

γ -Al₂O₃ as acid catalyst for dehydration of glucose to 5-hydroxymethylfurfural

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Keywords: alumina, heterogeneous catalysis, dehydration, glucose, 5-Hydroxymethylfurfural

Introduction

Currently, the search and development of sustainable feedstocks for chemicals derived from petrol have gained worldwide attraction because of the instability of the price of crude oil, the reduction of fossil oil reserves, and the environmental concerns associated to the greenhouse effect caused by CO₂ emissions, being biomass one of the world's most important renewable carbon sources [1,2]. The major component of plant-derived biomass are carbohydrates, being of great importance to develop efficient and green approaches to their valorization by conversion into high value-added products. Thus, glucose can be transformed by dehydration into 5-hydroxymethylfurfural (HMF), which is a versatile and key intermediate for the production of a wide variety of biobased chemicals and it is attracting much attention in biofuels and chemical industry [3].

Different catalytic systems have been evaluated for HMF production from C₆ carbohydrates as glucose, mostly based on heterogeneous catalysis as alternative to the use of liquid mineral acids [4]. On the other hand, the high surface area, large pore size and thermal and hydrothermal stabilities of some mesoporous solids make them suitable for many catalytic processes. In the present work, the dehydration of glucose to HMF has been evaluated by using different mesoporous γ -Al₂O₃ with acid, neutral or basic character, in a biphasic water–MIBK solvent system to avoid the HMF degradation and its possible reaction with the intermediates from glucose to give soluble polymers and humins or acetalization with glucose. Different experimental parameters, such as reaction temperature and time, as well as the addition of inorganic salts have been studied in order to reach the maximum HMF yield.

Materials and Methods

Three different commercial γ -alumina (acid, neutral and basic) supplied by Alfa-Aesar have been used, which have been denoted as Al-*x*, where *x*=*a*, *n* or *b* indicates its acid, neutral or basic character, respectively.

These catalysts have been characterized by X ray diffraction (XRD), N₂ adsorption–desorption isotherms at -196°C, X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption of ammonia (NH₃-TPD) and pyridine adsorption coupled to FTIR spectroscopy.

Batch catalytic experiments has been performed in a glass pressure tube with thread bushing with magnetic stirring bar. In a typical experiment, 150 mg of glucose (Sigma-Aldrich, >99%), 50 mg of catalyst, 1.5 mL of

deionized water and 3.5 mL of MIBK (Methyl Isobutyl Ketone, Sigma-Aldrich) are poured into the reactor. The reaction mixture was heated with a thermostatically controlled oil bath. The products are quantitatively analyzed by HPLC, equipped with a multiwavelength UV-visible and refractive index detectors in isocratic mode.

Results and Discussion

The characteristic peaks of γ -Al₂O₃ are clearly observed in the powder XRD patterns of Al-*x* catalysts (Figure 1) (Powder Diffraction File reference code 01-074-2206).

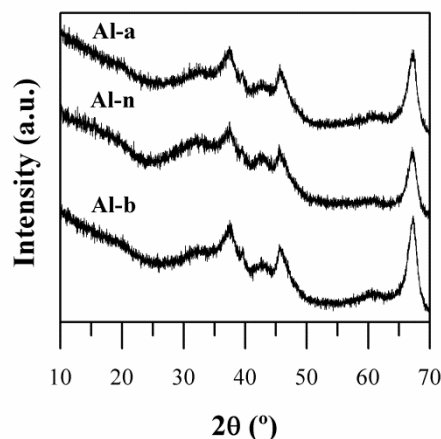


Fig. 1. XRD of Al-*x* catalysts

The textural properties have been evaluated from the nitrogen adsorption–desorption isotherms at -196 °C, showing type IV isotherms according to the IUPAC classification, typical of mesoporous solids. The average pore sizes are centred in the mesoporous range, as it can be inferred from data gathered in Table 1. Moreover, the BET surface areas and pore volumes are very similar for different alumina catalysts.

Table 1. Textural and acidic properties of Al-*x* catalysts

Catalyst	S _{BET} (m ² ·g ⁻¹)	V _p (cm ³ ·g ⁻¹)	dp (nm)	μmol NH ₃ ·g ⁻¹
Al- <i>a</i>	158	0.236	4.7	478
Al- <i>n</i>	137	0.237	4.8	401
Al- <i>b</i>	143	0.252	5.1	232

As the activity in the glucose dehydration into HMF depends on the acid properties, the total acidity has been evaluated by NH₃-TPD. Thus, as expected, the highest total acidity value (478 μmol NH₃·g⁻¹) is found in Al-*a*, whereas the lowest acidity is shown for the

basic alumina. On the other hand, the NH₃-TPD profiles (not shown) reveal the presence of acid sites with a broad range of strength. In addition, it is generally accepted that the acid strength depends on the ammonia desorption temperature, being also observed that ammonia desorbed from stronger sites at higher temperatures.

