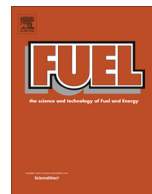




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Synthesis and characterization of functionalized alumina catalysts with thiol and sulfonic groups and their performance in producing 5-hydroxymethylfurfural from fructose

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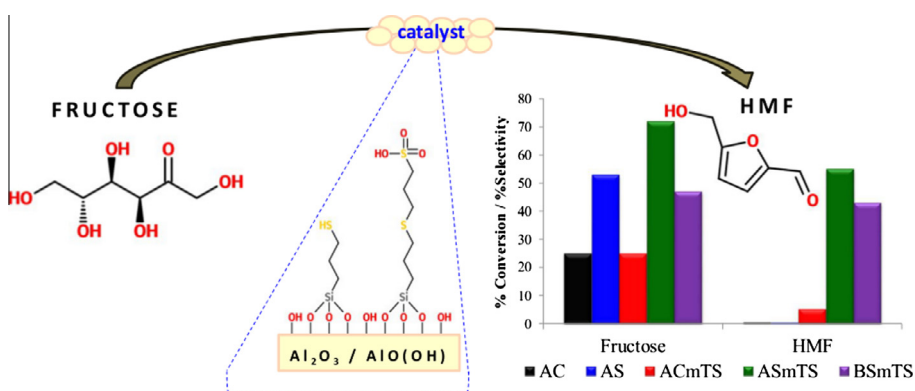
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HIGHLIGHTS

- Two aluminas (synthetic and commercial) were modified with –SH and –SO₃H groups.
- The functionalization with the –SH group was done via the grafting and sol-gel methods.
- NMR confirmed the higher presence of the –SH group on the synthesized alumina catalyst.
- Modified synthesized alumina presented the best catalytic activity.

GRAPHICAL ABSTRACT



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ABSTRACT

5-Hydroxymethylfurfural (HMF) has been identified as a potential candidate for biofuels and a high-potential intermediate chemical compound. The obtention of HMF from fructose is efficiently carried out using acid catalysts. In this work, a new catalyst of alumina synthesized by sol-gel as support was bifunctionalized with thiol (–SH) and sulfonic (SO₃) groups by the grafting method and compared with other supports, i.e., synthesized boehmite and commercial alumina. The 3-mercaptopropyl-trimethoxysilane was utilized as a source of the thiol group to promote fructose tautomerization to its furanose form. The sulfonic group was obtained from 1,3-propanesultone, which carries out the dehydration of the fructose molecule. The prepared bifunctionalized catalysts were tested in the fructose dehydration reaction. The functional groups were identified through Fourier transform infrared spectroscopy (FTIR) as the primary characterization. The type of acid site was identified by Fourier transform infrared spectroscopy (–pyridine (FTIR-py)) and quantified by temperature-programmed desorption of ammonia (TPD-NH₃). The molecular structures of thiol and the sulfonic groups anchored on the supports were resolved by nuclear magnetic resonance with cross-polarization (CP) and magic angle spinning (MAS)

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(CP-MAS-NMR). The bifunctionalized catalyst of alumina synthesized by sol-gel, being a very competitive material, reached a 55% selectivity to HMF at a 72% conversion at 453 K.

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1. Introduction

There is growing interest in the use of renewable carbon sources for chemical product production and biofuel production. The carbohydrates available in biomasses are a very promising resource because they are the main sources of natural carbon, renewable and relatively economic [1].

Fructose, glucose and sucrose are considered as higher carbon hydrate compounds, and furan chemical products can be obtained from these compounds, such as 5-hydroxymethylfurfural (HMF) [2,3]. The HMF could be synthesized from sugar dehydration catalyzed by acids. The investigation of Van-Putten et al. showed the works most important to HMF as a flexible chemical platform from the renewable sources [4], and it is also very important to consider HMF as a partial step in biomass conversion, such as the hydro-deoxygenation (HDO) process [5–7]. Alternately, the work by the group of Scott and Dumesic is currently the most important and promising for the dehydration reaction of fructose to form HMF [8].

Many researchers have been working with homogeneous acids in the dehydration reaction of fructose in HMF, such as mineral acids [9], organic acids [10] or ionic liquids [11,12]. The homogeneous acid catalysts have shown good percentages of performance of HMF; however, there are some serious troubles regarding the separation and recycling, as well as the corrosion of materials, and heterogeneous acid catalysts have been shown to be best; some of the recently reported heterogeneous acid catalysts are niobium oxide [13], sulfated zirconia [14] and zirconia with tungsten [15]. The functionalization with sulfonic groups in the SBA-15 catalyst increases the acidity in the solid surface; these acid sites of Brønsted are found in a more available way, improving the selectivity to HMF in fructose dehydration [16–18]. Nevertheless, the acid sites anchored in a mesoporous material, such as SBA-15, are often unstable; because the collapse of the silica mesostructure blocks the active sites or the separation of themselves [16], the functional groups in co-condensed silicas tend to be more hydrothermally stable than those of grafted sites [19].

