of the few successful examples of a heterogeneous catalyst capable of carrying out this reaction in a continuous process. Importantly, catalytic activity held steady during four hours on stream, and slight deactivation occurring could be practically overcome by thermal regeneration of the catalyst.

Introduction

Non-edible biomass is an attractive and sustainable starting material for renewable liquid fuels and chemicals that can diminish our dependence on petroleum and moderate greenhouse gas emissions concerns.^[1,2] Recent developments in the field of biomass valorization have enabled efficient chemical transformations of carbohydrates as a critical factor for the production of bio-based fuels and commodity chemicals.^[3] Monosaccharides comprise a vast family of carbohydrates present in most non-edible biomass, mainly derived from cellulosic waste materials.^[4] Among all monosaccharides, great attention has been given to glucose principally due to its versatility, and because by carrying out its isomerization, fructose could be attained. Thus, fructose becomes the platform to produce many other chemicals that could replace those synthesized using fossil fuel resources, such as 5-hydroxymethylfurfural or levulinic acid, both considered within the top 12 platforms and/or value-added chemicals from biomass.^[5] In this context, the development of fast, cheap and reusable systems able to perform the selective isomerization of glucose seems essential for advancing biomass conversion. Many approaches have been studied for this reaction. Nonetheless, both heterogeneous and homogeneous catalysts have mostly been developed to carry out the reaction in batch-type systems.^[6]

As far as continuous isomerization processes are concerned, a distinction between biocatalytic and chemocatalytic processes must be done. In the former case, the technology is well established and, since 1967, the immobilization of the enzyme enables the continuous production of a high fructose syrup (HFCS).^[7] Several inert carrier materials can be used for the immobilization of the active enzyme, being DEAE-cellulose (diethylaminoethyl cellulose), porous synthetic anion-exchange resin^[8] or porous glass^[9] some examples. Besides that, the last decades abound with studies providing insight into the kinetics and modeling^[10,11] of this packed bed system. On the other hand, deactivation has been broadly studied and, consequently, there is a good understanding of how key factors such as structural parameters (i.e., pore structure, particle morphology),^[12] thermal deactivation of the enzyme^[13,14] or resistance to internal diffusion^[15] could influence on the effectiveness of the process. Nonetheless, even though the immobilization of glucose isomerase has made its recyclability possible, chemocatalytic continuous processes are required to address the main issues of enzyme-based systems, such as their high cost and the need of using more versatile catalysts to make the coupling of this reaction with other processes involved in the production of renewable platform chemicals.^[6,16]

Regarding the continuous chemocatalytic isomerization, there is still plenty of room for improvement as just a few examples can be found in the literature. HY zeolite was claimed as efficient catalyst for the acid-type isomerization of glucose-to-fructose in γ -butyrolactone (GBL)/H₂O (80/20) system over a fixed bed reactor (at 100 °C, 5 bar of N₂ pressure, 3 wt% of glucose, 4 g of catalyst, WHSV = 0.02 h⁻¹), with superior activity to other H-zeolites tested.^[17] Excellent selectivity to fructose (96%) was reported at moderate glucose conversion (\approx 26%), with slight decay in both conversion (> 24%) and selectivity (> 90%) after 480 h on stream. The HY catalyst needed thermal regeneration for further use, while the use of GBL as co-solvent became a disadvantage. In addition, NaX zeolites with moderate basicity were used to carry out experiments in continuous mode over a 50 h period (100 g/l of glucose, 14 g of catalyst,

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0.15 ml/min of flow rate, and 95 °C of temperature). For this catalyst, the initial conversion of glucose (20%) decreases to 10% at 25 h, remaining stable up to 50 h. However, substantial leaching of the Na⁺ cation from the solid is reported.^[18] On the other hand, a few years ago, Palkovits and Delidovich^[19] claimed that, by working under continuous conditions with Mg–Al-Hydrotalcite-type catalysts (180 mL, 12 g of catalyst, 90 °C, 430 rpm), it was possible to notably reduce the destruction of fructose together with the leaching of Mg during the reaction. Although a yield of 5–25% of fructose could be obtained, the 1–2% of Mg leached from the catalyst during the experiment (time-on-stream, TOS = 100 h) led to a gradual catalytic deactivation. Nevertheless, it was possible to regenerate the catalyst by calcination and rehydration of the mixed oxide to yield the desired hydrotalcite.^[19] It is worth noting that the described systems are not packed bed reactors, but reactors that have been modified by coupling a continuous set-up to the system, thereby allowing the entrance and the exit of the solution (CSTR: Continuous Stirred-Tank Reactor). More recently, Souzanchi et al. performed the isomerization of glucose to fructose in a continuous packed bed reactor.^[20] For that purpose, they use Mg/Al-based hydrotalcite type materials as catalysts, thus reaching high selectivity (78.1%) but at intermediate conversion 25% (at 100 °C). The catalyst demonstrates good stability in the continuous flow reactor at least until TOS = 4 h. Catalyst deactivation was mainly due to the deposition of insoluble organic by-products on the catalyst surface, that caused a slight decrease in conversion, rather than by metal leaching.

