



## Beneficial effects of calcium chloride on glucose dehydration to 5-hydroxymethylfurfural in the presence of alumina as catalyst

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### ABSTRACT

Aluminas with different acid-base properties (acid, neutral and basic) have been characterized by using XRD, N<sub>2</sub> sorption at –196 °C, XPS and NH<sub>3</sub>-TPD, and tested for the dehydration of glucose to 5-hydroxymethylfurfural (HMF). Under the operating conditions used, the acid alumina showed the highest total acidity and the best catalytic performance, but the HMF yield hardly exceeded 20% since  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> apparently favored the secondary reactions. The presence of CaCl<sub>2</sub> in the reaction medium notably improved the catalytic performance, even at very short reaction times, due to the interaction between Ca<sup>2+</sup> ions and glucose molecules, which favors the  $\alpha$ -D-glucopyranose formation, thus enhancing glucose conversion and HMF yield up to 96% and 52%, respectively, at 175 °C after 15 min in presence of 0.65 g<sub>CaCl<sub>2</sub></sub> · g<sub>aq.sol.</sub><sup>-1</sup> and acid  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as catalyst. The isomerization of glucose to fructose and subsequent dehydration to HMF does not seem to take place when CaCl<sub>2</sub> is present in the reaction medium, as inferred from <sup>1</sup>H NMR spectroscopy. Moreover, the catalyst was reused at least for three runs maintaining the catalytic activity, without an intermediate regeneration step.

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### 1. Introduction

Currently, the depletion of fossil fuel reserves, together with the unsteady price of crude oil and the environmental concerns due to global warming and pollution, are boosting the development of alternative and clean synthetic routes for producing chemicals and fuels from non-fossil carbon sources. Biomass is a very promising sustainable feedstock for this purpose since it is the only widely available and renewable carbon source [1–3]. Lignocellulosic biomass is the most abundant source of biomass with an estimated annual production about  $2 \times 10^{11}$  metric tons [4], and it is composed of three major components: cellulose (40–50%), hemicellulose (25–35%) and lignin (15–20%), and other extractable components, as small amounts of organic compounds [3,5]. Cellulose is a biopolymer consisting of D-glucose units linked via  $\beta$ -1,4-glycosidic bonds, being required a hydrolysis step to make

available glucose monomers. Thus, carbohydrates are the largest natural source of carbon, constituting up to 75% of the annual production of biomass and being a promising raw material with industrial applications in several areas of chemistry, food, paper and pharmaceutical industries [6]. However, the main drawback of carbohydrates as feedstock is the excess of oxygen of their molecular structures, which can be reduced by several chemical processes, as for example, their dehydration into a broad spectrum of important chemicals, such as furanic derivatives (furfural, 5-hydroxymethyl-furfural (HMF) or 2,5-furandicarboxylic acid) and levulinic acid [2]. HMF has been listed among the top 10 value-added bio-based chemical platforms by the US Department of Energy, due to its great potential as key intermediate to synthesize a wide range of value-added compounds currently derived from petroleum, as 2,5-furandicarboxylic acid, 5-hydroxymethylfurfuroic acid, 2,5-dimethylfuran, hydroxymethyl tetrahydrofurfural, 2,5-hydroxymethyl furan, 2,5-hydroxymethyl tetrahydrofuran, 5-ethoxymethylfurfural, levulinic acid, adipic acid,  $\gamma$ -valerolactone, caprolactam, caprolactone, among others [2,6–8]. Nevertheless, HMF is not yet produced at industrial scale

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in spite of its versatility and multifunctionality because of its high production cost. The HMF production is carried out by triple dehydration of  $C_6$  carbohydrates in the presence of an acid catalyst. Although higher HMF selectivities are attained employing fructose as feedstock [9–14], glucose is preferred due to its abundance and availability. Mineral inorganic acids are traditionally used as acid catalysts, but they are corrosive and harmful for environment, in such a way that heterogeneous acid catalysts are preferred because they are environmentally friendly and human healthy, and they can be more easily separated and reused. In this sense, different solid acid catalysts have been tested for dehydration of glucose to HMF: cation exchange resins together with hydrotalcites [15], zeolites [16–18], sulfated zirconia [19,20], metal oxides such as  $TiO_2$  [21–24],  $ZrO_2$  [21–23,25],  $Nb_2O_5$  [10,26], metal phosphates [27–29], among others.

On the other hand, aluminum oxides have been extensively employed as supports and catalysts, because they are abundant, cheap and hence commercially available, being  $\gamma-Al_2O_3$  the most widely used. Thus, alumina has been utilized as such or in mixed oxides for dehydration of different sugars, such as glucose, fructose or xylose [30–35]. García-Sancho et al. [30] found that  $\gamma-Al_2O_3$ , used as support of  $Nb_2O_5$ , increased conversion in xylose dehydration, although it favored secondary reactions, considerably decreasing the furfural selectivity. It is well known that a key factor in the HMF production, from glucose dehydration, is to minimize side reactions leading to HMF rehydration, producing levulinic and formic acids, as well as to the formation of humins and other soluble and insoluble polymers [2,6,36,37]. In order to increase the HMF yield, different strategies have been followed, as the use of biphasic systems, where the presence of an organic solvent allows the continuous extraction of HMF, immediately after its formation in the aqueous phase, minimizing side reactions and consequently improving HMF yield. Different solvents have been evaluated as extracting agents of HMF, such as toluene [38–40], tetrahydrofuran [39,41], 1-butanol [41,42], 2-butanol [10,43,44], acetone [45,46], diethyl ether [47,48] and mainly methyl isobutyl ketone [38,39,49–52].

