Direct conversion of xylose to furfuryl alcohol on single organic–inorganic hybrid mesoporous silica-supported catalysts

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ABSTRACT

One-step conversion of xylose to furfuryl alcohol was investigated over Pt catalysts supported on ordered mesoporous SBA-15 bearing —SO_3H acid groups. Samples were characterized by SAXRD, FTIR, ^{29}Si CP-NMR, XRF, FE-SEM and TG-MS, and they were all tested in aqueous-phase conversion of xylose in a semi-batch reactor. It was found that the presence of acid sites enhances catalytic activity, confirming that they are also playing a role in xylose conversion. A coupled activity of both metal and acid surface centres was thus suggested. The distribution of products was also found to be significantly modified by grafting organosulfonic groups on catalyst surface; while xylitol was the main product on unmodified Pt/SBA-15 catalyst (selectivity of 45%), a remarkable selectivity of 83–87% to furfuryl alcohol was accomplished over the catalysts supported on organic–inorganic hybrid mesoporous silica. Additionally, no furfural was detected along the aqueous-phase reaction, evidencing that no remote surface acid sites were playing a sole role. It was suggested that direct highly chemoselective conversion of xylose to furfuryl alcohol takes place on vicinal acid–metal surface sites. Finally, the hybrid catalysts were found to be stable regarding their mesostructure framework upon aqueous-phase processing but acid groups resistance to leaching is still the major challenge for one-pot conversion.

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1. Introduction

Lignocellulosic biomass is a valuable renewable feedstock, which is largely available worldwide and comes from a wide variety of sources, mostly agroindustrial and forestry residues such as corn, wheat and rice straws and sugarcane bagasse and straw. These are all by-products of active industrial sectors whose relevance for a country economy depends on its production profile. In Brazil, where ethanol replaces about 40% of gasoline [1] due to the extensive use of flex fuel cars, the agroindustry of sugarcane is a quite significant activity. Nowadays, over 300 sugarcane-processing units are operating in Brazil and they are able to process around 650 million tonnes of sugarcane per year [2], which leads to considerable amounts of lignocellulosic residues (∼30 wt.%).

The ever-growing Brazilian demand for ethanol, which is currently used as a biofuel and a platform molecule for industrial production of green chemicals [3], drives the use of cellulose fraction in that abundant biomass to the biochemical production of second-generation (2G) ethanol. The non-fermentable hemicellulose-derived sugars as well as the lignin fraction from lignocellulosic waste biomass are important sidestreams in 2G ethanol process, which may themselves become a valuable renewable feedstock for green chemicals production. Indeed their conversion into more high added-value compounds in a biofuel integrated production model would provide an additional income, leading to a cost-competitive 2G ethanol.

Hemicellulose is the second-most abundant carbohydrate yielded from fractionation of lignocellulosic biomass, accounting for up to 30% of the total mass. This branched heteropolysaccharide is mainly composed of a mixture of C5 and C6 sugars (pentoses and hexoses), which are easily unlocked by hydrolysis and whose concentration may vary according to the biomass source. However, xylose is the most often primary monossacharide, which makes it a target molecule to be transformed into alternative biofuels, biofuels additives and biobased products [4,5].

So far, xylose is mostly industrially used to produce furfural from dehydration using mineral acids as homogeneous catalysts [4]. Over the last years, many efforts have been done to develop alternative heterogeneous acid catalysts to establish a more environmentally friendly process [6–8] since furfural is certainly the main industrial chemical produced from hemicellulose. It is indeed

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reckoned as a key derivative for the production of a wide range of green chemicals as well as a potential biofuel precursor [9,10]. Polymeric resins, heteropolyacids, 3D and 2D zeolites and either functionalized or simple metal oxides have already been exploited as catalysts in this process [6,11–14].

Amongst the furfural-derived industrial chemicals, furfuryl alcohol stands out as 60% of the whole produced aldehyde is consumed for the alcohol production [15]. Furfuryl alcohol is widely used in the manufacturing of chemical resistant furanic resins [13], especially poly(furfuryl alcohol), and a wide range of other chemical intermediates [4,5]. This alcohol is produced from selective hydrogenation of C=O bond of furfural over metal catalysts. Accomplishing chemical selectivity is quite a challenging though as the reduction of C=C bond in the furan ring or the hydrogenation of all C=O and C=C unsaturated bonds of furfural, which may respectively lead to tetrahydrofurfural or tetrahydrofurfuryl alcohol, must be hindered. Copper chromite is the industrially catalyst applied for the gas-phase furfural hydrogenation [16]. The extensive and severe impact of using chromium on the environment and human health has motivated the search for alternative noble metal catalysts, especially Pd [17] and Pt [17–19].

Nevertheless, it has to be outlined that despite whatever novel catalytic systems used either to xylose dehydration or to furfural hydrogenation, furfuryl alcohol would still mandatorily be produced in a two-step process. Furthermore the distinctive catalysts should bear different surface features and operate at distinct conditions, especially temperature, pressure and reaction medium (liquid or gas phase). Some technical difficulties should be overcome to develop a process for the direct conversion of xylose to furfuryl alcohol since many competitive side reactions may occur.