Thus, considering the few examples in the literature, every research involving chemocatalytic continuous systems for glucose isomerization to fructose is especially exciting, not only because of the potential industrial applicability but also to deepen the knowledge on issues like metallic leaching due to different causes, such as the chelating properties of saccharides, acidification or basification of reaction media, or even deactivation by strong adsorption of certain by-products.^[6] In these cases, the use of aqueous systems without the need of organic solvents represents an outstanding advantage.

In the present work, we evaluated a novel type of Ca–Al hydrotalcite-derived material as catalyst for the continuous production of fructose through the isomerization of glucose by using only water as solvent. Owing to the high potential that this Ca–Al-based catalyst showed in previous experiments on a batch-type reactor,^[21] reaching high glucose conversion (≥ 50%) and high fructose selectivity (≥ 87%), the continuous reaction in a tubular fixed bed catalytic reactor was here evaluated. After the required catalyst optimization, the most active and selective solid was chosen to be assessed as the catalyst in this flow system. Operational parameters such as temperature, catalyst loading, time of stream (TOS), and stability of the catalyst were studied and reported herein.

Results and Discussion

Catalyst characterization

A series of Ca–Al-based materials with different Ca/Al ratios were prepared by co-precipitation, whose characterization has been thoroughly discussed in previous work.^[21] Therefore, the main textural and physicochemical properties (including acidity and basicity measurements) of selected samples are briefly summarized in Table 1. It was taking into account that the Ca–Al(3.0) material (with Ca/Al molar ratio of 3.0/1.0) was previously selected as a suitable catalyst to perform the glucose-to-fructose isomerization.^[21] Therefore, this catalyst was here selected for further development and optimization in the continuous process, and its characterization data will be more in detail commented below.

To elucidate base and acid sites present in the Ca–Al solid catalysts temperature program desorption measurements with probe molecules were done, with CO₂ to assess the basic sites and with NH₃ for the acid sites, respectively. The results showed that Ca–Al-based materials are solids with a predominantly basic character, especially in the case of the Ca–Al(3.0) sample in which, moreover, all of the centers are strong basic sites (see SI, Figure S1). Concerning the BET surface area, all of these types of Ca–Al hydrotalcite-derived materials presented low values between 5 and 7. Nonetheless, it was previously demonstrated that this parameter is not a pivotal factor in modifying the isomerization activity.^[21,22] XRD analysis of the samples (Figure 1A) showed the typical pattern for the Ca–Al-based hydrotalcite phase without the presence of other phase impurities. After calcination (Figure 1B), mainly a CaO phase was observed. Interlayer distance, calculated by the Bragg's law, was more prominent than those distances found for the typical hydrotalcite-type materials based on Mg/Al,^[23] a fact attributed to the bigger atomic radius of calcium.

The SEM micrograph of the Ca–Al(3.0) material before calcination (Figure 2) clearly showed the layers of the hydrotalcite-type phase. After calcination, these layers collapsed, thus establishing a decrease in the interlayer space between each layer of the structure. Homogeneity of the Ca–Al(3.0) sample is

Table 1. Main textural and physicochemical properties of the Ca–Al-based materials.

Catalyst	Ca/Al molar ratio ^[a]	Basic sites ^[b] [μmol CO ₂ /m ²]	Acid sites ^[c] [μmol NH ₃ /m ²]	Surf. area ^[d] [m ² /g]	Basal spacing ^[e] [Å]
Ca–Al (2.3)	2.3/1.0	142	0	6	8.56
Ca–Al (3.0)	3.0/1.0	181	4	5	8.62
Ca–Al (3.4)	3.4/1.0	185	0	7	8.56

[a] Measured by ICP of the hydrotalcite-type precursor (before calcination); [b] Concentration of basic sites measured by CO₂-TPD analysis on the mixed oxide; [c] Concentration of acid sites measured by NH₃-TPD analysis on the mixed oxide; [d] Values calculated from N₂ adsorption isotherms (BET method) of the mixed oxide; [e] Basal spacing (interlayer distance + one layer) of the hydrotalcite-type precursor (before calcination) calculated based on Bragg's law.

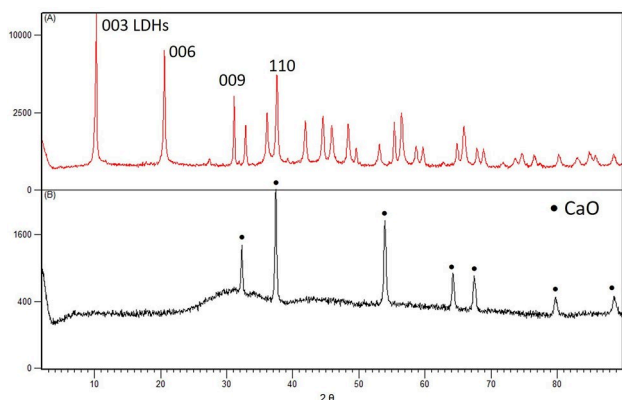


Figure 1. XRD patterns of Ca–Al(3.0) material before (A) and after (B) calcination.

