Catalytic upgrading of furfuryl alcohol to bio-products: Catalysts screening and kinetic analysis

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ABSTRACT

The conversion of furfuryl alcohol, a highly versatile biomass-derived platform molecule, into a large variety of bio-products, including ethers, lactones and levulinates, has been evaluated in alcohol media using different solid acid catalysts, such as commercial zeolites, sulfonic acid-functionalized materials, and sulfated zirconia. Reaction pathways and mechanisms have been correlated to the particular type of catalyst used, aiming to establish the influence of the main physico-chemical properties of the materials on the extent of furfuryl alcohol conversion, as well as on the predominant reaction pathway followed. Mechanistic and kinetics modelling studies for each type of catalyst have been developed and compared, providing an useful tool for the selection of the most suitable solid acid catalyst for the production of each of the reaction intermediates in the cascade from furfuryl alcohol to alkyl levulinate.

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1. Introduction

As a response to the depletion of petroleum resources, increasing demand for oil and environmental concerns over greenhouse gas emissions, the conversion of lignocellulosic biomass into fuels and chemicals is receiving much attention. Lignocellulose is the most important source of biomass, being a sustainable alternative obtainable from forest/agricultural residues, municipal wastes, and as a by-product of some industries. It mainly comprises cellulose, hemicellulose and lignin. Selective depolymerization of hemicellulose and cellulose provides sugars, which can be subsequently transformed into platform chemicals such as levulinic acid, 5-hydroxymethyl furfural (5-HMF) and furfural [1,2]. Among the biomass derived chemicals, furfuryl alcohol, coming from furfural hydrogenation, is an attractive intermediate compound for the production of levulinic acid, alkyl levulinate esters, alkyl furfuryl ethers and angelica lactones [3–5], which find numerous applications, either as themselves or as starting points for other synthetic routes. Likewise, furfural route (via xylose) is an interesting alternative to the use of glucose in terms of atom economy for the production of these bio-products.

Furfuryl ethers are used as blending components of gasoline and as flavours [6,7]. Alkyl levulinates have strong potential to be used in various applications, substituting current chemicals pro-duced through petro-chemical routes such as in the perfume and flavour industries, as blending agents for diesel fuel formulation, as plasticizers or solvents [8]. On the other hand, angelica lactones have been proposed for the preparation of fuel additives, useful flavours and cigarette additives [9]. Noticeably, levulinic acid has been identified by the U.S. Department of Energy as one of the top 12 most important biomass-derived platform chemicals. It is a versatile platform molecule that can be further reacted to produce a wide range of chemicals, polymers, fuel additives, agrochemicals, etc. [10].

In aqueous media, the hydration of furfuryl alcohol mediated by an acid results in the production of levulinic acid [10]. However, the substrate furfuryl alcohol is highly reactive under these conditions, leading to undesired oligomers formation by condensation [11]. Using an alcohol as solvent instead of water allows for minimizing the formation of oligomers, driving the reaction towards the formation of alkyl levulinate esters. However, side reactions such as alcohol consumption by auto-etherification – driven by the strong acid catalysts employed for this transformation – can be a serious drawback for this route. By the proper selection of catalyst and reaction conditions, this problem can be overcome.

Many acid catalysts have been used for the conversion of furfuryl alcohol into bio-products. The use of heterogeneous acid catalysts has attracted much more attention than homogeneous mineral acids, because of the well-known drawbacks that the latter group presents. For instance, solid catalysts with sulfonic acid groups have been used for the transformation of furfuryl alcohol, such us sulfonic acid-functionalized carbon and carbon-silica composites

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[12], mesoporous silica [13], ion-exchange resins [14–16], and heteropoly acid supported catalysts [17,18]. Although high yields of levulinate are obtained, this kind of catalysts is not stable through typical regeneration by coke burn-off. Mesostructured zirconium-based mixed oxides containing tungsten and/or aluminium are also versatile solid acid catalysts for chemical valorisation of biomass, leading to high yields of bio-products [19]. Zeolite materials have also been tested in this reaction, displaying good results in terms of alkyl levulinate esters production when ethanol is used as solvent [14,16], though alkyl furfuryl ether, an intermediate compound, reveals as the main product with larger alcohols [3,4].

Therefore, many acid catalysts have previously demonstrated a suitable activity in the transformation of furfuryl alcohol into bio-products. Herein, a systematic analysis of the conversion of biomass-derived furfuryl alcohol into bio-products over a wide variety of heterogeneous acid catalysts and alcoholic media is presented. Evaluated acid catalysts include several zeolites with different framework topology and loading and strength of acid sites, sulfonic acid-functionalized materials (mesostructured silicas and resins) and sulfated zirconia. The main purpose of the current study is to settle the relationship between the physico-chemical properties of each catalyst, i.e. acid sites loading, strength and accessibility, and its catalytic performance. Moreover, a throughout mechanistic and kinetic modelling has been developed and discussed in order to determine the most favoured reactions for each catalyst.

