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POROUS ALUMINOSILICATES AS ACID CATALYSTS FOR GLUCOSE DEHYDRATION TO 5-HYDROXYMETHYLFURFURAL

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Introduction

The instability of oil prices and the diminishing fossil fuel reserves, as well as the growing concerns about global warming, have led to the search of new sustainable sources of energy and chemicals from renewable resources. Biomass is considered as a renewable and sustainable feedstock for fuel and chemical production. 5-hydroxymethylfurfural (HMF) is an important building blocks derived from biomass, particularly from glucose, a versatile and key intermediate for production of a large spectrum of biobased chemicals, such as levulinic acid, furandicarboxylic acid, dimethyl furan, γ -valerolactone and dihydroxymethylfurfural [1,2].

Many studies have reported glucose and fructose conversion to HMF using not only homogeneous catalysts, but also a large variety of solid acid catalyst, such as sulphated zirconia/titania [3], layered Zr and Ti phosphates [4], heteropolyacids [5], and zeolites [6], among others. The state of the art of the catalytic dehydration of C6 carbohydrates has been reviewed by Chheda *et al.* [7] and Wang *et al.* [8]. It is well known that the use of mineral acids as catalysts in this reaction involves several problems such as toxicity, corrosion, catalyst waste, use of large amount of catalyst and difficulty of separation. Therefore, their replacement by solid acids is highly recommended owing to their absence of corrosiveness, environmentally friendly nature and easy separation and recovery. Lucas *et al.* [9] have evaluated the catalytic behavior of mesoporous Al-SBA-15 catalysts and different commercial zeolites in the dehydration of fructose to HMF, and they found a maximum HMF selectivity of 88% at 59 mol% conversion of fructose, by using a Al-SBA15 catalyst with a Si/Al molar ratio of 65, at 165°C, with a 10% aqueous solution of fructose, in a biphasic water:MIBK (5:1, v/v) solution, after 1 h of reaction time. However, leaching of non-framework aluminum was observed when water is used as solvent, thus limiting the reusability of this solid catalyst. The use of non-aqueous solvents, like DMSO, overcomes this drawback. Nevertheless, under the same experimental conditions, glucose dehydration only gives conversion and HMF selectivity values lower than 30 mol%.

In the present work, the catalytic behavior of micro- and mesoporous aluminosilicates in glucose dehydration is compared. In this sense, different commercial zeolites (Beta, Y and ZSM-5, in their protonic form) and aluminum-doped mesoporous MCM-41 silica have been characterized by using different physico-chemical techniques and the

dehydration of glucose has been studied by using bi-phasic systems, where the influence of experimental variables, such as nature of co-solvent, inorganic salt addition, catalyst loading and temperature and time reaction, has been optimized.

Experimental

Three commercial zeolites were used: H-Y (CBV400, Zeolyst International), Beta (CP814E, Zeolyst International) and ZSM-5 (CBV3024E, Zeolyst International). Their H-form was obtained after treatment with ammonium nitrate aqueous solution and subsequent thermal treatment of the resulting solid at 450°C in air.

Mesoporous Al doped MCM-41 silica was prepared by a sol-gel method in two reaction steps (acid and alkaline hydrolysis), by following the method reported by Araujo et al. [10], by using tetraethylortosilicate and aluminium triisopropoxide, in the presence of a n-dodecylammonium chloride hydro-alcoholic solution. Two catalysts with different Si/al molar ratios were prepared after removing after thermal treatment at 550°C for 3h.

The glucose dehydration was performed by using 50 mg of catalyst, 0.15 g of glucose, 1.5 mL of deionized water and 3.5 ml of organic solvent to extract the HMF and avoid its degradation. After reaction time, liquid phases were separated and filtered, and the analysis of products was done in both phases by HPLC.

Results and Discussion

The structural and textural characterization has confirmed the mesoporous nature of the synthesized xAl-MCM catalysts. Total acidity of these porous aluminosilicates has been measured by NH₃-TPD, and high acidity values have been found for zeolites (Table 1).

Table 1. Textural and acid properties of catalysts

Catalyst	SiO ₂ /Al ₂ O ₃ molar ratio	S _{BET} (m ² /g)	V _p (cc/g)	pore dimension (Å)	acidity (μmol NH ₃ /g)	T (°C)*
H-ZSM-5	30	404	0,3	5.4 x 5.6 5.5 x 5.1	1259	165
H-Beta	25	441	0,85	5.7 x 7.5 6.5 x 5.6	1282	183
H-Y	5.1	595	0,34	7.4	1676	213
10Al-MCM	30	587	1,45	22	528	278
5Al-MCM	10.8	734	1,7	28	956	160

* maximum temperature peak in the NH₃-TPD curve

As expected, the acidity increases with the amount of aluminum, in both family of micro- and mesoporous aluminosilicates, and the presence of octahedral and tetrahedral aluminum has been studied by ²⁷Al NMR.

