Chemoselective hydrogenation of furfural to furfuryl alcohol on ZrO$_2$ systems synthesized through the microemulsion method

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ABSTRACT

Different solids consisting in hydrous zirconia were synthesized by the water in oil microemulsion technique (ME series). For comparative purposes, diverse solids were also obtained by the conventional sol-gel method (P-series). The solids were tested for liquid-phase selective hydrogenation of furfural to furfuryl alcohol, using propan-2-ol as the hydrogen donor (Meerwein–Ponndorf–Verley process). The best results corresponded to catalysts calcined at 200 °C which consisted in amorphous solids with surface areas of ca 200 m^2/g. The presence of some surfactant remaining from the synthetic process in solids obtained through the microemulsion technique favored selectivity to furfuryl alcohol with values ≥98%. Results were explained by the steric hindrance of furfural by the surfactant molecules in micelles thus favoring the interaction of the substrate with hydroxyl groups in hydrous zirconia through the C=O group. Application of microwave irradiation accelerated the reaction (15–30 times) as compared to conventional heating.

1. Introduction

Nowadays, biomass valorization is one of the most interesting research topics in the context of sustainable chemistry [1]. Biomass can be used as an energy source [2–4]. There is, however a unique feature of biomass as compared to other renewable energy sources: it can also provide chemicals [5–7]. Furfural and furfural derivatives are among the so-called platform molecules obtained from biomass which can be used for the synthesis of chemicals and fuels [8,9]. Furfural selective hydrogenation can lead to furfuryl alcohol, which has important applications in the production of resins, fibers or as a solvent, just to cite some of them [10,11].

Copper-based solids are the most widely used catalysts for furfural hydrogenation into furfuryl alcohol [10,11], though some other non-noble (Fe, Co, Ni) [12–14] or noble metals (Pt, Pd, Au, Ru) [15–18] have also been described. Hydrogenation is normally conducted using molecular hydrogen. Nevertheless, carbonyl groups can also be reduced to the corresponding alcohol through hydrogen transfer from an alcohol (the so-called Meerwein–Ponndorf–Verley, MPV, reaction) [19–21]. The process, traditionally conducted in the homogeneous phase using aluminium alkoxides as the catalysts, has also been successfully described in the heterogeneous phase using a wide range of solids such as magnesia or zirconia [22–27]. In the present piece of research different zirconium-based systems were obtained through the micro-emulsion technique. For comparative purposes, the solids were also synthesized through conventional sol-gel process. The systems were tested for liquid-phase selective hydrogenation of furfural to furfuryl alcohol using propan-2-ol as the hydrogen donor (MPV process).

2. Experimental

2.1. Materials

Chloroform anhydrous ≥99% (Ref. 288306-2L), 2,2,4-Trimethylpentane anhydrous 99.8% (36006-1L), cetyltrimethylammonium bromide (CTAB) ≥98% (H5882-500G), 1-Butanol (360465-2.5L), ethanol (02860-2.5L), ammonium hydroxide solution (0.1N) (318620-2L), zirconium (IV) oxynitrate hydrate (346462), furfural (185914) and furfuryl alcohol (185930) were purchased from Sigma-Aldrich. Ammonium hydroxide solution (5.0N) (318612-2L) and hydrochloric acid solution (318949-2L) were purchased from Fluka analytical. Milli-Q water was used for preparation of solutions.

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2.2. Synthesis of the solids

2.2.1. Precipitation method (P series)

A 0.4 M zirconium (IV) oxynitrate hydrate solution was dropwise added to a 200 mL solution of NH_4OH (pH 10, prepared from NH_4OH 5 N). pH 10 was kept during the whole process adding NH_4OH 5N or HCl 0.2 M using a Syrris Atlas pump, with constant agitation (500 rpm). Once the addition had finished, typically after 1 h, the solution was aged overnight. Then the white precipitate was filtered and dried overnight at 120 °C. Afterwards, the solid was calcined at the desired temperature (200, 300, 400, 500, 600 or 700 °C) for four hours with a temperature ramp of 5 °C/min under synthetic air flow (50 mL/min). Finally, the solids were ground and sieved (particle size < 0.149 mm). The nomenclature used for the solids was P-Zr-X, where X indicates the calcination temperature.

2.2.2. Microemulsion method (ME series)

For the synthesis of zirconium systems through reverse (water in oil) microemulsion, two microemulsion systems, ME1 and ME2, for NH_4OH and the Zr precursor, respectively, were prepared.

Under optimized conditions, the composition of microemulsions (ME) was surfactant: CTAB (15 wt%), oil: 2,2,4-trimethylpentane (53%), co-surfactant: butan-1-ol (12%), water solution: 20 wt%. In the case of ME1, water solution contained 5 M NH_4OH whereas for ME2 0.4 M $ZrO(NO_3)_2 \cdot xH_2O$ was used.

Similarly as for precipitation method, ME2 was dropwise added to ME1 at a stirring rate of 500 rpm. In order to ensure complete precipitation of zirconium precursor, the used amount of NH_4OH was three times that stoichiometrically required.

Once both microemulsions had been mixed, a white precipitate was observed, which was kept aging overnight under constant agitation. The precipitate was then filtered and divided into two parts. One portion was washed 5 times with 200 mL of a 50/50% chloroform/ethanol mixture, with the intention to remove the residual surfactant. The solid was then dried in an oven at 120 °C overnight.

