Mesoporous niobium oxide for dehydration of D-xylose into furfural

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1 Introduction

Carbohydrates are considered as a renewable feedstock for green chemistry because they represent 75% of the annually renewable biomass. Furfural has a large spectrum of industrial applications, being an excellent example of a major chemical platform that can be produced from biomass. Furfural can be obtained from the hydrolysis of hemicellulosic pentose fractions of biomass and successive cyclodehydration of pentose monomers, being the most common D-xylose.

In most industrial processes for the production of furfural, conventional mineral acids are used as catalysts. However, these acids are toxic and corrosive, and their use generates large amounts of toxic wastes. Therefore, their replacement for solid acid catalysts seems very attractive to overcome these drawbacks, besides the advantages resulting from the easy separation and reutilisation of solid catalysts, longer catalyst lifetime or stability in a wide range of temperatures and pressures. In this sense, many different solid acid catalysts have been tested for the dehydration of xylose to furfural: zeolites [1], exfoliated titanate, niobate and titanoniobate nanosheets [2] or bulk and mesostructurated sulphated zirconia [3].

The development of water-tolerant heterogeneous catalysts is crucial for this reaction because water is the preferred solvent for this reaction. Niobium oxide has acid properties and is insoluble in water, but exhibits a low specific surface area. Therefore, the synthesis of mesoporous niobium oxide can be very interesting for this reaction. In the present work, a mesoporous niobium oxide has been prepared, as described Lee *et al.* [4], and tested as solid water-tolerant acid catalyst for the dehydration of xylose into furfural.

2 Experimental

Mesoporous niobium oxide has been synthesized following the method proposed Lee *et al.* [4]. The material was calcined at 450ºC during 5 hours in air. A commercial bulk Nb_2O_5 (Sigma-Aldrich) was also studied to compare.

The synthesized material was characterized by X-ray diffraction (XRD), N_2 adsorption–desorption isotherms at -196ºC, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption of ammonia (NH_3-TPD) and Transmission Electron Microscopy (TEM).

Batch catalytic experiments were performed in a glass pressure tube with thread bushing with magnetic stirring bar. In a typical experiment, 150 mg of D-xylose (SigmaUltra, >99%), 50 mg of catalyst, 1.5 mL of deionized water and 3.5 mL of toluene (Sigma-Aldrich, >99.5%) were poured into the reactor. The reaction mixture was heated with a thermostatically controlled oil bath. The products were quantitatively determined by HPLC equipped with a multiwavelength detector and a refractive index detector in isocratic mode.

3 Results and discussion

The powder XRD pattern of mesoporous niobia at low range exhibited a broad and intense diffraction peak which is characteristic of the hexagonal structure of mesoporous materials, which can be assigned to the (100) diffraction line. The presence of this peak reveals that the mesoporous structure is preserved after calcination at 450 ºC. However, this peak disappeared when the calcination temperature was 550ºC. The textural properties of this catalyst were assessed from the nitrogen adsorption-desorption isotherms at -196 ºC. The isotherm is of type IV according to the IUPAC classification, confirming its mesoporous nature (S_{BET}= 123 m^2/g and average pore size centered in 3.9 nm). The total acidity of this catalyst (198.6 µmoles NH_3/g) was evaluated by NH_3-TPD and the corresponding curve revealed the presence of acid centers with a wide range of strength.

This mesoporous niobium oxide catalyst was tested in the dehydration of xylose to furfural under batch operation in aqueous solution, using toluene as a co-solvent for the extraction of the furfural formed during the reaction. The effect of temperature, time of reaction and xylose-catalyst ratio were studied.

Firstly, it was carried out a study at 150 ºC and a reaction time of 45 minutes to check xylose conversion and furfural yield are higher than bulk niobium oxide and the non-catalyzed reaction (Table 1), attaining a conversion of 76.8% and a furfural yield of 25.9% for mesoporous Nb_2O_5.

Table 1. Conversion and furfural yield over different ca5alysts at 170ºC, 45 min and xylose/catalyst weight ratio = 3.