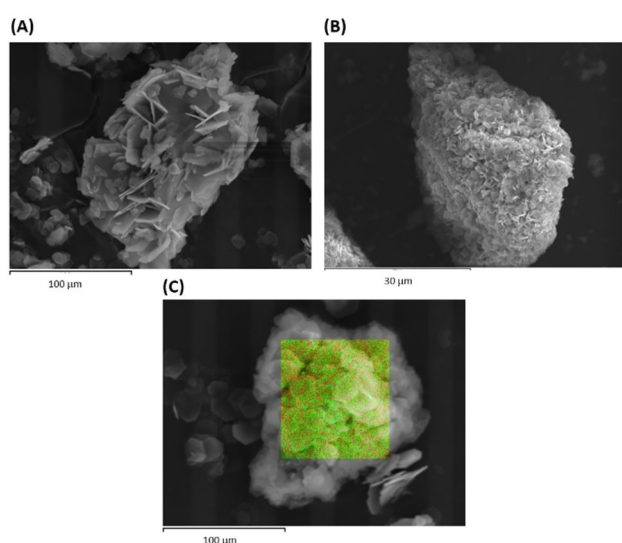


Figure 2. SEM images of the Ca–Al(3.0) material before (A) and after calcination (B), and SEM-EDX mapping (C) where red is Al and green is Ca.

also demonstrated by carrying out a SEM-EDX mapping of the solid surface, as shown in Figure 3C.^[21]

Catalytic isomerization of glucose

Previous experiments on batch reactor showed that, under optimal conditions, the Ca/Al(3.0) mixed oxide $\text{Ca}_3\text{AlO}_{4.5}$ was the most efficient catalyst in the glucose-to-fructose isomerization, with $\approx 50\%$ glucose conversion and $\approx 87\%$ fructose selectivity, thus allowing achieving an isomerization rate of 1806 mmol/ $\text{g}_{\text{cat}}\text{h}$. The solid catalyst could be recovered after reaction and reused without significant efficiency loss.^[21] In light of these results, we decided to use the same catalyst, $\text{Ca}_3\text{AlO}_{4.5}$, to develop a continuous flow fixed-bed catalytic system since it showed excellent behavior in terms of glucose conversion and fructose selectivity. Different technical and operational parameters that could affect the performance of the new continuous-

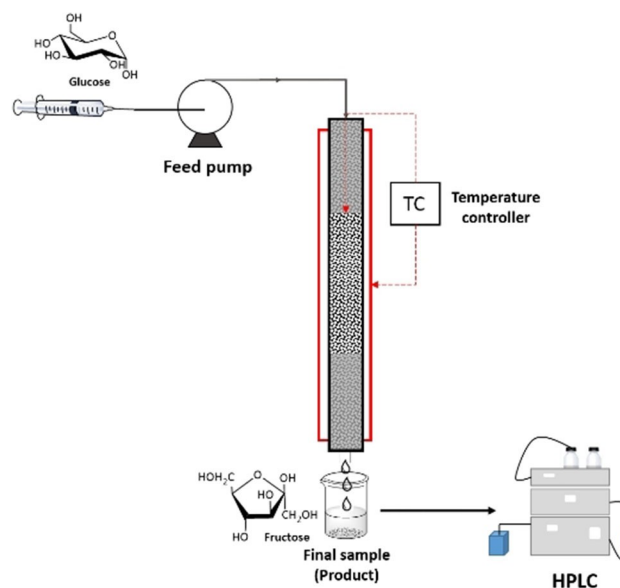


Figure 3. Schematic representation of the lab-scale continuous-flow fixed-bed catalytic reactor system.

flow system for isomerization of glucose to fructose in an aqueous media were studied. The schematic diagram of the designed lab-scale continuous-flow fixed-bed tubular reactor used in this work is presented in Figure 3.

Some preliminary tests were carried out on the continuous-flow fix-bed reactor to evaluate the system and accurate that experiments are performed under kinetic control and out of range of internal and external diffusion limitations (see in SI, Figures S2, S3). Besides, the optimization of the main operational parameters of the reaction system was carried out and the catalytic results attained are summarized in Tables 2 and 3, respectively. Temperature optimization was performed first since it is considered a key parameter in many isomerization processes.^[6,24] The attained results are depicted in Table 2 in terms of average conversion, selectivity and yield to fructose, and carbon balance. These reactions were done by maintaining the flow rate, the quantity of catalyst, and the time on stream (TOS, h).

A decrease in the temperature impaired glucose conversion, a clear reduction in the average conversion being observed.

Table 2. Catalytic results on the selective isomerization of glucose-to-fructose in a continuous flow fix-bed reactor over Ca–Al(3.0) catalyst at different temperatures.^[a]

T [°C]	Average glucose conversion [mol.%]	Average fructose selectivity [mol.%]	Average yield to fructose [mol.%]	Carbon balance [%]
90	89	50	45	65
65	76	62	47	85
45	68	80	54	95
25	17	87	15	87

[a] Reaction conditions: Feed flow rate = 2 mL/h, catalyst = 0.50 g, feed concentration = 100 g/L (glucose in water), TOS = 4 h.

