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Efficient production of 5-ethoxymethylfurfural from fructose by sulfonic mesostructured silica using DMSO as co-solvent

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ABSTRACT

The use of sulfonic acid-functionalized heterogeneous catalysts in conjunction with the use of dimethyl sulfoxide (DMSO) as co-solvent in the catalytic transformation of fructose in ethanol to produce 5-ethoxymethyl furfural (EMF) is shown as an interesting alternative route for the production of this advanced biofuel. Arenesulfonic acid-modified SBA-15 mesostructured silica (Ar-SO_3H-SBA-15) has been the most active catalyst, ascribing its higher catalytic performance to the combination of excellent textural properties, acid sites surface concentration and acid strength. Noticeably, DMSO promotes the formation of EMF and HMF, reducing the extent of side reactions. Reaction conditions (temperature, catalyst loading and DMSO concentration) where optimized for Ar-SO_3H-SBA-15 via response surface methodology leading to a maximum EMF yield of 63.4% at 116 °C, 13.5 mol% catalyst loading based on starting fructose and 8.3 vol.% of DMSO in ethanol after 4 h of reaction. Catalyst was reused up to 4 consecutive times, without regeneration treatment, showing a slight gradual decay in activity attributed to the formation of organic deposits on the catalyst's surface.

1. Introduction

Diminishing fossil fuel reserves along with the need for greening of land transport, aiming to reduce air pollution, are key concerns for the present century. Such environmental objectives are driving society towards the search for new renewable energy sources for transport that may advantageously substitute fossil sources. Lignocellulosic biomass is abundant, and it has the potential to significantly displace petroleum in the production of not only fuels but also valuable chemicals, especially through the transformation of sugars coming from the hydrolysis of cellulose and hemicellulose [1]. Limitations of conventional biofuels (first generation biodiesel and bioethanol) and new trends in legislation have stimulated the search for new technologies providing energy-dense (i.e., lower oxygen content) biomass-derived fuels. Such advanced biofuels could be easily implemented in the existing hydrocarbon-based transportation infrastructure (e.g. engines, fuelling stations, distribution networks and petrochemical processes) and, importantly, not depending on edible biomass for their production.

Among the wide range of possibilities, an interesting approach is the transformation of lignocellulosic platform molecules into oxygenated compounds, which can be used as blend components for the reformulation of conventional fuels (gasoline and diesel), in some cases even improving certain fuel properties [2]. In this context, 5-ethoxymethylfurfural (EMF), the main representative of the 5-alkoxymethylfurfural ethers family, is considered as an excellent component for diesel-range fuels. It has relatively high energy density, similar to regular gasoline and nearly as good as diesel fuel, and significantly higher than the bioethanol, currently the most extended biofuel [3]. EMF has been evaluated admixed with commercial diesel in engine tests, leading to promising results in terms of engine performance, accompanied by a significant reduction of soot (fine particulates), and SO_x emissions [4]. Consequently, there is currently a remarkable interest in the synthesis of EMF from renewable resources such as cellulosic materials. Most of the studies in literature have been focused on the synthesis of EMF from 5-hydroxymethylfurfural (HMF). HMF is the dehydration product of biomass hexoses (mainly glucose and fructose) and can be easily etherified with ethanol by means of acid catalysis, advantageously using solid acid catalysts [5]. While relative high EMF yields can be obtained using this approach, the direct use of HMF as a precursor for the preparation of EMF is not still industrially interesting. The reason is that HMF is a very reactive molecule, difficult to isolate in good yields. Another proposed strategy is via 5-chloromethylfurfural by substitution with an alcohol. This proposal seeks to replace the OH group within the HMF molecule by

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a chlorine atom, leading to 5-(chloromethyl)furfural (CMF) [6,7]. Thereafter, the nucleophilic substitution of the Cl with ethanol easily leads to the formation of EMF, giving HCl as by-product. Although high EMF yields are achievable, the presence of HCl may generate serious problems in the industrial processing. Likewise, SBA-15-supported sulphated zirconia, a bifunctional catalyst showing both Lewis and Brønsted acid sites, has also been successfully applied to HMF etherification with ethanol, demonstrating the existence of a quantitative relationship between the concentrations of each type of acid sites within the catalyst [8].

A more appealing methodology is the one-pot combination of the dehydration of cheap and renewable source such as fructose into HMF, together with the etherification into EMF using ethanol as solvent and a heterogeneous acid catalyst. Both transformations are driven by acid catalysis, being feasible to optimize the selectivity towards EMF through the proper selection of the acid catalyst and the reaction conditions. For instance, a conventional mineral acid such as sulfuric acid has been used as catalyst in this one-pot system [9]. In this work, a mechanistic study of the reaction pathway indicated that the dehydration of EMF into EL is the slowest transformation, not being the sole pathway responsible for EL formation. On the other hand, the implementation of solid acid catalysts would have several advantages over mineral acids, especially in terms of selectivity and management of the transformation. Therefore, the use of selective solid catalysts is of great interest in this transformation. In a pioneering work, Brown and co-workers evaluated the preparation of ethers of HMF, together with HMF itself and alkyl levulinates, from fructose using ion-exchange resins in non-aqueous solvents [10]. However, both the selectivity to EMF and the reaction rates were low. In a similar way, more recently, a catalyst based on silica-sulfuric acid provided 70% EMF yield at 110 °C, but still requiring excessively long reaction times [11]. In another example, Liu et al. proposed the use of a heteropolyacid-based organic-inorganic hybrid catalyst, $[\text{MIMBS}]_3\text{PW}_{12}\text{O}_{40}$, leading to high EMF yields at moderate temperatures [12]. Kraus et al. used recyclable sulfonic acid-functionalized ionic liquids (ILs), providing a biphasic system that was shown as a key factor to significantly enhance both yield and selectivity, avoiding interferences from humins-type by-products [13]. As an indication of the current relevance of the investigation on EMF production from fructose, during the last year several other heterogeneous catalytic systems have been reported: magnetic sulfonic nanoparticles (Fe_3O_4@C-SO_3H) [14]; acid-base bifunctional hybrid nanospheres prepared from the self-assembly of basic amino acids and phosphotungstic acid (HPA) [15]; H-USY, dealuminated H-beta zeolite, Amberlyst-15, SO_3H-SBA-15 [16].