These mesoporous Al-*x* catalysts have been tested in the dehydration of glucose to HMF at 175 °C under batch operation in aqueous solution, using MIBK as co-solvent for the extraction of HMF formed during the reaction (Figure 2). In all cases, high values of glucose conversion are reached, being slightly greater for acid alumina, with a value of 85% after 90 minutes of reaction. The acidic alumina gives rise to the highest HMF yield after 90 min (14%), although after 120 min the values of all the catalysts are very similar. However, these values are not high enough in spite of the high glucose conversion attained, because γ -Al₂O₃ enhances the secondary reactions as previously confirmed García-Sancho *et al.* [5] for dehydration of xylose to furfural.

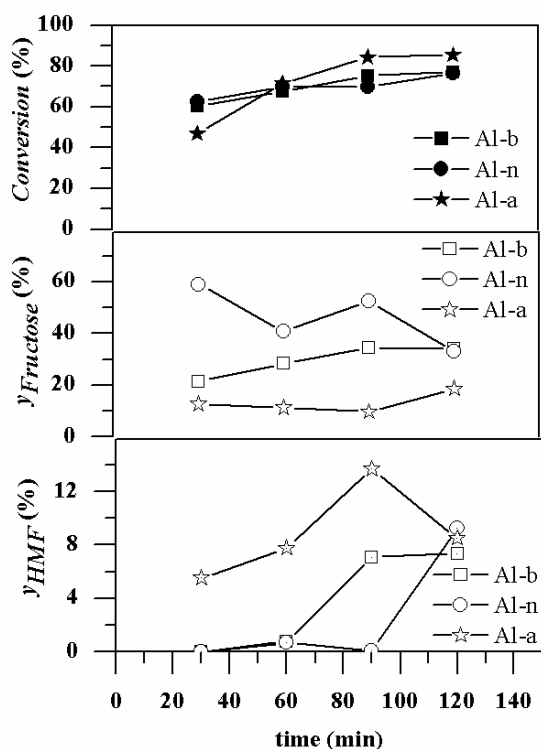


Fig. 2. Glucose conversion, fructose and HMF yields for Al-*x* catalysts as function of time at 175 °C (Glucose/catalyst ratio=3)

In order to minimize these side reactions, the addition of inorganic salts has been proposed by different authors, and they have observed its positive effect in dehydration of sugars [6,7]. In the present research work, it has been observed that glucose conversion is almost complete at a very short reaction time (30 min) in the presence of CaCl₂.

Likewise, a considerable increase of HMF yield is obtained in presence of CaCl₂, reaching a value of 48% after 30 minutes at 175 °C. Therefore, it can be affirmed that the use of calcium chloride improves the HMF selectivity, minimizing the secondary reactions. It should be also noted that the fructose yield also decreases by using Al-*a*. This fact would indicate that the reaction mechanism changes due to the presence of calcium chloride, as confirmed by Marcotullio *et al.* [7] who evaluated the effect of chlorides in dehydration of xylose to furfural, although other authors have pointed out that the effect is mostly over the partition coefficient of HMF in the aqueous and organic phases.

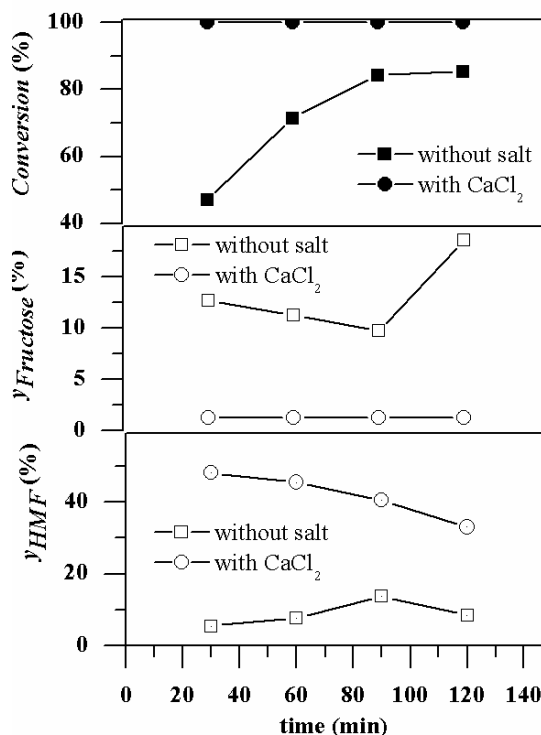


Fig. 3. Influence of the addition of CaCl₂ on glucose conversion, fructose and HMF yields for Al-*a* catalyst as function of time at 175 °C (Glucose/catalyst ratio=3)

Acknowledgements

The authors are grateful to financial support from the Spanish Ministry of Economy and Competitiveness (CTQ2012-38204-C04-02 project), Junta de Andalucía (RNM-1565) and FEDER funds.

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