The existence of both Brönsted and Lewis acid sites has been corroborated by using pyridine adsorption coupled to FTIR spectroscopy and the concentration has been correlated with the nature of aluminum species.

Concerning the catalytic behavior, by using a biphasic water/MIBK as reaction medium and a 30 wt.% of the 10Al-MCM catalyst with respect to the substrate weight (glucose),

87 % of glucose conversion and 36 % of HMF yield were attained at 195°C after 150 min of reaction time. However, a very positive effect was observed by using a sodium chloride aqueous solution. The large pore dimensions of aluminium doped MCM-41 silica and H-Beta catalysts together with their high acidity, with both Brönsted and Lewis centres, have led to very active acid catalysts in the dehydration of glucose to HMF. Thus, by using a biphasic water/MIBK solution, after addition of a 20 wt% NaCl, the catalytic activity is largely improved, attaining glucose conversion values higher than 94 % and 70 % of HMF yields, in a short reaction time (30 min). Moreover, no levulinic acid nor furfural were detected (Figure 1).

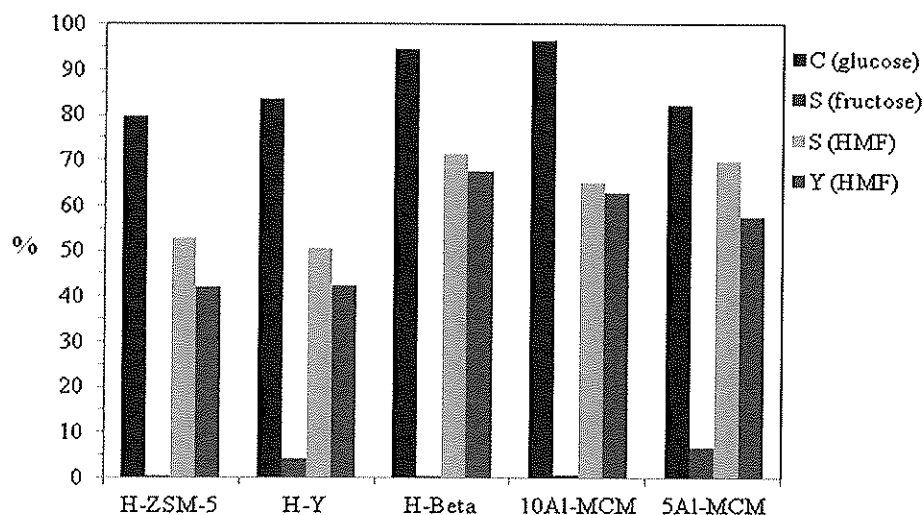


Figure 1. Catalytic behavior in the dehydration of glucose (Experimental conditions: 50 mg of catalyst, 0.15 g of glucose, 1.5 ml of NaCl aqueous solution (20 wt% NaCl) and 3.5 ml of organic, T= 195°C, time= 30 minutes)

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References

- [1] M.J. Climent, A. Corma, S. Iborra, , Green Chemistry, 13 (2011) 520.
- [2] P. Gallezot, Chemical Society Reviews 41 (2012) 1538.
- [3] J. Zhang, S. Wu, H. Zhang, B. Li, BioResources 7 (2012) 3984.
- [4] F. Benvenuti, C. Carlini, P. Patrono, A.M. RaspolliGalletti, G. Sbrana, M.A. Massucci, P. Galli, Applied Catalysis A 183 (2000) 147.
- [5] Q. Zhao, L. Wang, S. Zhao, X. Wang, S. Wang, Fuel 9 (2011) 2389.
- [6] R. Kourieh, V. Rakic, S. Bennici, A. Auroux, Catalysis Communications 30 (2013) 5.
- [7] J.N. Chheda, Y. Roman-Leshkov, J.A. Dumesic, Green Chemistry, 9 (2007) 342.
- [8] T. Wang, M.W. Nolte, B.H. Shanks, Green Chemistry 16 (2014) 548.
- [9] N. Lucas, G. Kokate, A. Nagpure, S. Chilukuri, Microporous and Mesoporous Materials, 181 (2013) 38.
- [10] R.S. Araujo, D.C.S. Azevedo, E. Rodríguez-Castellón, A. Jiménez-López, C.L. Cavalcante Jr., Journal of Molecular Catalysis A 281 (2008) 154.