Table 3. Catalytic results on the selective isomerization of glucose-to-fructose in a continuous flow fix-bed reactor over Ca–Al(3.0) catalyst at different temperatures.^[a]

T [°C]	Average glucose conversion [mol.%]	Average fructose selectivity [mol.%]	Average yield to fructose [mol.%]	Carbon balance [%]
90	35	65	23	75
65	27	90	22	83
45	24	85	21	85
25	16	87	14	86

[a] Reaction conditions: Feed flow rate = 2 mL/h, catalyst = 0.25 g, feed concentration = 100 g/L (glucose in water), TOS = 4 h.

Simultaneously, average selectivity to fructose increased as temperature decreased, the converted glucose being almost entirely transformed into fructose when the reaction was carried out at room temperature. A more reliable comparison is obtained by checking yield values, the best result achieved at 45 °C, with a fructose yield comparable to that attained with the enzymatic industrial system.^[25,26] Carbon balance is a trustworthy parameter as well, the best results being reached at this intermediate temperature. These results evidenced that the operational parameters will be crucial in finding an adequate balance between glucose conversion, selectivity and yield to fructose, and carbon balance. When low selectivity is observed by-products derived from the retroaldolization of glucose were detected, for example glycolaldehyde, similarly to that previously observed when the reaction was carried out in batch.^[21] Mannose was also detected in a minor proportion (yield ≈ 4–7%). Taking these results into consideration, it seems that 45 °C is the optimal temperature. In addition, the dependence of the catalytic results with the catalyst loading was evaluated to ascertain the appropriate operating conditions for the system and to facilitate the wisest decision. Therefore, experiments at different reaction temperatures (as those shown in Table 2), but with 0.25 g of catalyst instead of 0.50 g in the reactor, were carried out, and the results are disclosed in Table 3.

Comparison of the results of Tables 2 and 3 show that the average conversion of glucose decreased by decreasing temperature in both cases. However, selectivity to fructose did not follow the same trend by getting a moderate boost at lower catalyst loading (see values of Table 3) when the reaction was completed at 90 and 65 °C, while keeping approximately the same values like those shown in Table 2 for 45 and 25 °C. This means that non-desired secondary reactions mainly take place at higher temperatures, and need the presence of enough catalytic active sites.

Taking note of these results, 45 °C and 0.50 g of catalyst, were finally fixed as the optimal parameters for isomerization of glucose-to-fructose, thus tuning after the rest of the operational parameters such as feed flow rate, feed concentration and TOS. In this sense, three different flow rates were evaluated, such as 5, 3 and 1 mL/h; the attained results are presented in Figure 4. As can be seen, a decrease in the average conversion of glucose was observed by increasing the feed flow rate. Carbon balance kept constant with the feed flow, which means that low carbon

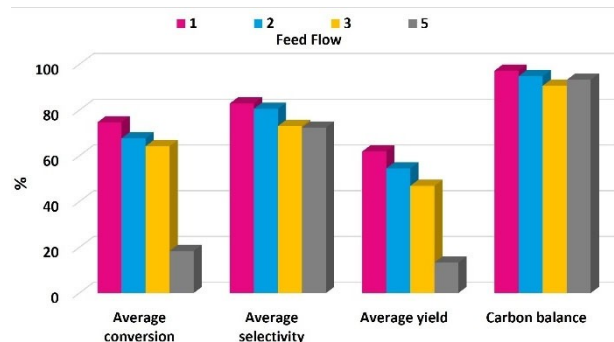


Figure 4. Dependence on feed flow rate (mL/h) in the glucose-to fructose isomerization over Ca–Al(3.0) catalyst.

deposition and low decomposition were achieved in this case. On the other hand, contact time (W/F = amount of catalyst in grams/feed flow in grams per hour) and space velocity (WHSV) parameters were calculated and correlated with glucose conversion, yield and selectivity to fructose, in order to find out the optimal values for these reaction parameters (see Figure 5).

Contact time (CT) is inversely proportional to the space velocity (WHSV) ($CT = 1/WHSV$), for instance. The highest CT leads to the highest glucose conversion, selectivity and yield to fructose but to the lowest WHSV, an indicator of the reactant retention/residence time within the catalytic bed, desirable to enhance catalyst activity, although not too high, thus allowing to avoid undesirable side reactions. Under this premise, the highest ($CT = 5$ h) and the lowest ($CT = 1$ h) CT values have been discarded. Among the two intermediates values, $CT = 2.5$ h ($Flow = 2$ mL/h) was the selected value due to the higher glucose conversion levels, yield and selectivity to fructose. Particularly, fructose yield is higher than the value achieved in the enzymatic isomerization reaction after long reaction times (42% fructose, at 52% glucose conversion).^[26]

Interestingly, the stability of the Ca–Al(3.0) catalyst under reaction conditions was evaluated in the glucose isomerization

