ARTICLE IN PRESS

Catalysis Today xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Zr-USY zeolite: Efficient catalyst for the transformation of xylose into bio-products

Clara López-Aguado[a], Marta Paniagua[a], Jose Iglesias[a], Gabriel Morales[a,*], José L. García-Fierro[b], Juan A. Melero[a]

[a] *School of Experimental Sciences and Technology, Universidad Rey Juan Carlos, C/Tulipán s/n, E-28933, Móstoles, Madrid, Spain*
[b] *Institute of Catalysis and Petrochemistry (ICP), CSIC, C/Marie Curie 2, E-28049, Cantoblanco, Madrid, Spain*

ARTICLE INFO

Keywords:
Bifunctional catalyst
Zr-USY zeolite
Zirconium
Cascade reaction
Xylose
Furfural

ABSTRACT

A series of bifunctional USY zeolite catalysts with different Al/Zr ratios were synthesised. The incorporation of Zr into the structure was accomplished after partial dealumination of H-USY. Structural and spectroscopic characterization confirmed the preservation of the zeolite network as well as the isolated incorporation of Zr atoms in Al vacancies, with no evidence of large zirconia domains. The catalytic evaluation in the transformation of xylose in 2-propanol allowed to obtain interesting mixtures of bio-products, and to identify the presence of two competitive routes: the formation of GVL following alternating acid-driven and hydrogen-transfer (MPV) steps, and the retro-aldol condensation of xylose. The extent of each of these two competing reaction cascades is strongly dependent on the Zr loading. Thus, the catalyst with the lowest Al/Zr ratio favours the xylose retro-aldol condensation. When considering furfural as starting substrate, only products involved in the cascade to GVL are obtained. In this case, the incorporation of Zr in the catalyst favoured the MPV reactions, enhancing furfural conversion rate. Thus, increasing concentrations of products coming from the reduction of furfural–furfuryl alcohol, furfuryl 2-propyl ether, lactones-, were detected over Zr-USY samples, with the Zr-USY-3 yielding 13.5% of the final product, GVL. The catalysts are reusable after thermal regeneration at 550 °C.

1. Introduction

Chemical industry, strongly dependent on crude oil as raw material, is driving towards the search for new sustainable and efficient alternatives that can substitute fossil sources. Among the different renewable options, abundant lignocellulosic biomass has the potential to produce fuels and valuable chemicals through the transformation of sugars coming from the hydrolysis of cellulose and hemicellulose, major components of this biomass [1]. Currently, a great variety of catalytic processes involving the transformation of the biomass carbohydrate fraction into value-added products have been proposed. Such processes usually require complex multi-step transformations, suffering from low overall yields, which can seriously compromise the economic efficiency. This limitation can be partly ameliorated by using integrated processes based on the direct one-pot transformation of lignocellulose derivatives into value added chemicals. In such systems, the use of a multifunctional catalyst, able to catalyse several steps in one pot avoiding the isolation of intermediate platform molecules, would be highly desirable [2].

In this field, an interesting route for the valorisation of waste lignocellulosic biomass is the synthesis of different bio-products starting from xylose, an abundant monosaccharide derived from the hemicellulose fraction of plant biomass. An approximation to the sequence of reactions leading to the production of the different interesting molecules is represented in Scheme 1, considering γ-valerolactone (GVL) as the final product. When this transformation is performed in alcohol media, some of the bio-products that can be obtained comprise furfural, furfuryl alcohol, furfuryl ether, levulinic acid/levulinates, angelica lactones and GVL. All of them have commercial value: furfuryl ethers can be used as blending components of gasoline and as flavours [3,4]; levulinic acid is considered as a platform molecule that can be transformed in a wide range of chemicals, polymers, fuel additives, agrochemicals, etc. [5]; levulinates have applications in perfume and flavouring industries, as blending agents for diesel fuel formulation, and as plasticizers or solvents [6]; angelica lactones, like levulinates, have been proposed as flavourings and fuel additives [7]; finally, GVL is a molecule identified as fuel additive, polymer precursor and starting material for the production of other advanced biofuels [8,9].