Catalyt	Conversion (%)	Furfural yield (%)
Temperature effect (non catalytic)	5.5	2.8
Commercial Nb_2O_5	22.3	3.4
Mesoporous Nb_2O_5	76.8	25.9

The catalytic activity of the heterogeneous process using mesoporous Nb_2O_5 as a function of reaction time was evaluated at two different reaction temperatures (150 and 170ºC) (Fig. 1). It can be observed that conversion and furfural yield were increased with the temperature and reaction time, obtaining a conversion of 81.4% and a furfural yield of 41.1% at 150ºC and 90 minutes, which increase until 92% and 49.3%, respectively, at 170ºC.

Fig. 2 displays the evolution of the turnover frequency (TOF), expressed as mmol·xylose converted (furfural produced) $g_{cat}^{-1}\cdot s^{-1}$ as a function of xylose-catalyst ratio. It can be noted that the highest amount of mmoles furfural · $gcat^{-1}$ · s^{-1} is obtained when the xylose:catalyst ratio = 3:1. Furfural selectivity is higher for this ratio and it may be due to a decrease of possible secondary reactions in this conditions.

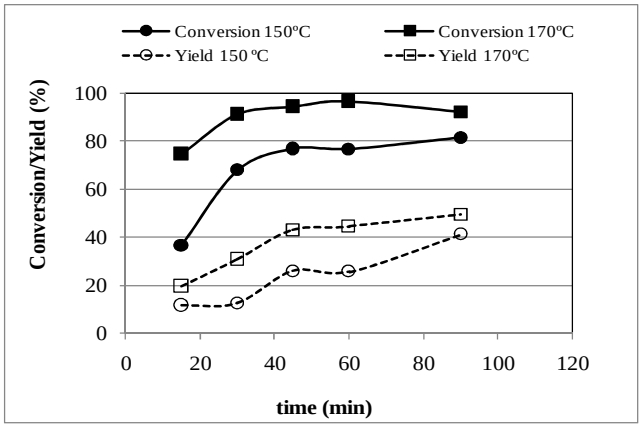

Fig. 1. Conversion of xylose and furfural yield as a function of reaction time (xylose/catalyst weight ratio = 3).

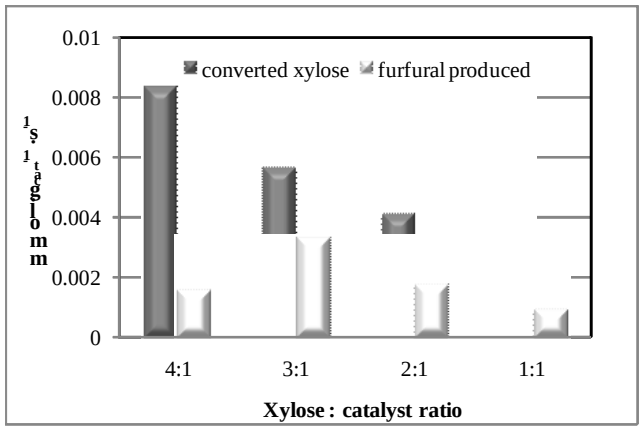

Fig. 2. Evolution of xylose conversion and furfural yield (mmol·$g_{cat}^{-1}\cdot s^{-1}$) as a function of xylose-catalyst ratio at 150ºC and after 45 min.

Leaching of Nb from the solid catalyst to the aqueous phase was measured by ICP-MS, and the amount of Nb in solution was lower than 0.5% of initial niobium.

4 Conclusions

Mesoporous niobium oxide has been found to be effective catalyst for the dehydration of D-xylose to furfural, reaching a conversion of 92% and a furfural yield of 49.3% at 170ºC and 90 minutes. Leaching of Nb from the solid catalyst was measured by ICP-MS and the amount of Nb in solution was lower than 0.5 wt% of the Nb initially present in the solid, thus confirming the stability of the solid acid catalyst.

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References

[1] C. Moreau, R. Durand, D. Peyron, J. Duhamet, P. Rivalier, *Ind. Crop. Prod*. 7 (1998) 95.

[2] A.S. Dias, S. Lima, D. Carriazo, V. Rives, M. Pillinger, A.A. Valente, *J. Catal*. 244 (2006) 230.

[3] A.S. Dias, S. Lima, M. Pillinger, A.A. Valente, *Catal. Lett*. 114 (2007) 151.

[4] B. Lee, D. Lu, J.N. Kondo, K. Domen, *J.Am. Chem. Soc*., 124 (2002) 11256.