



Mesoporous Al-promoted sulfated zirconia as an efficient heterogeneous catalyst to synthesize isosorbide from sorbitol

Yi Zhang^{a,b}, Tong Chen^{a,*}, Gang Zhang^{a,b}, Gongying Wang^a, Hua Zhang^a

^a Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, China

^b University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Keywords:

Biomass
Mesoporous sulfated zirconia
Aluminum promoter
Sorbitol dehydration
Isosorbide

ABSTRACT

Mesoporous aluminum-promoted sulfated zirconia (named as mAl-SZ) was directly prepared by grind method, and firstly used to catalyze the solvent-free dehydration of sorbitol to isosorbide. The physicochemical properties of as-prepared catalysts were characterized by FT-IR, TGA, XRD, N₂ sorption, NH₃-TPD and pyridine-infrared (IR) spectroscopy techniques in order to elucidate the relevance of the catalyst properties and the catalytic performance. It was found that the catalysts prepared by grind method possessed mesoporous structures with high surface area, pure tetragonal phase as well as high sulfur contents, which were advantage to eliminate diffusion limitation and generate abundant acidic sites, especially Brønsted acidic sites. Furthermore, aluminum promoters could contribute to the considerable increase of the strong acidic sites and ratio of Brønsted to Lewis acidic sites. Consequently, the mesoporous sulfated zirconia with 6 mol% Al-promoter (6Al-SZ) attained porous structure with improved acidic properties, thus showing the optimal catalytic behavior. The full sorbitol conversion with 73% isosorbide selectivity was achieved under milder conditions (175 °C, 2 h) than those of similar type of catalysts. In addition, the 6Al-SZ exhibited favorable reusability with insignificant drop in isosorbide yield during five reaction cycles.

1. Introduction

Currently, continuous efforts have been paid to the utilization of biomass as renewable and sustainable feedstocks for the production of high-value chemicals or liquid fuels to fulfill sustainable development [1]. Sorbitol is considered to be one of the most promising platform chemicals for biomass conversion, which is easily obtained from cellulose via glucose hydrogenation [2]. Among the various sorbitol-derived chemicals, isosorbide is regarded as one of the most potential derivatives in view of its typical application in the medicine and surfactant fields due to its special molecular structure [3]. Especially, incorporation of isosorbide monomer into the poly (ethyleneterephthalate) polymer (PET) might greatly enhance its glass transition temperature and impact resistance [4]. In recent years, isosorbide is also regarded as a promising alternative of bisphenol A in the synthesis process of epoxy resins or polycarbonate to eliminate environmental pollution [5,6].

Generally, isosorbide is produced by double dehydration of sorbitol as displayed in Scheme S1 [7]. In the view of green chemistry, the process for dehydration of sorbitol under solvent-free and milder conditions would be highly promising [8]. However, this is not a simple

and easy synthetic route, which requires strong acidity, especially strong Brønsted acidic sites to enhance selectivity of isosorbide [7,9]. This process is industrially carried out under homogeneous catalysis in the presence of strong mineral acids such as H₃PO₄, H₂SO₄ and HCl [10,11]. Although a high value about 75% of isosorbide yield is achieved under mild condition, these liquid acids bring obstacles from the standpoint of environment, safety, corrosiveness, separation and operating cost. Therefore, the development of green heterogeneous solid acid catalyst to replace conventional mineral acids have prompted an extensive demand from an economic and environmental perspective. The various heterogeneous solid acid catalysts, such as metal (IV) phosphates [12–14], phosphoric acid modified Ta₂O₅ [15], supported heteropolyacid [16] and cellulose-derived solid acid catalyst [17] had been studied for the catalytic dehydration of sorbitol. Most of those catalysts usually required high reaction temperature but obtained unsatisfactory isosorbide yield. An acceptable isosorbide yield of 70–80% was obtained under long reaction time in the presence of H β zeolite [18–20], but a large amounts of catalyst loading was required. Furthermore, the H β zeolites have the disadvantages of being expensive catalysts. On the other hand, sulfonic acid resins and mesostructured SBA-15 silica functionalized with organic sulfonic acid groups were

* Corresponding author.