The other portion was directly dried in an oven at 120 °C overnight without washing.

The rest of the preparation procedure was analogous to that described for the precipitation method: after the drying process, all solids were calcined at the desired temperature (200, 300, 400, 500, 600 or 700 °C) for 4 h (ramp temperature of 5 °C/min under 50 mL/min synthetic flow). Catalyst nomenclature is ME-Zr-X- Y were X denotes the calcination temperature and Y whether the solid was washed (W) or unwashed (UW).

2.3. Characterization

Thermogravimetric analyses (TGA–DTA) were performed on a Setaram SetSys 12 instrument. An amount of 20 mg of sample was placed in an alumina crucible and heated at temperatures from 30 to 1000 °C at a rate of 10 °C/min under a stream of synthetic air at 50 mL/min in order to measure weight loss, heat flow and derivative weight loss.

Surface areas of the solids were determined from nitrogen adsorption–desorption isotherms obtained at liquid nitrogen temperature on a Micromeritics ASAP-2010 instrument, using the Brunnauer–Emmett–Teller (BET) method. All samples were degassed to 0.1 Pa at 120 °C prior to measurement.

Transmission electron microscopy (TEM) images were obtained using a JEOL JEM 1400 microscope. All samples were mounted on 3 mm holey carbon copper grids.

X-ray diffraction (XRD) of all catalysts were performed on a Siemens D-5000 X-Ray diffractometer using a cobalt source, Co Kα, and a graphite monochromator. The voltage and current intensity were 20 kV and 25 mA, respectively. Scans were performed at 0.05° intervals over the 2θ range from 10° to 70°.

Surface acidity in the catalysts were determined by thermal programmed desorption (TPD) of a pre-adsorbed probe molecule, pyridine (Py) monitored by TCD. An amount of 50 mg of sample was placed under a He stream flowing at 75 mL/min in a reactor 10 mm in diameter that was placed inside an oven. He stream was used to clean the solids by heating to 350 °C (200 °C in the case of solids calcined at 200 °C) at a rate of 10 °C/min and then cooling to 50 °C. At that point, the surface of the solid was saturated with the Py for 30 min. Pyridine was supplied by bubbling the He stream through liquid pyridine at room temperature over the samples. After saturation, excess physisorbed Py was removed increasing the temperature up to 50 °C and passing a He stream at 75 mL/min for 60 min. Then temperature was increased up to 400 °C (200 °C in the case of solids calcined at 200 °C) at 10 °C/min, holding the final level for 30 min. Desorbed pyridine was quantified against a calibration graph previously constructed from variable injected volumes of pyridine.

Additionally, Raman analyses of solids pre-saturated with pyridine were performed in order to determine the type of surface acid sites. First the solids were cleaned by heating up until 120 °C during 30 min under nitrogen flow. Then temperature was cooled down to 50 °C and the pyridine was saturated for 1 h. Physisorbed pyridine was removed by heating up to 120 °C for 1 h under nitrogen flow. Finally, the Raman spectra were recorded at 300 mW using a portable Raman spectrometer EZRaman-N series 785-B, (Manufactured by TSI, Irvine CA, USA) with an excitation laser of 785 nm.

2.4. Catalytic tests

The solids were tested for selective hydrogenation of furfural to furfuryl alcohol using propan-2-ol as the hydrogen donor. Catalytic test were conducted in two reaction systems:

2.4.1. Multi-reactor (conventional thermal heating)

A Carrusel Reaction Station TM multi-reactor (Radley Discovery Technologies) with twelve 50 mL vials was used. The reaction mixture consisted in 1 mL furfural, 9 mL isopropanol and 50 mg catalyst. Temperature and stirring rate were adjusted at 100 °C and 1000 rpm, respectively. The top part of the vials was always refrigerated at 5 °C thus preventing lost in the reaction volume as a result of evaporation.

2.4.2. Microwave oven

Microwave assisted reactions were carried out in a computer-controlled CEM Discover microwave reactor. Reactions were performed in a closed 10 mL vial at 100 °C, with a maximum pressure of 200 psi. The reaction mixture consisted in 0.5 mL furfural, 2.0 mL isopropanol and 25 mg catalyst (i.e. same substrate/catalyst ratio as for conventional heating).

After the reactions, the solids were filtered using a PTFE syringe filter 0.45 μm and the liquid phase was analyzed by gas chromatography, GC-FID (Agilent Technologies 7890, with a Supelcowax-10 capillary column) with confirmation by GC–MS (CP-3800 Gas Chromatograph connected to a Varian 1200 QuadrupoleMS). Quantification of furfural and furfuryl alcohol was performed using the corresponding calibration curves.

3. Results and discussion

TGA-DTA profiles of P-Zr, ME-Zr-W and ME-Zr-UW gels are represented in Fig. 1. From that figure it is evident that weight loss is significantly higher in the case of ME series, especially for the unwashed system, due to the presence of surfactant (weight losses percentages of 17.0, 36.9 and 72.5%, for P-Zr, ME-Zr-W and ME-Zr-UW, respectively). As for the heat flow profiles, in the case of P-Zr (Fig. 1A), there are two main peaks. The first endothermic peak centered at ca. 106 °C corresponds to the loss of water whereas the sharp exothermal peak at ca. 453 °C (the so-called glow exotherm) is attributed to the