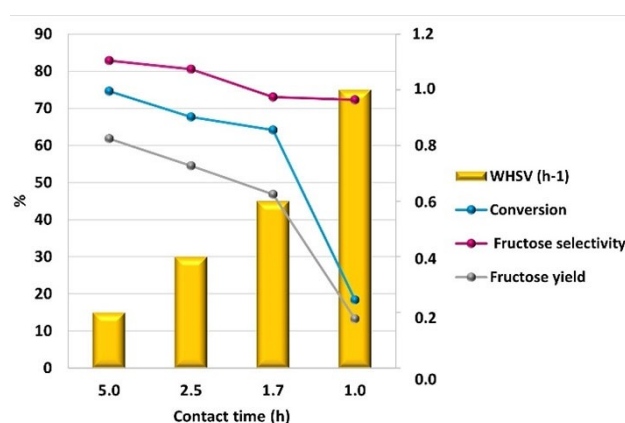


Figure 5. Correlation between contact time (h), glucose conversion, yield and selectivity to fructose, and WHSV (h^{-1}) in the glucose-to-fructose isomerization over Ca–Al(3.0) catalyst at 45 °C during 4 h.

process, thus affording the potential industrial application of the catalytic system. For that purpose, a catalytic test was conducted by continuously monitoring the reaction during one day on stream (TOS = 24 h). Figure 6 shows that a decrease in the activity of Ca–Al(3.0) catalyst is observed after 10 h of TOS (Figure 6A). This drop in the conversion of glucose, as well as in the yield of fructose, could be attributed to the hydration of the catalyst resulting in a regeneration of the hydrotalcite structure, less active for the isomerization of glucose-to-fructose. XRD measurements of the used catalyst confirm this hypothesis (see Figure 7), in line with the results previously reported of experiments performed in a batch reactor, where the catalyst recovered from the reaction mixture presented the crystalline structure of the hydrotalcite phase.^[21]

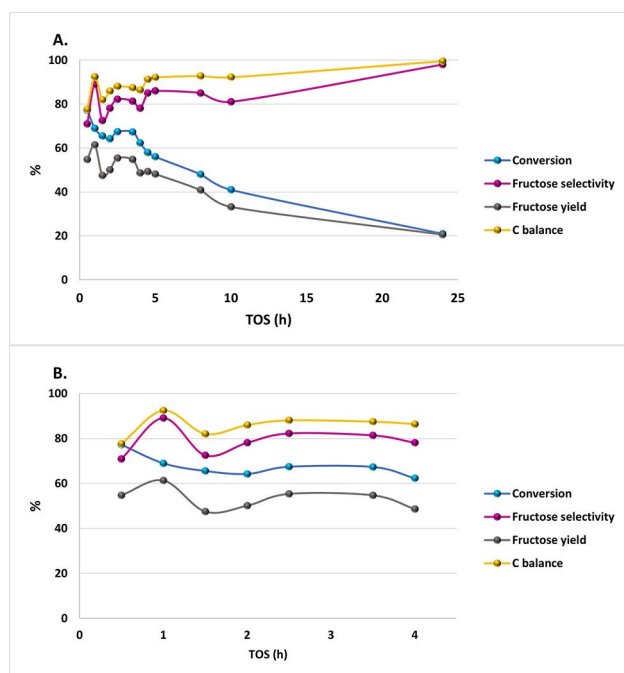


Figure 6. Effect of continuous time on stream (A) TOS = 24 h, and (B) TOS = 4 h on glucose isomerization to fructose over Ca–Al(3.0) catalyst at 45 °C (Reaction conditions: glucose concentration = 100 g/L, feed flow rate = 2 mL/h, catalyst = 0.50 g).

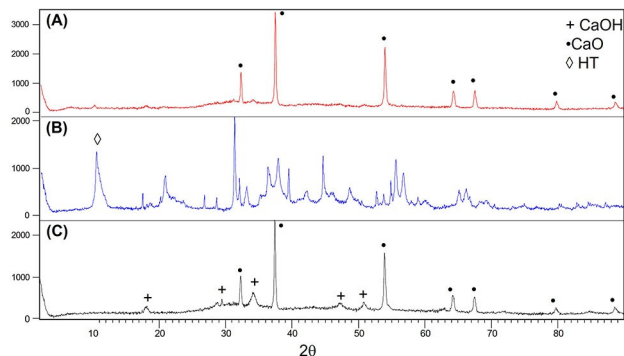


Figure 7. XRD patterns of the (A) fresh, (B) used, and (C) used + calcined Ca–Al(3.0) catalyst.

The stability of the catalyst in the glucose-to-fructose isomerization was evaluated by varying the feed flow rate from 1 to 5 mL/h, as shown in Figure 8. As can be seen, the catalyst showed high stability when carrying out the reaction with a feed flow rate from 1 to 3 mL/h (see Figure 8A and Figure 8B). Nevertheless, the use of a higher feed flow rate (5 mL/h, Figure 8C) has a negative effect on the catalyst stability, and a decrease in the glucose conversion and the yield to fructose was observed after 2 h of reaction. Remarkably, and despite the catalytic activity suffered a substantial decay after 5 h of reaction, it was wholly recovered again after thermal treatment (calcination in air) of the solid catalyst (Figure 8C). However, when the reaction was performed at a lower temperature (25 °C) with the optimal flow rate a higher stability of the catalyst was observed, thus offering an excellent and constant selectivity to fructose ($\approx 85\%$) during 100 h on stream, at an expense of a decrease in the glucose conversion and, consequently, on the fructose yield (Figure 9).

