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Mesoporous zirconia-based mixed oxides as versatile acid catalysts for producing bio-additives from furfuryl alcohol and glycerol

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ABSTRACT

Mesostructured zirconium-based mixed oxides (MZM) are versatile solid acid catalysts for the chemical valorisation of biomass, within sugar and fatty acid platforms of biorefineries. MZM catalysts containing tungsten and/or aluminium were prepared via a templating route that allows the texture and acid properties to be improved. Their catalytic potential was explored for synthesising different types of interesting oxygenated fuel bio-additives, specifically levulinate esters, furfuryl alkyl ethers and glycerol acetals of the type 1,3-dioxolane and 1,3-dioxane. Levulinate esters are synthesised from furfuryl alcohol (FA), which is produced industrially from lignocelluloses; the acetals are obtained from glycerol, which is a coproduct of the industrial production of biodiesel. The performances of the MZM catalysts have been compared with those of zirconium–(tungsten and/or aluminium) mixed oxides synthesised via conventional co-precipitation (without a template). Structure–activity relationships were established which reveal advantages of the templating route used for the synthesis of the MZM catalysts. The MZM catalysts were more active and led to higher total yields of bio-additives (e.g. up to 86% yield at 100% FA conversion, 140 °C, 30 min reaction) than the catalysts prepared by co-precipitation (e.g. up to 45% yield at 88% FA conversion), under similar reaction conditions. Detailed catalytic and characterisation studies were carried out for the used catalysts.

1. Introduction

The use of renewable sources for energy, materials and chemicals is an important approach towards sustainable development. Of the existing renewable sources, biomass is the most appropriate for producing organic products and liquid biofuels [1–6]. This approach demands the development of economically feasible and environmentally friendly biomass conversion processes, where heterogeneous catalysis plays an important role [7–11].

The chemical valorisation of biomass via acid-catalysed reactions allows the synthesis of interesting bio-products with comparable applications to many petrochemicals [12–15]. In particular, levulinate esters (LEs) such as ethyl levulinate (EL) and butyl levulinate (BL) possess interesting properties as oxygenated fuel additives, improving the fuels' quality while being eco-friendly by reducing emissions [16–19]. 2-(Ethoxymethyl)-furan (EMF) is an interesting bio-based blending component of gasoline [20–22]. These bio-products can be formed via the acid-catalysed reaction of furfuryl alcohol (FA, which is produced industrially from hemicelluloses [23–27]) with aliphatic alcohols (Scheme 1) [28–33]. Glycerol acetals are another type of interesting candidates for oxygenated fuel additives, and can be produced by reacting glycerol (Gly, which is a side product of the industrial production of biodiesel from triglycerides) with butanal, for example, to give the corresponding cyclic acetals (denoted GBAs), Scheme 1 [5,20,34]. It has been demonstrated that the use of mixtures of glycerol acetals as bio-additives allows significant reduction in pour point temperature of fuels [35]. Glycerol acetals may find other applications in different sectors of the chemical industry, such as flavours, surfactants, disinfectants and anti-freezing agents [35–39]. Different types of inorganic solid acid catalysts possessing Brönsted and Lewis acidity

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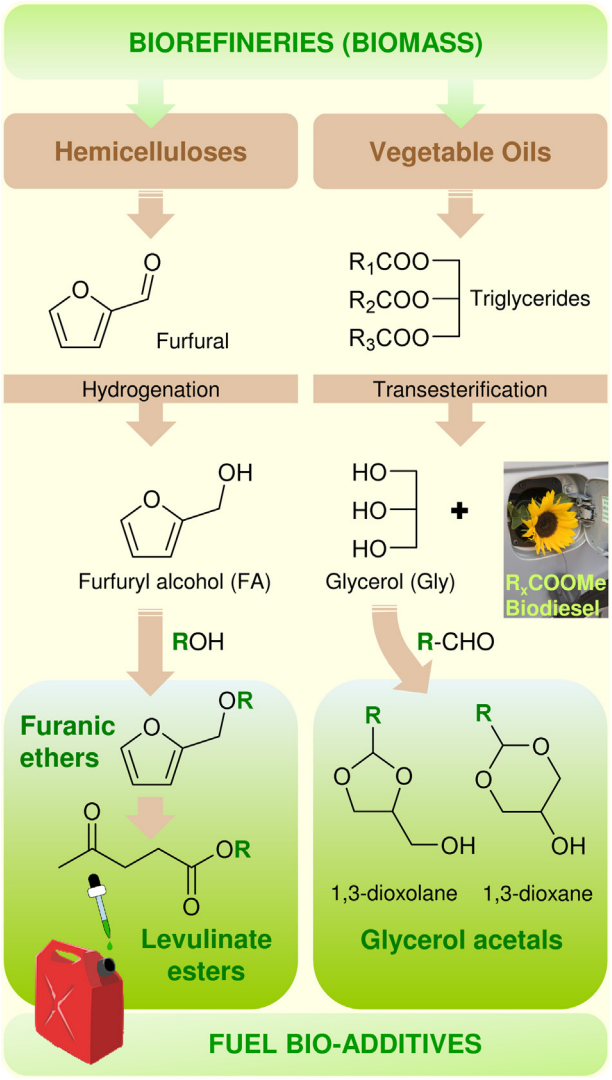

Scheme 1. Catalytic routes for converting biomass to fuel additives involving the acid-catalysed conversion of furfuryl alcohol (FA, derived from lignocelluloses) with an aliphatic alcohol (ROH) to furfuryl alkyl ethers (e.g. EMF) and levulinate esters (LEs), and of glycerol (Gly, a coproduct of biodiesel production) with an aldehyde (R-CHO, R = alkyl) to the corresponding glycerol acetals (1,3-dioxolane and 1,3-dioxane).

have been successfully tested for producing EL and/or BL, e.g. mesoporous aluminosilicates of the type TUD-1, composites of zeolite beta embedded in TUD-1 silica, and microporous aluminosilicate zeolites [28–30], and for producing GBAs, e.g. MoO_3 supported on silica [40] and zeolites [41].