On the other hand, during the production of EMF from fructose in ethanol using solid acid catalysts it is particularly important to prevent formed HMF from rehydrating to yield levulinic acid, reaction favoured in the presence of strong acid catalysts even in the presence of very small amounts of water. Such consumption of HMF limits the formation of EMF, while increases the production of ethyl levulinate (EL) from the esterification of levulinic acid in ethanol medium (Scheme 1). Thus, though EL might also be considered a target fuel additive [17], if the desired product is EMF, the rehydration must be prevented. In this sense, many authors have previously reported on the use of an aprotic organic solvent such as dimethylsulfoxide (DMSO) in the dehydration of hexoses to 5-hydroxymethylfurfural [18–22]. DMSO can stabilize the formed HMF, significantly reducing undesired side-reactions leading to the formation of humins, as well as levulinic acid. Furthermore, DMSO can play an active role in the reaction, since at high temperature it has the effect of modifying the tautomeric forms of fructose, increasing the presence of furanose versus pyranose forms, making easier the dehydration into HMF, precursor to EMF [23]. A recent work by Wang et al. demonstrated the benefits of using DMSO in the production of EMF from fructose in ethanol using a commercial homogeneous heteropolyacid HPW catalyst [24]. On the other hand, several authors have brought the attention on the main drawback of using DMSO in HMF production, which is the difficulty of the separation of both chemicals by conventional processes such as distillation, due to the high boiling point of HMF and its sensitivity to high temperatures. However, a recent work on the room temperature separation of HMF from DMSO by selective adsorption on porous activated carbons, have provided a cost-effective recovery process [25], avoiding the disadvantages of high temperature separation.

In this context, sulfonic acid-functionalized mesostructured materials have demonstrated an excellent behaviour in the catalytic transformation of biomass-derived compounds into added-value products, such as biodiesel from non-conventional feedstocks [26], glycerol derivatives from crude glycerin [27,28], HMF from glucose [22], levulinates from levulinic acid [29], etc. These materials, featured by high surface area, large uniform pores, high thermal stability, and the capability to control the surface hydrophilic/hydrophobic balance as well as the strength and concentration of acid sites, appear as promising catalysts for this sort of acid-catalyzed reactions. More broadly, solid acids with SO_3H acid sites and tunable surface properties appear to have a large potential in the valorization of biomass [30].

In this contribution, we have studied the catalytic performance of several sulfonic-containing heterogeneous acid catalysts in the conversion of fructose to EMF, investigating the effect of using DMSO as co-solvent, followed by a multivariate analysis to assess the optimal reaction conditions – catalyst loading, temperature and DMSO content – to maximize the production of EMF over these catalysts.

2. Experimental

2.1. Materials

Fructose (99% purity), 5-(hydroxymethyl) furfural (HMF, 99% purity), 5-ethoxymethylfurfural (EMF, 97% purity) and ethyl levulinate (EL, 99% purity) were purchased from Sigma-Aldrich. Ethanol (99.9% purity) and dimethyl sulfoxide (DMSO, 99.8% purity) were obtained from Scharlab. Decane (99% purity) was acquired from Across Organics. All the chemicals were used as received without previous purification.

2.2. Catalysts

Several sulfonic acid-containing heterogeneous catalysts have been evaluated in the dehydration of fructose. Propylsulfonic acid and arenesulfonic acid functionalized mesostructured silicas (Pr-SO_3H-SBA-15 and Ar-SO_3H-SBA-15, respectively) were synthesized following previously reported procedures [31,32]. As reference catalysts, commercial acid catalysts were also evaluated in this work. Acidic macroporous resin, Amberlyst-15, and a homogeneous catalyst, *p*-toluenesulfonic acid (PTSA), were supplied by Sigma-Aldrich.

2.3. Catalysts characterization

The textural properties of the sulfonic acid-modified mesostructured silicas were obtained by means of nitrogen adsorption-desorption isotherms recorded at 77 K using a Micromeritics TRISTAR 3000 system. Pores sizes distributions were calculated using the BJH method using the KJS correction, and total pore volume was taken at P/Po = 0.975. Structural characterization was performed by X-ray powder diffraction (XRD) patterns, which were acquired on a PHILIPS X'PERT diffractometer using the Cu Kα line.

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