Considering the results above mentioned the reusability of the Ca–Al-based hydrotalcite-derived catalyst in the selective isomerization of glucose was also evaluated. Thus, after a

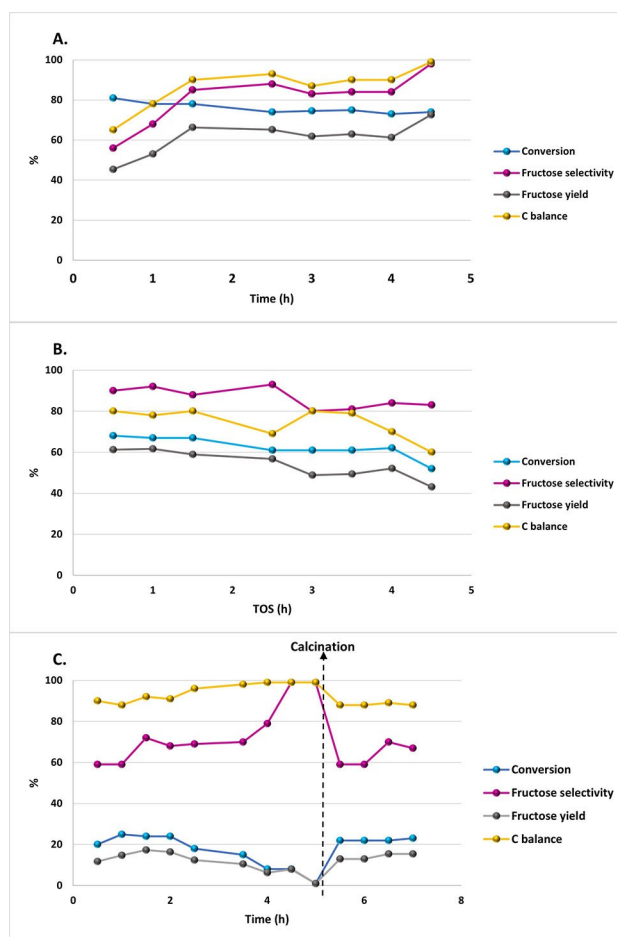


Figure 8. Results of glucose-to-fructose isomerization over Ca–Al(3.0) catalyst at different flow rates. (A) Flow = 1 mL/h; (B) Flow = 3 mL/h; and (C) Flow = 5 mL/h. (Reaction conditions: glucose concentration = 100 g/L, catalyst = 0.50 g, at 45 °C).

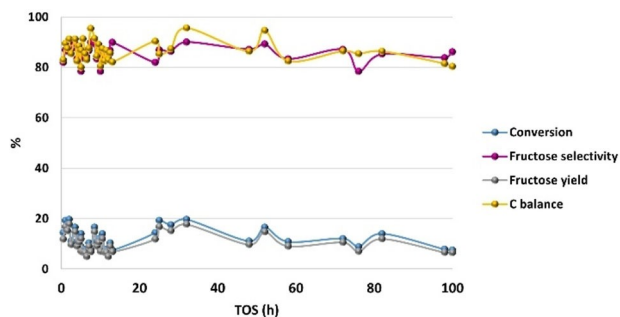


Figure 9. Effect of continuous time on stream TOS = 100 h, on glucose isomerization to fructose over Ca–Al(3.0) catalyst at 25 °C (Reaction conditions: glucose concentration = 100 g/L, feed flow rate = 2 mL/h, catalyst = 0.50 g).

catalytic experiment carried out during TOS = 4 h, the solid catalyst was separated from the inert solid for recovering, washed three times with pure water, and then calcined (see Experimental Section). A considerable decrease ($\approx 40\%$) in both glucose conversion and yield to fructose was observed after TOS = 4 h. Therefore, this time was chosen as the time limit where the catalyst needs to be regenerated. This regenerated (calcined) catalyst was used again to fill the tubular reactor and do a new catalytic experiment. This process was repeated at least 3 times, always following the same experimental procedure. Results obtained in terms of average conversion of glucose, selectivity to fructose, and carbon balance in four consecutive runs under standard reaction conditions are depicted in Figure 10.