E-mail address: chentongw@sina.com.cn (T. Chen).

favorable for the conversion of sorbitol into isosorbide, while high-cost and low thermal stability constrained their industrial applications [21–24].

Among the various solid acids catalysts, the sulfated metal oxides such as ZrO_2 , SnO_2 , TiO_2 , and Nb_2O_5 have attracted considerable attentions as the promising catalysts for industrial processes, which are used in various hydrocarbon reactions due to their high thermal stability, eco-friendly, as well as strong acidic properties [25,26]. In recent years, several groups reported the utilization of sulfated metal oxides for the conversion of sorbitol to isosorbide [27–30]. Among these sulfated metal oxides, $\text{SO}_4^{2-}/\text{ZrO}_2$ have been extensively concerned due to its relatively high Brønsted acid strength and acidic sites, which are preferable to sorbitol dehydration [31]. Also, sulfated zirconia is less expensive and readily available at industrial scale. However, conventional preparation of sulfated zirconia is generally accomplished by post-sulfonation and calcination method, which contribute to a relatively weak interaction between SO_4^{2-} and ZrO_2 framework with low sulfur content, thereby the low ratio of Brønsted to Lewis acidic sites and low activity. Some control on sulfur loading of sulfated zirconia can be achieved by varying the calcination temperature, but the favorable tetragonal phase and crystallinity are affected. Additionally, poor porosity such as small pore size and low pore volume inhibits their inherent catalytic activities for bulky biomass-derived molecules like polyalcohol [32]. Therefore, some unconventional preparation methods were conducted to improve its porosity and strengthen its interactions between sulfate species and ZrO_2 framework, which could lead to an enhanced catalytic activity and stability [33–35].

In the present study, a mesoporous aluminum metal promoted sulfated zirconia with the high sulfur contents and ratio of Brønsted to Lewis acidic sites was synthesized by a simple grind method and used as an efficient catalyst in solvent-free dehydration of sorbitol to isosorbide. This study systematically evaluated the correlations between catalyst structure and catalytic performance in sorbitol dehydration at different reaction parameters such as catalyst amount, reaction temperature and reaction time. In addition, its catalytic performance was compared with that of conventional sulfated zirconia prepared by post-sulfonation and calcinations method. It was found that grinding prepared 6Al-SZ exhibited superior catalytic activity and reliable reusability under relatively mild reaction conditions.

2. Experimental

2.1. Catalysts preparation

Mesoporous Al-promoted sulfated zirconia was prepared by simple grind method under solvent-free condition. Typically, a mixture of 3.22 g $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 7.92 g $(\text{NH}_4)_2\text{SO}_4$ and desirable amounts of Al $(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was ground for 20 min. After standing for 24 h, the sample was calcined at 600 °C in air for 5 h, which was denoted as mAl-SZ, m referred to molar percentage ratio of Al/Zr. Accordingly, mesoporous sulfated zirconia was prepared by the same method with the exception of a mixture only containing $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{SO}_4$. The as-prepared catalyst was labelled SZ.

For comparison, conventional sulfated zirconia, denoted as SZ-C, was prepared by post-sulfonation and calcinations method as previously described [30]. Briefly, 2.0 g of zirconium (IV) hydroxide was added into 40.0 mL of 0.05 M aqueous H_2SO_4 , then vigorously stirred for 5 h at room temperature. The suspension was centrifuged to obtain the white solid powders. After dried at 100 °C overnight, the obtained solids were calcined at 600 °C for 5 h.

2.2. Catalysts characterization

Fourier transform infrared (FT-IR) spectra was obtained with a Nicolet Magna-IR 560 spectrometer in the wavelength range of 4000–400 cm^{-1} and the resolution was 4 cm^{-1} , using KBr powders.