2. Experimental

2.1. Materials

Furfuryl alcohol (FOL, 98%), angelica lactone (LACT, 98%) and levulinic acid (LA, 98%) were purchased from Sigma–Aldrich. Methanol (99%), ethanol (99.9%) and 2-propanol (98%) were obtained from Scharlab. Decane (99%) was acquired from Across Organics and ethyl furfuryl ether (EFE, 97%) was supplied by Manchester Organics. All the chemicals were used as received without previous purification. Isopropyl levulinate (i-LEV) was synthesized by esterification of levulinic acid in 2-propanol with sulfuric acid as catalyst. Purification of the levulinate was accomplished following a previously described procedure [20]. After removal of 2-propanol by distillation under reduced pressure, the product mixture was dissolved in MTBE and extracted 3X with saturated $KHCO_3$ solution and 3X with distilled water. The solution was dried with anhydrous Na_2SO_4 and then filtered to eliminate Na_2SO_4. Finally, solvent was removed by distillation under reduced pressure. Purification grade was assessed by ^1H NMR and ^{13}C NMR spectra. ^1H NMR spectrum (400 MHz, $CDCl_3$): δ 4.97 (sep, J = 6.3 Hz, 1H), 2.72 (t, J = 6.7 Hz, 2H), 2.52 (dt, J = 0.4, 6.7 Hz, 2H), 2.17 (s, 3H), 1.2 (d, J = 6.3 Hz, 6H) ppm; ^{13}C NMR spectrum (100 MHz, $CDCl_3$): δ 206.98 ($CH_3C(O)–$), 172.45 ($–C(O)OiPr$), 68.18 ($–C(CH_2)CH_2$), 38.19 ($CH_3C(O)C–$), 30.07 ($CH_3C(O)CH_2C–$), 28.58 ($CH_3C(O)–$), 21.96 ($–C(CH_2)CH_2$) ppm.

Propylsulfonic functionalized SBA-15 (Pr-SO_3H-SBA-15) was prepared as described elsewhere [21]. Molar composition of the synthesis mixture for 4 g of templating block-copolymer (Pluronic 123, BASF) was: 0.0369 tetraethylorthosilicate (TEOS, Aldrich); 0.0041 mercapto-propyltrimethoxysilane (MPTMS, Aldrich); 0.0369 H_2O_2; 0.24 HCl; 6.67 H_2O. Likewise, arenesulfonic functionalized SBA-15 (Ar-SO_3H-SBA-15) was synthesized following a previously reported procedure [22]. In this case, the molar composition of the synthesis mixture for 4 g of pluronic 123 was as follows: 0.0369 TEOS:0.0041 chlorosulfonylphenylethyltrimethoxy-silane (CSPTMS, Gelest):0.24 HCl:6.67 H_2O. In both materials, the amounts of sulfur precursors (MPTMS and CSPTMS) have been selected to provide 10% of total silicon moles. Ion-exchange sulfonic resin Amberlyst 70 (Amb-70) was provided by Rohm & Haas

and before use, it was washed with methanol to remove absorbed water. Acid zeolites with different structures were supplied by Zeolyst International (H-Beta and H-USY) and by Süd-Chemie (H-ZSM-5). Sulfated zirconia (ZrO_2-SO_4^{2-}) was kindly provided by Mel Chemicals. Before their use in catalytic experiments, all the inorganic solids were thermally treated in air at 550 °C for 5 h under static conditions in order to remove water adsorbed over acid sites.

2.2. Catalysts characterization

Textural properties of the tested acid catalysts were calculated from nitrogen adsorption–desorption isotherms, which were recorded at 77 K using a Micromeritics TRISTAR 3000 system. Pores sizes distributions were calculated using the BJH method applying the KJS correction, and total pore volume was taken at P/P_0 = 0.975. Acid capacity of sulfonic materials (Pr-SO_3H-SBA-15, Ar-SO_3H-SBA-15, and Amb-70) was measured by the determination of cationic-exchange capacity using 2 M NaCl as the cationic-exchange agent. In a typical experiment, 0.05 g of solid was added to 15 g of aqueous solution containing the sodium salt. The resulting suspension was titrated potentiometrically by the drop-wise addition of 0.01 M NaOH(aq). The acid capacity of inorganic materials was determined by means of temperature programmed desorption of NH_3 in a Micromeritics 2910 (TPD/TPR) equipment fitted with a TCD detector. Samples were outgassed at 550 °C under flowing He for 2 h prior to NH_3 pulse at 180 °C (30 min). Thermal programmed desorption under a He flow consisted in increasing the temperature from 150 °C to 550 °C at 15 °C min^{-1}. Elemental analysis of zeolites was performed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) with a Varian Vista AX spectrometer to confirm the Si/Al ratios provided by the commercial supplier.

2.3. Catalytic tests

Catalytic experiments were performed in liquid phase in a stainless-steel stirred autoclave (500 mL) fitted with temperature control and a pressure gauge. Typically, 7.6 g of furfuryl alcohol were mixed with 3 g of catalyst and 300 mL of the corresponding alcohol used as reaction media (methanol, ethanol or 2-propanol). Catalytic tests were also carried out using α-angelica lactone, levulinic acid and iso-propyl levulinate as substrates. Decane was added as internal standard for analytical purposes in a concentration of 10 g L^{-1}. After closing the reactor, stirring was fixed in 1000 rpm and a heating rate of 2.5 °C min^{-1} was established. Samples were taken periodically and the solution filtered into a vial. Selected catalysts were tested in the temperature range of 130–170 °C.

2.4. Product analysis

Reaction samples were analyzed by gas chromatography, using a Varian 3900 gas chromatograph fitted with a ZB-WAX Plus column (30 m × 0.25 mm, DF = 0.25 μm) and a FID detector. Compounds detected by GC included unreacted furfuryl alcohol and alkyl furfuryl ethers, alkyl levulinates, levulinic acid, α/β-angelica lactones and di-alkyl ethers as main reaction products. The identification of the bio-products was checked by GC–MS using a Bruker 320-MS GC Quadrupole Mass Spectrometer equipped with a capillary column (BR-SWax, 30 m × 0.25 mm × 0.25 μm), and He as the carrier gas. Product quantification was based on a previous calibration of the analysis unit with standard stock solutions of pure commercially-available chemicals using decane as internal standard. Degradation products named as humins was calculated as the amount of furfuryl alcohol no transformed into detected products. Catalytic results are