



Short communication

Arenesulfonic acid functionalized ordered mesoporous silica as solid acid catalyst for solvent free dehydration of sorbitol to isosorbide



Aasif A. Dabbawala, Jung J. Park, Anil H. Valekar, Dinesh K. Mishra, Jin-Soo Hwang*

Bio-refinery Research Center, Korea Research Institute of Chemical Technology (KRICT), Yuseong, Daejeon 305-600, Republic of Korea

ARTICLE INFO

Article history:

Received 2 April 2015

Received in revised form 17 May 2015

Accepted 22 June 2015

Available online 27 June 2015

Keywords:

Dehydration

Sorbitol

Selectivity

Isosorbide

Mesoporous organosilica

ABSTRACT

Organosulfonic acid functionalized ordered mesoporous silicas with different moieties have been synthesized and used as solid acid catalysts for solvent free dehydration of sorbitol to isosorbide. In screening experiments with distinct solid acids, the arenesulfonic acid functionalized SBA-15 (Ar/SBA-15) showed higher catalyst performance as compared to propyl and fluorosulfonic acid sites. Under optimum reaction condition, Ar/SBA-15 afforded 100% sorbitol conversion with 71% isosorbide selectivity in 2 h at moderate temperature of 170 °C. The high activity of catalyst ascribed to its ordered mesoporous structure and ease to access Brønsted acid sites with high acid strength.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The catalytic conversion of cellulosic biomass or biomass-derived carbohydrates to value added chemicals has received considerable interest in the recent years due to the depletion of fossil fuel and environmental concern [1–7]. The sorbitol (a sugar alcohol) can be obtained from cellulose via glucose hydrogenation and is considered as an important platform molecule to synthesized number of chemicals [6,7]. By acid catalyzed dehydration, sorbitol is converted into anhydro-sugar alcohols such as sorbitan and isosorbide (Scheme 1). Both anhydro-sugar alcohols can be extensively useful to synthesize a variety of intermediates applicable in the preparation of surfactants, pharmaceuticals, cosmetics and synthetic polymer industries [8–11].

The dehydration of sorbitol to isosorbide (IS) was studied first using homogeneous mineral acids especially in the presence of sulfuric acid [9]. It is known that mineral acid based process has many disadvantages, such as risk in handling of acid, corrosion of equipments and required tedious product purification. Consequently, the research in the field of sorbitol cyclodehydration has been focused to develop solid acid catalyst and process alternate to mineral acids [10–17]. The various solid acid heterogeneous catalysts, such as metal (IV) phosphates (65% IS selectivity, 300 °C) [12], phosphoric acid modified Ta₂O₅ (48% IS selectivity, 225 °C) [13], supported heteropolyacid (65% IS selectivity, 250 °C) [14], sulfated CuO (67% IS selectivity, 200 °C) [15] and sulfated ZrO₂ (61% IS selectivity, 210 °C) [16] have been employed for the dehydration of sorbitol to isosorbide. All the studied solid acid catalysts have

their own advantages compared to homogeneous mineral acids. However, the most of studied solid acid catalysts require comparatively high reaction temperature (200–300 °C) for significant production of isosorbide. Therefore, the development of efficient solid acid catalyst that catalyzed this reaction at moderate temperature and produced high isosorbide selectivity is highly desirable.

The functionalized ordered mesoporous silicas (OMSs) possess superior physicochemical properties and their applications in the field of catalysis and adsorptions have greatly been explored [18]. The use of sulfonic acid modified OMS as catalyst has been increased for the conversion of biomass-derived carbohydrates due to their ordered porous structure and number of accessible Brønsted acid sites [19,20]. However, the proper studies on cyclodehydration of sorbitol to isosorbide using functionalized mesoporous materials are limited [21]. Herein, we synthesized sulfonic acid functionalized OMS having different organic moieties and evaluated their catalyst performance in solvent free cyclodehydration of sorbitol to isosorbide. The experimental results of catalysts are discussed based on their organic functionalities and anhydro-alcohol selectivity. Moreover, the effects of reaction temperature, catalyst amount and reaction time on sorbitol conversion and isosorbide selectivity were studied and the catalyst was also reused.