After the first run, a slight decrease in glucose conversion was observed that could be attributed to a decrease in the number of active sites due to a minimal Ca loss in the solid, as well as to a blockage of the sites by deposition and accumulation of insoluble (refractory) organic matter,^[19] the latter being evidenced by the color change in the recovered catalyst (from white to brown). Although most of the carbonaceous materials deposited on the solid surface are eliminated upon prior calcination to a new run, a small decrease in surface

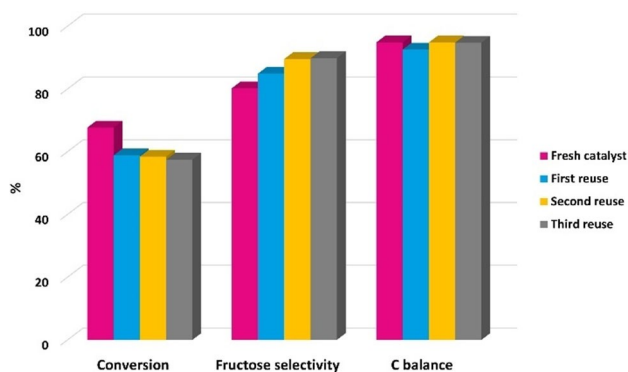


Figure 10. Reusability of the Ca–Al(3.0) catalyst in the glucose isomerization to fructose (Reaction conditions: glucose = 100 g/L in water, flow rate = 2 mL/h, with 0.5 g of catalyst, at 45 °C and TOS = 4 h).

area of the used and calcined catalyst was encountered. In the three consecutive runs after the first use of the catalyst, any remarkable loss on glucose conversion was detected, whereas a slight increase in fructose selectivity was observed, thus keeping a regular yield value. It is worth noting that this fructose production is higher than the best reference found to date where a heterogeneous catalyst (Mg–Al-hydrotalcite, with [Glucose] = 0.01 g/L and 0.25 g catalyst at 90 °C) is used with 25.1 % yield.^[19]

The used catalyst was analyzed by ICP. After the first run, a Ca loss of $\approx 5\%$ (with respect to the initial amount of Ca in the solid) was detected, while after the last run, the cumulative loss reached 6.2%, suggesting a stabilization after the first cycle. XRD measurements of the used and then calcined catalyst were also performed (see Figure 7C), and a new minority phase was observed that corresponds with the pattern of Ca(OH)_2 , (relative phase amount of 5.1% estimated from the area of the main diffraction peaks observed in the XRD diffractogram). This Ca hydroxide is formed by the well-known hydration of CaO; the Ca–Al mixed oxide stays a long time in contact with water, which entails its rehydration. Since thermal degradation of Ca(OH)_2 to CaO occurred at 512 °C,^[27] and the calcination of the catalyst took place at 450 °C, it is reasonable to think that the Ca(OH)_2 formed did not degrade and persists together with CaO in the solid (Figure 7C). This fact, together with the Ca loss and the lower activity observed by Ca(OH)_2 ,^[21] explains the slight decrease in conversion over the 4 catalytic cycles.

Conclusions

In this research work, the isomerization of glucose to fructose performed in a continuous flow fixed-bed catalytic reactor using a Ca–Al mixed oxide (derived from hydrotalcite-type precursor) as catalyst was presented. The main conclusions extracted from the study are listed below:

- 1) The Ca–Al mixed oxide, $\text{Ca}_3\text{AlO}_{4.5}$, exhibited excellent performance in the glucose-to-fructose isomerization, with fructose yields higher than those attained with other heterogeneous catalysts found in the bibliography and comparable to that of the enzymatic system currently used in industry (see SI).^[28]
- 2) After an exhaustive study on the reaction conditions, the optimal operational conditions for a continuous flow catalytic system have been established, allowing for an average glucose conversion of 68% with a fructose yield of 54%.
- 3) A catalyst deactivation was detected by lengthening the time on stream (after TOS = 4 h). XRD measurements of the used catalyst showed the hydration of the mixed oxide, regenerating the hydrotalcite structure, less active in the isomerization of glucose to fructose. Also, the production of small amounts of Ca(OH)_2 in the solid catalyst after its use leads, not only to a slight decrease in the conversion, only observed from the first to the second run, but to an increase in the selectivity to fructose with consecutive catalytic runs. Nonetheless, catalyst deactivation could be solved via the

regeneration of the catalyst by introducing a convenient calcination step, which allows for the complete recovery of the initial catalytic activity.

Experimental Section

Materials

Glucose and fructose (Sigma-Aldrich, 99.5%), were used as reagents in the isomerization tests. For the analysis, glucose and fructose ($\geq 99.99\%$) were purchased from Sigma-Aldrich and used as received. Water (Milli-Q quality, Millipore) was used as the solvent. Hydro-talcite-precursors were prepared by using the suitable metallic precursor bought from Sigma-Aldrich: $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ($\geq 99\%$), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ($\geq 98\%$), and an aqueous solution of NaOH (98%) in Milli-Q water. Single oxides CaO and Al_2O_3 and $\text{Ca}(\text{OH})_2$ were also purchased from Sigma-Aldrich. Nitrogen (99.999%) was acquired from Abelló Linde S.A.