The sol-gel method provides an attractive, convenient route to manipulate the structural and textural properties and purity of a compound [20–22]. The alumina is a mesoporous material and presents various advantages, such as low cost, good thermal and chemical stability, and high specific surface and acid surface. It is widely used as a support and exhibits good catalytic properties. Some authors have focused on controlling the acidity of the alumina (Lewis and Brønsted acid sites) through the use of inorganic acid groups [20,23]. It is worth noting that the alumina has abundant superficial hydroxyl groups, which is very adequate for the organic acid group connection and modifying the acidity [24].

The selectivity to HMF in the fructose dehydration depends on the temperature, quantity and type of solvent used in the reaction. Different solvents have been evaluated in biphasic systems: dimethylsulfoxide (DMSO), methyl isobutyl ketone (MIBK), and tetrahydrofuran (THF) [25], as well as ethanol, ethylacetate, methanol, isopropanol, *tert*-butanol, acetone and deionized water to prepare the aqueous solution [26]. Román-Leshkov et al. evaluated the solvent effect in the fructose dehydration to HMF in a series of biphasic systems with primary alcohols, secondary ketones and ethers [27]. It has been proved that the thiol group promotes

the fructose tautomerization to its furanose form and, beside a sulfonic group, favors the dehydration reaction. The bifunctional sites are a strategy to present high selectivity to form HMF [19].

In the present work, the bifunctionalization of the alumina was carried out with thiol and sulfonic groups. The scope is to demonstrate that the thiol and sulfonic functional groups were incorporated on the surface of the different supports: sol-gel synthesized alumina, boehmite and a commercial alumina by deep characterization. The catalytic activity in the dehydration reaction of fructose was tested, but the most important parameter to obtain is a competitive selectivity in the formation of HMF.

2. Experimental

2.1. Synthesis of alumina by sol-gel

For the synthesis of alumina by sol-gel (labeled as AS), the aluminum-tri-sec-butoxide (ATB, 97%, Aldrich) was dissolved in 2-propanol (99.8%, Aldrich) at 353 K using reflux for 3 h. After that, it was taken to a temperature of 298 K; then, the deionized water was added, and it was left in agitation (800 rpm) for 24 h. The synthesized gel was left in an ageing process for 24 h and then dried at 353 K; finally, it was calcinated at 823 K for 4 h. The molar relations were the following: 2-propanol/ATB (60:1), and H₂O/ATB (1:1) as Valente et al. previously reported [20,23,28].

2.2. Functionalization of the alumina with a thiopropyl group

2.2.1. Incorporation of the thiol group by the grafting method

1.5 g of the commercial alumina catalyst (AC) brand name CATALOX[®] SBA-200 Alumina (Sasol) or the synthesized alumina (AS) was taken and suspended in 50 mL of toluene (Aldrich); after that, 0.9 mL (4.60 mmol) of 3-mercaptopropyl-trimethoxysilane (MPTMS, 95%, Aldrich, Fig. 1a) was added, and the result was left in agitation (800 rpm) with reflux for 36 h at 298 K. The mix was filtered, and the solid obtained was washed three times with 15 mL of ethanol (99.5%, Aldrich) and finally was dried under vacuum (50 kPa) at 353 K for 12 h. The commercial alumina and the synthesized alumina were functionalized and labeled as ACmT and ASmT, respectively [8,20,23].

2.2.2. Incorporation of the thiol group by the sol-gel method

The aluminum-tri-sec-butoxide (ATB, 97%, Aldrich) was dissolved in 2-propanol (99.8%, Aldrich) with reflux for 3 h at 353 K. The reaction was taken at 298 K, and the 3-mercaptopropyl-trimethoxysilane was incorporated *in situ* (MPTMS, 95%, Aldrich) with a time of contact of 1 h. Later, the deionized water was added, and the result was left in agitation (800 rpm) for 1 h. The synthesized gel was left in the ageing step for 24 h, was dried at 353 K, and lastly was calcinated at 513 K for 4 h. The solid obtained was labeled BSMT. The same molar relation was used for AS (2-Propanol/ATB (60:1), H₂O/ATB (1:1)) [8,20–23].

2.3. Bifunctionalization with the sulfonic group

The placing of the propyl-sulfonic group was carried out under conditions of N₂ flux (1.6 mL/s) in a three-necked flask, and the result was cooled down at 195 K; 25 mL of tetrahydrofuran was

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