



Aqueous-phase dehydration of xylose to furfural in the presence of MCM-22 and ITQ-2 solid acid catalysts

Margarida M. Antunes^a, Sérgio Lima^a, Auguste Fernandes^b, Martyn Pillinger^a, Maria F. Ribeiro^b, Anabela A. Valente^{a,*}

^a Department of Chemistry, CICECO, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal

^b Institute for Biotechnology and Bioengineering, Centre for Biological and Chemical Engineering, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

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ABSTRACT

The H-MCM-22 zeolite possessing an MWW (medium-pore) framework and its delaminated counterpart, ITQ-2, with enhanced external surface area, are effective and recyclable solid acid catalysts in the batch-wise, aqueous-phase dehydration of xylose, at 170 °C. Up to 71% furfural (Fur) yield is reached at 98% conversion using a biphasic aqueous–organic solvent system (for the simultaneous extraction of Fur); using solely water as the solvent gives up to 54% Fur yield at 97% conversion. Sulfuric acid, used in an approximately equivalent amount to the total acid site concentration of the solid acids, gave 55% Fur yield at 93% conversion. Decreasing the Si/Al ratio of H-MCM-22 zeolite improves the acid properties and consequently the catalytic activity, without affecting significantly the Fur selectivity. While the delamination process considerably enhanced the external surface area of ITQ-2 in comparison to H-MCM-22, it caused modifications in the acid properties, leaving the two prepared materials with the same Si/Al atomic ratio of 24, on a comparable footing in terms of catalytic performance in the studied catalytic reaction. Nevertheless, these solid acid catalysts are fairly stable (similar Fur yields are reached in recycling runs; no structural modifications and no leaching phenomena were detected).

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1. Introduction

Furfural (Fur; C₅H₄O₂) is a platform chemical derived from lignocellulosic biomass and has been commercialised since the beginning of the last century (from cereal waste stockpiles) [1]. The Fur market extends to different sectors of the chemical industry (e.g., oil refining, resins, agrochemicals and pharmaceuticals) and is attracting increasing attention in the biofuels sector [1–4]. The synthesis of Fur involves the primary hydrolysis of pentosans (polysaccharides, which may be found in agricultural/forestry wastes/surpluses) to give the respective pentoses (monosaccharides), followed by the dehydration of the latter to Fur (Scheme 1); theoretically, water is the sole co-product. The hydrolysis/dehydration reactions are promoted by acid catalysts and sulfuric acid is most commonly used in the industrial production of Fur. While being quite effective, H₂SO₄ poses risks to human health, the environment (difficult catalyst recovery/recycling, possible formation of sulfur-containing by-products, neutralisation of effluents) and the process equipment (e.g., corrosion hazards).

There has been growing interest in the search for heterogeneous catalytic routes for the production of Fur. Different types of porous solid acids have been investigated as catalysts in the reaction of xylose in the aqueous phase, such as: (organic) acid resins [5] and modified carbonaceous spheres [6], (hybrid) silicas functionalised with sulfonic acid groups [7–9], (inorganic) bulk/supported heteropolyacids (HPAs) [10,11], micro/mesoporous transition metal oxides (Zr, Zn, Ti [12], ZrW [5], Ti/Nb [13], NbSi [14]), sulfated metal oxides (ZrAl [15,16]), silicoaluminophosphates [17] and aluminosilicates [5,18–21]. Important requirements to be put on solid acid catalysts for this reaction system include water-tolerance (minimal levelling-off of the acid strength in water), hydrothermal stability (crystalline structure integrity and stability towards metal leaching) and good thermal stability if the catalyst regeneration requires thermal decomposition of accumulated carbonaceous deposits (typically in the range 350–550 °C), or chemical stability if carbonaceous deposits are to be removed by harsh chemical treatments (e.g., lower temperature, liquid-phase oxidising conditions).

From the literature data, certain families of porous inorganic solids can be pinpointed as fairly robust materials for this catalytic application, and in particular aluminosilicates (bulk catalysts) are relatively cheap and versatile materials with respect to the type of crystalline and porous structures (micro/meso/macropores; 1,

* Corresponding author. Tel.: +351 234 370603; fax: +351 234 401470.

E-mail addresses: atav@ua.pt, avalente@dq.ua.pt (A.A. Valente).