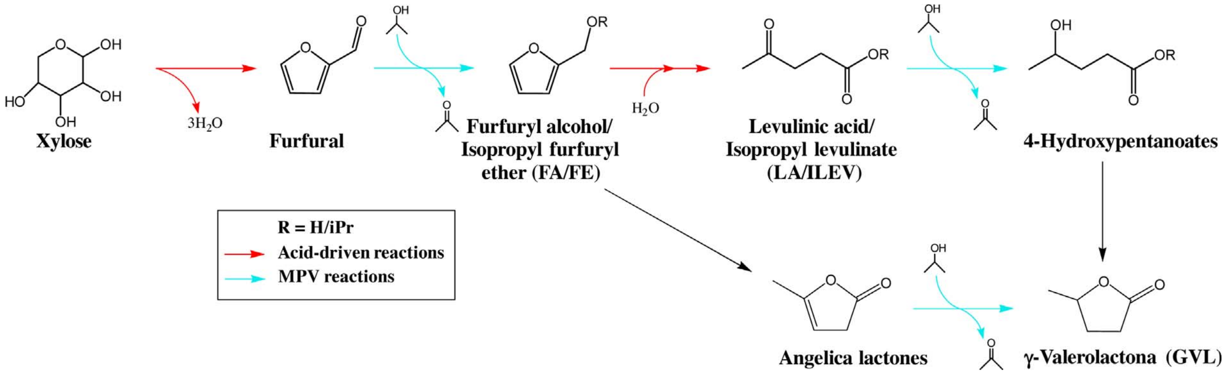
The cascade process starts with the dehydration of the monosaccharide to furfural, promoted by an acid catalyst [10]. Furfural can

---

* Corresponding author.
E-mail address: gabriel.morales@urjc.es (G. Morales).

http://dx.doi.org/10.1016/j.cattod.2017.08.031
Received 28 April 2017; Received in revised form 1 July 2017; Accepted 14 August 2017

Please cite this article as: López-Aguado, C., Catalysis Today (2017), http://dx.doi.org/10.1016/j.cattod.2017.08.031



Scheme 1. Reaction network for xylose conversion in 2-propanol into bio-products through alternative acid catalysed and MPV reactions.

subsequently be reduced by hydrogenation to furfuryl alcohol and etherified to furfuryl ether, which in alcohol media evolves by hydration and isomerization to a mixture of levulinic acid and alkyl levulinate in the presence of an acid catalyst. Finally, the hydrogenation of these compounds followed by lactonization produces GVL [11]. The direct and selective transformation of xylose into the different above-described bio-products through a single-pot reaction would be highly desirable, as the overall investment and operation costs would be reduced. Therefore, the rational design of a multifunctional catalyst which can drive the chain of reactions to the diverse desirable bio-products is of paramount importance in this field. In this case, the proposed reaction pathway requires of a bifunctional catalyst, since acid-driven transformations need to be combined with Meerwein-–Ponndorf–Verley (MPV) reductions, using the adequate sacrificing alcohol in the reaction media, to allow the reduction of carbonyl groups. The use of such catalytic-hydrogen-transfer reaction avoids the use of elevated H_2 pressures and expensive precious-metal catalysts. In this regard, catalysts containing Lewis acid sites have been successfully applied to this kind of MPV carbonyl moieties reduction [12]. On the other hand, xylose dehydration and furfuryl alcohol transformation into alkyl levulinates are mainly promoted by Brønsted acid sites [13].