Thermogravimetric analysis (TGA) was carried out by means of a NETZSCH STA 449F3 instrument, a heating rate of 10 K min^{-1} , an air gas flow of 100 ml min^{-1} , over the 313–1273 K temperature range. The sulfur content was calculated based on the weight loss from 873 to 1273 K. The weight loss corresponded to the content of SO_3 , and sulfur content could be 40% of this weight loss [36].

X-ray diffraction (XRD) patterns were recorded in the 2θ range of 20–70° on a Bruker D8 ADVANCE diffractometer with Cu K α radiation source (1.5418 Å). The crystalline size of crystal phase was determined from the peak width of characteristic peak using Scherrer's equation: $D = K\lambda/\beta\cos\theta$, where $K = 0.9$, D represented crystallite size, λ represented the wavelength of Cu K α radiation, and β represented the corrected half-width of the diffraction peak.

A Micromeritics ASAP 2010 was used to determine BET surface area, pore volume and pore size at 77 K using N_2 adsorption. The BET surface areas were determined by the BET method. The total pore volume was calculated from the amount of vapor adsorbed at a relative pressure (p/p^0) close to unity. Pore size distribution curves were established from the desorption branches of isotherms using the Barrett–Joyner–Halenda (BJH) model.

Temperature-programmed desorption of ammonia (NH_3 -TPD) measurement was performed on a Micro TP-5080 automatic adsorption instrument equipped with a thermal conductivity detector (TCD) to determine the acid strength and acid amount of catalysts. Before adsorption, 100 mg catalyst loaded in a quartz reactor was pretreated at 300 °C for 2 h under N_2 flow (50 mL min^{-1}). After cooling down to room temperature, NH_3 adsorption was performed by N_2 flow to a stream of 10 vol% NH_3/N_2 (50 mL min^{-1}) and maintaining the temperature for 1 h. After a purge with N_2 to remove physically adsorbed ammonia, NH_3 -TPD measurements were taken up to 650 °C at a heating rate of 10 °C min^{-1} in flowing N_2 at a flow rate of 50 mL min^{-1} and the process was monitored by a thermal conductivity detector (TCD).

The types of acid sites of the as-prepared catalysts were determined by pyridine-infrared (IR) spectroscopy (Nicolet 5700), self-supporting wafers of samples were placed into a quartz cell and evacuated at 300 °C for 2 h (10^{-2} Pa) to remove the adsorbed impurities over the catalyst surface. After cooling to 30 °C, the pretreated samples were exposed to pyridine for 1 h and then outgassed at 150 °C or 300 °C for 1 h to remove the physically adsorbed pyridine, after which the FT-IR spectra were recorded. The ratios of Brønsted to Lewis acid sites were calculated from integrated areas of the peaks located about 1540 and 1446 cm^{-1} .

2.3. Activity measurements

The solvent-free dehydration of sorbitol was carried out in a 50 mL round bottom glass reactor attached to a vacuum pump to maintain the reaction pressure of 40 kPa. Typically, 10 g sorbitol and a certain amounts of catalyst were placed into the flask and allowed to melt at 130 °C under mechanical agitation. The reaction mixture was quickly heated to designed temperature. After reaction, the reaction products were cooled to room temperature and an appreciable amount of water was added. The resulting mixture was centrifuged to separate the catalyst. Liquid solution was analyzed by HPLC (Waters e2695) equipped with a 2414 refractive index (RI) detector and Asahipak column ($\text{NH}_2\text{P-50 4E}$, No. N1670026). Acetonitrile/water (80/20) mixture was used as an eluent for the analysis with the flow rate of 1.0 mL/min. The temperature of RI detector was maintained at 35 °C throughout the analysis.

The recovered catalyst was washed with a large amounts of alcohol and then regenerated by calcined at 500 °C for 2 h to recover its original white. Thereafter, it was used again for the dehydration of sorbitol as previously described process to evaluate its reusability.

Conversion of sorbitol (C_{sorbitol}) and product selectivity (S_i) were defined according to the following equation:

Download English Version:

<https://daneshyari.com/en/article/6496561>

Download Persian Version:

<https://daneshyari.com/article/6496561>

[Daneshyari.com](https://daneshyari.com)