Catalyst preparation:

The Ca/Al mixed oxide was prepared by calcination of the hydro-talcite precursor. The hydro-talcite was synthesized by the co-precipitation modified-method described in ref. [18]. Two different solutions, solution A containing the metallic species (Ca, Al) in the desired concentrations, and solution B containing the basic solution in the wanted concentration that is: $[\text{OH}^-] = 2[\text{Ca}^{2+}]$ were mixed at room temperature under N_2 atmosphere keeping constant the addition rate at 20 mL/h. The precipitates were aged for 18 h at 60°C in an oven, under N_2 atmosphere. After that, the solid was washed with deionized water until $\text{pH} \leq 8$ and calcined, prior to their use in the catalytic experiments, at 450°C for 4 h with a temperature rate of $2^\circ\text{C}/\text{min}$. The solid was cooled down for 8 h under N_2 atmosphere and kept under N_2 atmosphere to prevent CO_2 and H_2O adsorption and/or degradation.

Catalyst characterization

HTs and mixed oxides materials were characterized by inductively coupled plasma (ICP) with a Varian 715-ES ICP-Optical emission spectrometer, after solid dissolution in HNO_3 aqueous solution. Phase purity was determined by X-ray diffraction (XRD) in a Philips X'pert MPD diffractometer equipped with a PW3050 goniometer ($\text{CuK}\alpha$ radiation, graphite monochromator). Surface areas of the solid samples (150 mg) were calculated by applying the BET method to the N_2 adsorption isotherms obtained by carrying out liquid nitrogen adsorption experiments at -196°C , in a micro-meritics flowsorb apparatus.

The temperature-programmed desorption of ammonia (NH_3 -TPD) was carried out to evaluate the total surface acidity of the catalysts. After cleaning the catalysts (80 mg) with helium, and subsequent adsorption of ammonia at 373 K, the NH_3 -TPD measurement was performed by raising the temperature from 100 to 550°C , under a helium flow of 40 mL/min, with a heating rate of 10 K/min and maintained at 550°C during 15 min. The evolved ammonia was analyzed using a TCD detector of a gas chromatograph (Shimadzu GC-14A).

A scanning electron microscope (SEM, Zeiss instrument, AUR-IGA Compact) has been employed to determine the morphology of the solid samples before and after calcination.

Continuous flow reactor setup and experimental procedure

The schematic diagram of the lab-scale continuous flow fixed-bed catalytic reactor is shown in Figure 3. The experimental setup consists of a tubular reactor surrounded by an electrical heater consisting of a thermal blanket. The tubular reactor is controlled with a thermocouple placed next to the catalyst bed, directly connected to the temperature controller. In a typical test, 0.50 g of the catalyst is mixed with 0.50 g of SiC, the tubular reactor is then filled, keeping this mixture in the middle of the reactor. Empty spaces were filled with 2×0.5 g of SiC. The reactor then is conditioned under a N_2 flow and the temperature is increased until reaching the desired one (standard test = 45°C). A perfusion syringe pump allowed for fixing the liquid feed (100 g/L aqueous solution of glucose) at an adequate flow rate (from 1 to 5 mL/h). The relationship between feed flow rate, amount of catalyst, and time is given by weight hourly space velocity (WHSV), defined as the feed weight flowing per weight unit of the catalyst per hour [Eq. (1)].

$$\text{WHSV}(\text{h}^{-1}) = (\text{Feed concentration} \times \text{Feed flow rate}) / (\text{Mass of catalyst}) \quad (1)$$

Liquid samples are collected at different times at the outlet of the reactor in an ice-refrigerated vessel, and then filtered off prior to their analysis.

Product analysis

The liquid samples collected from the experiments were analyzed using HPLC (LC-1100 Agilent) equipped with a refractive index detector (RI) with internal temperature of 50°C to determine the amount of products and substrates. Bio-Rad Aminex HPX-87C column (9 μm , 7.8×300 mm) maintained at 60°C was used with a mobile phase of 100% Milli-Q HPLC grade water at a flow rate 0.5 mL/min. Determination of the product concentration in samples was done by means of external calibration curves generated for all the suitable products separately, by using standard solutions with known concentrations. The results are reported in terms of glucose (substrate) conversion, yield and selectivity to the different products, and Carbon balance which are calculated according to Equations (2)–(5):

$$\text{Substrate conversion} = (\text{Mol substrate converted}) / (\text{Initial mol substrate}) \times 100\% \quad (2)$$

$$\text{Product yield} = (\text{Mol product produced}) / (\text{Initial mol substrate}) \times 100\% \quad (3)$$

$$\text{Product selectivity} = (\text{Mol product produced}) / (\text{Mol substrate converted}) \times 100\% \quad (4)$$

$$\text{Carbon balance} = (\text{Moles of carbon produced}) / (\text{Moles of carbon in the substrate}) \times 100\% \quad (5)$$

Catalyst reusability

In a standard experiment, after checking the activity loss of the catalyst, the solid was washed by flowing pure water at 0.05 mL/min overnight. After that, the catalyst was dried at 100°C , taken out of the reactor, and separated from SiC, which could be done because of the size difference. The catalyst was then calcined in a tubular furnace, for 4 h at 450°C with a rate temperature increase

of 2 °C/min, and cooling under a N₂ atmosphere for 23 h to room temperature. The solid was packed at the desired size, mixed with SiC, and the tubular reactor was finally filled for the next catalytic test.

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Conflict of Interest

The authors declare no conflict of interest.

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