The process using furfural as starting point of the cascade reaction has been studied in previous works in literature. Román-Leshkov et al. used a mixture of catalysts, Zr-beta and Al-MFI zeolites, for the efficient production of GVL [14]. The combination of Brønsted and Lewis acid sites in one single zeolite catalyst was investigated by the group of Valente, analysing several combinations of metal species and loadings, e.g. Sn-Al and Zr-Al-containing beta zeolites. They reached a mixture of useful bio-products, though without achieving the final product in the cascade, GVL [15,16]. More recently, Song et al. prepared a hierarchical *meso*-Zr-Al-beta zeolite that exhibited remarkable catalytic activity in the production of GVL from furfural [17]. All these works demonstrate the potential of Zr & Al bifunctional zeolites in this kind of multi-step reactions from furfural. Taking a further step, we have recently reported the direct successful transformation of xylose into GVL over bifunctional Zr-Al-Beta zeolite, being to the best of our knowledge the first work using a single catalytic system for the whole process [18]. In such system, the incorporation of the zirconium species is achieved after dealumination of a parent Al-beta zeolite in order to fix the zirconium atoms in the lattice Al vacancies generated. The so-incorporated framework Zr exhibits high activity in the MPV steps of the reaction cascade. The adjustment of the Brønsted/Lewis acid sites ratio by controlling the loadings of both Al and Zr in the beta zeolite turned out to be a key aspect in the promotion of the alternating MPV and acid driven reaction steps. Additionally, both the pore size and the pore structure of the zeolite support could be important factors. Hence, in this research, we propose the incorporation of Zr species, as MPV sites, into the structure of a partially dealuminated zeolite H-USY. It can be expected that the relatively large size of FAU-type framework pores help in the progression of the reaction cascade by facilitating the formation of bulky intermediates.

2. Experimental

2.1. Catalysts preparation

The synthesis procedure of zirconium-modified USY zeolites (Zr-USY) was slightly modified from that reported in literature for zeolite beta [18,19]. Thus, as parent support, a commercial H-USY (8.4 Si/Al atomic ratio) was purchased from Zeolyst international. Partial dealumination was carried out by treatment in nitric acid solution (65% aq. HNO_3, Scharlau): two samples were prepared with a concentration of 0.5 and 2 M at RT (1 h, 20 mL g^{-1}); and a third sample was prepared under harsher conditions (10 M HNO_3, 100 °C, 20 h, 20 mL g^{-1}). After washing with deionized water and centrifugation to recover the solid product, the resulting materials were dried overnight (110 °C). Zirconium incorporation was accomplished by impregnation in water with the appropriate amount of Zirconium (IV) nitrate (Chemical Point), suspending the pre-dealuminated USY zeolite in deionized water. The solvent was removed under vacuum from the resultant slurry, and the solid was dried overnight and calcined in air at 200 °C for 6 h (3 °C min^{-1} heating ramp) and then at 550 °C for another 6 h with the same heating rate. The three so-synthesised Zr-modified USY zeolites were named as Zr-USY-n, wherein n is from 1 (softer dealumination conditions) to 3 (harsher dealumination conditions).

2.2. Catalysts characterization

Zirconium and aluminium contents were determined by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) with a Varian Vista AX apparatus. Textural properties of the tested catalysts were calculated from argon adsorption–desorption isotherms, which were recorded at 87 K using an AutoSorb equipment (Quantachrome Instruments). Average pore size was estimated using the NLDFT method, and total pore volume was taken at $P/P_o = 0.98$. X-ray powder diffraction (XRD) patterns were collected in a Philips X-pert diffractometer using the Cu Kα line in the 2θ angle range from 5° to 65° (step size of 0.04°). Structural characterization was completed by means of transmission electron microscopy (TEM) on a Philips Tecnai-20 electronic microscope operating at 200 kV. Solid state ^{27}Al MAS-NMR and ^{29}Si MAS-NMR spectra were acquired using a Varian Infinity 400 MHz spectrometer. Acid properties of the materials were determined by means of temperature programmed desorption of NH_3 in a Micromeritics 2910 (TPD/TPR) equipment fitted with a TCD detector. Additionally, acidity of the materials was further analysed by means of *n*-propylamine chemisorption and subsequent thermal analysis on a Mettler Toledo TGA/DSC1 Star System under a helium purge gas (60 cm^3 min^{-1}) interfaced to a ThermoStar TM GSD 301 T3 mass spectrometer. X-ray Photoelectron Spectroscopy (XPS) measurements were obtained using a Specs Phoibos 150 9MCD photoelectron