Recently, we have reported the one-pot synthesis of furfuryl alcohol straight from xylose over a dual catalytic system composed of a solid acid (sulfated zirconia, ZrO_2-SO_4) physically mixed with a hydrogenation metal catalyst (Pt/SiO_2) [20]. By adjusting the reaction conditions – temperature and solvent revealing to be the most pertinent variables – and the density of acid and metal catalysts in the dual system, selectivity towards furfuryl alcohol of around 50% could be accomplished. The unprecedented results reported allowed a proof-of-concept and stated the feasibility of establishing a process relaying on cascade reactions. Each reaction step proceeding on either catalyst surfaces that are set apart in the liquid phase since the dual system is formed by two separate heterogeneous catalysts [20]. A similar approach was reported by other authors [21], but exploiting a flow-reactor system instead of a batch operation. The use of separate double catalyst bed (an acid catalyst followed by a supported metal catalyst) allowed reaching a remarkable selectivity of 87% to furfuryl alcohol [21].

More lately, we investigated the performance of a single multifunctional catalyst in contrast to the acid/metal dual catalytic system both bearing sulfate groups as acid centres and platinum as metal sites [22]. We could see that setting both sites on the same surface indeed brings some advantages to xylose conversion allowing the straight formation of furfuryl alcohol. The balance between acid and metal sites and their positioning on catalyst surface were found to be crucial to determine product distribution. One-step xylose conversion was suggested to occur on vicinal surface sites. Nevertheless sulfate groups were seen to hydrolyse under reaction conditions leading to acid sites leaching and ultimately to catalyst deactivation [22].

In this contribution, the design of a more chemically-stable single catalyst for one-step conversion of xylose to furfuryl alcohol is further pursued. In the present approach the features of each required surface sites were taken into consideration to develop a single multifunctional hybrid catalyst. The disposal of more resistant active acid centres and the metal sites on the same surface was investigated by designing organo-functionalized mesoporous

silica-supported catalysts. Tailoring the arrangement of the surface centres on the catalyst allowed remarkable chemoselectivity to furfuryl alcohol.

2. Experimental

2.1. Synthesis of organic–inorganic hybrid mesoporous catalysts

SBA-15 was firstly synthesized from tetraethylorthosilicate, TEOS (Sigma–Aldrich), as silicon precursor and poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) symmetric triblock copolymer (Pluronic P123), molecular weight = 5800 g/mol – $EO_{20}PO_{70}EO_{20}$ (Sigma–Aldrich) as template, according to a procedure previously described by Yang et al. [23,24]. Firstly, 2 g of Pluronic P123 was dissolved in 15 g of deionized water and subsequently mixed with a 2 mol/L HCl aqueous solution at room temperature. The final homogeneous solution was heated to 40 °C and then 15.4 g of TEOS was added dropwise under vigorous stirring. The solution was kept under stirring at 40 °C for 20 h. After, it was filtered and the retained white powder was extensively washed with deionized water. It was next suspended in 60 g of H_2O_2 (30 wt.%), transferred to Teflon-lined stainless steel autoclave and hydrothermally treated at 110 °C for 24 h. The synthesized solid was finally filtered, copiously washed with deionized water followed by ethanol and calcined at 500 °C for 5 h following a linear heating rate of 1 °C/min.

A sulfonic-functionalized SBA-15 sample was prepared by grafting, following a post-synthetic functionalization procedure. Initially, thiol surface groups were anchored on silica surface by using 3-mercaptopropyltrimethoxysilane, MPTMS (Sigma–Aldrich) as precursor. In a typical procedure [25], pre-synthesized SBA-15 (1 g) was suspended in organic solution containing 20 mL of xylene and 24.7 g of MPTMS and refluxed for 14 h. Afterwards the powder was filtered, washed with hexane and dried at 100 °C. This organofunctionalized support was then oxidized at room temperature by suspending it in a solution with 10 mL of H_2O_2 (30 wt%) and 20 mL of methanol for 20 h. The powder was recovered by centrifugation, washed with ethanol and submitted to a final complementary oxidation step with a 0.1 mol/L H_2SO_4 aqueous solution. A volume of acid solution to mesoporous powder ratio of 100 mL/g was used. This suspension was remained for 20 h at room temperature under static conditions. Lastly, the powder was once again recovered by centrifugation and washed with ethanol. Propylsulfonic-functionalized sample was labelled as SBA-15-SO_3H.

Finally, the metal-supported catalysts were obtained by incipient wetness impregnation using a H_2PtCl_6 (Sigma–Aldrich) aqueous solution at a concentration to lead to catalysts with different metal loadings and acid/metal molar ratios. The supported samples were dried overnight at 100 °C and calcined in a synthetic air (20 vol%O_2/N_2) stream at 50 mL/min for 4 h at 200 °C, following a heating rate of 10 °C/min. After calcination the catalysts were activated by reduction at 200 °C under a pure hydrogen flow (50 mL/min) for 1 h. Samples were labelled as Pt/SBA-15-SO_3H (*x*), where *x* stands for the acid/metal molar ratio.

2.2. Physicochemical characterization

Small-angle X-ray powder diffraction (SAXRD) of all samples was performed using a Bruker D8 Advance with DaVinci design diffractometer equipped with a Lynx-eye position sensitive detector. Analyses were carried out with CuKα radiation in the angular range 0.5°–5° 2θ at a rate of 2°/min.

Porosity was assessed by collecting nitrogen adsorption-desorption isotherms at −196 °C in a Micromeritics ASAP 2020