Zirconia-based mixed oxides are interesting, versatile solid acids in that they can be prepared using relatively simple procedures which can be modified to give different acid and textural properties. These types of materials are commercially available (e.g. zirconium–tungsten mixed oxides), and have potential for growing market. Zirconium–(tungsten, aluminium) mixed oxides can be fairly stable catalysts [42]. These types of materials have been successfully applied in different acid-catalysed reactions for the chemical valorisation of biomass, such as the recently reported selective production of aromatics from alkylfurans [43] and the dehydration of glycerol to acrolein [44]. Aluminium–zirconium mixed oxides have been successfully tested in the reaction of glucose in hot compressed water, at 180 °C, and the acid–base properties could be tuned to produce target bio-products by changing the composition and structure of the materials [45]. The use of an appropriate template for preparing mesoporous zirconia-based mixed oxide catalysts can lead to improved texture and acid properties, as well as active site accessibility [42,46]. Superior performances of templated mesostructured zirconia-based mixed oxides (MZM), in comparison to the mixed oxides prepared by conventional co-precipitation routes, have been previously reported for the aqueous phase reaction of xylose to furfural, at 170 °C [46]. An advantage of these types of fully inorganic catalysts is the relatively enhanced chemical and thermal stability (e.g. compared to catalysts with organic components).

In the present work, mesostructured zirconium–aluminium and zirconium–tungsten–aluminium mixed oxides (ZrAl-mp and ZrAlW-mp) were synthesised by impregnating aluminium or tungsten precursors on a templated zirconium hydroxide material, and these materials were explored as solid acid catalysts in the reactions of FA with aliphatic alcohols to give LEs, and Gly with butanal to give the corresponding acetals (GBAs). The catalyst versatility of the prepared MZM materials is reflected by the fairly good catalytic results obtained for the two reaction systems which are interesting for producing (bio)fuel additives within different biorefinery platforms, namely the sugar and fatty acid platforms. The performances of the MZM catalysts were compared with those of zirconium–tungsten, zirconium–aluminium and zirconium–aluminium–tungsten mixed oxides synthesised via conventional co-precipitation (without a template). Structure–activity relationships have been tentatively established. Catalyst stability was studied by performing catalytic tests and characterising the used/recovered solids.

2. Experimental

2.1. Synthesis of the catalysts

The mesostructured catalysts ZrAlW-mp and ZrAl-mp were prepared by impregnation of a templated zirconium hydroxide material (Zr(template)) with tungsten and/or aluminium sources. The Zr(template) was synthesised following the procedure described by Ciesla et al. [47]. Hexadecyltrimethylammonium bromide (5 g; Fluka, ≥96%) was dissolved in a mixture of water (230 g) and 37 wt.% HCl (45.1 g; Aldrich), and a 70 wt.% solution of zirconium(IV) propoxide in 1-propanol (11.84 g; Aldrich) was slowly added with stirring. After stirring for 30 min, ammonium sulphate (3.4 g; Panreac, 99.5%) dissolved in water (46 g) was added. The resulting mixture was stirred for 1 h, transferred to a polypropylene bottle and heated at 100 °C for 72 h. The solid was recovered by filtration, washed with deionised water (200 mL), ethanol (200 mL), deionised water (200 mL) and finally dried at 100 °C overnight.

The impregnation of tungsten and aluminium on the Zr(template) to give ZrAlW-mp was carried out following the procedure described by Hwang et al. [42]: ammonium metatungstate hydrate (0.21 g; Aldrich, 99%) and aluminium nitrate nonahydrate (0.21 g; Riedel-de-Haën, ≥98.5%) were dissolved in an ethanol/water mixture (1:1, v/v; 10 mL). This solution was added dropwise with stirring to preheated (100 °C) Zr(template) (3.22 g), which was alternated with drying of the solid at 120 °C for 1 h until all of the solution had been added. Finally, the solid was dried at 100 °C for 24 h and calcined at 630 °C for 5 h. The ZrAl-mp was prepared in a similar fashion to ZrAlW-mp, by impregnating Zr(template) solely with aluminium; a solution of aluminium nitrate nonahydrate (0.15 g in ethanol/water (1:1, v/v; 10 mL)) was added to Zr(template) (2 g). For comparison, a zirconia material ZrO_2 (without W or Al) was prepared by calcining the Zr(template).

Zirconium–tungsten (ZrW), zirconium–aluminium (ZrAl) and zirconium–aluminium–tungsten (ZrAlW) mixed oxides were synthesised using a conventional method of co-precipitation (without