Moreover, it has been reported the salting out effect improves the HMF selectivity increasing the partition coefficient, but the role of inorganic salts is not clear in the literature [42,53–55]. On the one hand, Marcotullio et al. [56,57] studied the influence of halide salts on dehydration of xylose to furfural, concluding that anions promoted the formation of an acyclic intermediate, 1,2-enediol, whose subsequent acid catalyzed dehydration led to furfural. However, Rasrendra et al. [58] compared halide and sulfate salts of different metals, pointing out that the anion effect was less important than the influence of cation. On the other hand, Román-Leshkov et al. [54] saturated the aqueous phase of a biphasic system with inorganic salts for dehydration of fructose to HMF, and concluded that the salting-out effect cannot be attributed to individual cationic or anionic contributions, being related to the interaction of all ionic species. Thus, the highest HMF selectivity was found by using  $K^+$  and  $Na^+$  cations maintaining constant the amount of  $Cl^-$ . Nevertheless, significant differences with respect to systems without salt were not found when the anion was changed from  $Cl^-$  to  $Br^-$ . The influence of alkali and alkaline earth metal salts on HMF production was also evaluated by Combs et al. [55], demonstrating that  $Ca^{2+}$  and  $Mg^{2+}$  accelerated the glucose decomposition rate via glucose complexation, since it had been previously demonstrated that the alkaline earth metal cations can form bidentate complexes by interacting with two oxygen atoms of glucose [59,60]. However, the reason why these cations favor the glucose decomposition has not been hitherto understood unequivocally.

In this work, the dehydration of glucose to HMF has been evaluated by using different mesoporous  $\gamma-Al_2O_3$  with acid, neutral or basic character, in a biphasic water–MIBK solvent system to avoid

side reactions involving HMF. The addition of inorganic salts such as  $NaCl$  and  $CaCl_2$  in the reaction medium has been carried out in order to reach the maximum HMF yields. Likewise, the influence of  $CaCl_2$  on the possible reaction pathways from  $^1H$  NMR results has been elucidated for the first time. Different parameters such as the reaction time, the amount of catalyst and its possible reuse, have been also studied.

## 2. Experimental

### 2.1. Reagents

Three different commercial aluminas (Alfa-Aesar, Brockmann Grade I, 58 Å) have been employed as solid acid catalysts for glucose dehydration to HMF: acid, neutral and basic alumina, which have been denoted as Al-x, where x = a, n and b indicate their acid, neutral or basic character, respectively.

For the catalytic tests, the following chemicals have been utilized: glucose (Sigma-Aldrich, >99%), fructose (Sigma-Aldrich, >99%), sodium chloride (VWR, 99%) and calcium chloride (VWR, 97%). Deionized water and methyl isobutyl ketone (MIBK, VWR, 98%) have been used as solvents.

### 2.2. Characterization of catalysts

Powder diffraction patterns were collected on an PANalytical automated diffractometer, EMPYREAN model, using  $Cu-K\alpha$ -1,2 (1.5406 Å) radiation and a last generation PIXcel detector.

The textural parameters were determined from the nitrogen adsorption–desorption isotherms at  $-196^\circ C$ , obtained by using an automatic ASAP 2020 model of gas adsorption analyser from Micromeritics. Prior to  $N_2$  adsorption, the samples were degassed at  $200^\circ C$  and  $10^{-4}$  mbar for 10 h. Surface areas were determined by using the Brunauer–Emmett–Teller (BET) equation and taking a value of  $16.2 \text{ \AA}^2$  for the cross section of the adsorbed nitrogen molecule at  $-196^\circ C$ . Pore size distributions were calculated with the BJH method.

X-ray photoelectron spectra were obtained with a Physical Electronics PHI 5700 spectrometer with non-monochromatic Mg  $K\alpha$  radiation (300 W, 15 kV, and 1253.6 eV) with a multi-channel detector. Spectra were recorded in the constant pass energy mode at 29.35 eV, using a 720  $\mu m$  diameter analysis area. Charge referencing was measured against adventitious carbon (C 1s at 284.8 eV). A PHI ACCESS ESCA-V6.0 F software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gaussian–Lorentzian curves in order to determine accurately the binding energies of the different element core levels.

The temperature-programmed desorption of ammonia ( $NH_3$ -TPD) was carried out to evaluate the total surface acidity of catalysts. After cleaning of catalysts (80 mg) with helium up to  $550^\circ C$  and subsequent adsorption of ammonia at  $100^\circ C$ , the  $NH_3$ -TPD was performed by raising the temperature from 100 to  $550^\circ C$ , under a helium flow of  $40 \text{ mL min}^{-1}$ , with a heating rate of  $10^\circ C \text{ min}^{-1}$  and maintained at  $550^\circ C$  for 15 min. The evolved ammonia was analyzed by using a TCD detector of a gas chromatograph (Shimadzu GC-14A).

Thermogravimetric analyses (TGA) were performed with a TGA/DSC 1 model (Mettler-Toledo), under air flow of  $50 \text{ mL min}^{-1}$  with a heating ramp of  $10^\circ C \text{ min}^{-1}$ , from room temperature until  $900^\circ C$ . The carbon content of spent catalysts was measured with a LECO CHNS 932 analyser.

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