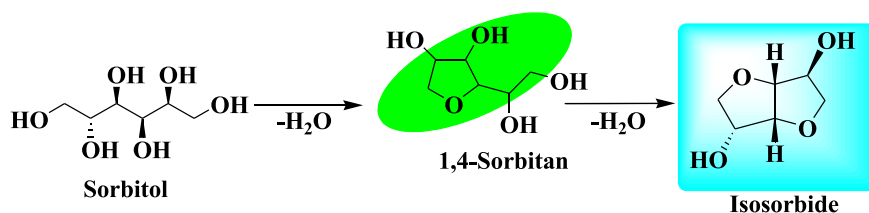
2. Experimental

2.1. General remarks

SBA-15 was prepared according to reported synthesis procedure [22]. The propylsulfonic acid functionalized SBA-15 (Pr/SBA-15) and arenesulfonic acid functionalized SBA-15 (Ar/SBA-15)

* Corresponding author.

E-mail address: jshwang@kRICT.re.kr (J.-S. Hwang).



Scheme 1. Cyclodehydration of sorbitol to isosorbide.

were synthesized in two steps according to reported method by changing precursors 3-mercaptopropyltrimethoxysilane (MPTMS) and 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (CSPTMS) respectively (Scheme 2) [20]. For comparison, Pr/SiO₂ was synthesized from amorphous silica (SiO₂) and MPTMS precursor. Sulfated zirconia (SZ) was prepared according to previously reported procedure [15]. The fluorosulfonic acid functionalized acidic resins such as NR-50 (DuPont™) and Nafion® SAC-13 (NF-SAC, fluorosulfonic acid Nafion® polymer on amorphous silica, 10–20 wt.%) were procured from Sigma-Aldrich. The total acid sites in catalyst samples were determined by acid–base back titration using molar solutions of NaOH and HCl with phenolphthalein as indicator [23]. In a typical experiment, 0.050 g of catalyst was added to a 0.01 M NaOH aqueous solution (20 mL). The mixture was stirred for 60 min at room temperature. After separating catalyst by centrifuge, the supernatant solution was titrated by a 0.01 M HCl solution using phenolphthalein as an indicator. The solvent free dehydration of sorbitol was performed in simple reactor setup under reduce pressure and the composition of products was analyzed using HPLC [24]. For catalyst reuse and regeneration, the water/ethanol was added to the reaction mixture to dissolve product and then filtered to separate solid catalyst from the product. The recovered catalyst was thoroughly washed with water and THF. The catalyst was then dried and finally calcined at 300 °C for 2 h to get regenerated catalyst.

3. Results and discussion

3.1. Characterization of the catalysts

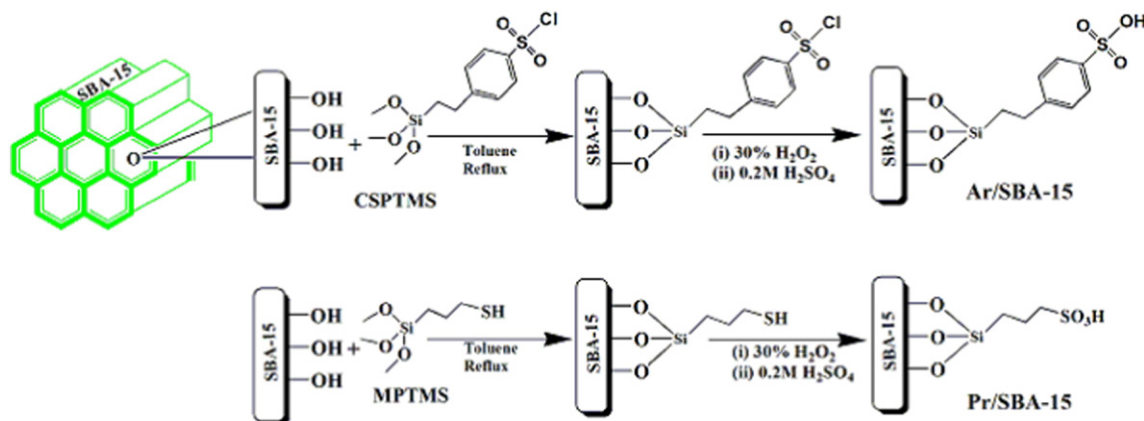
The synthesized Pr and Ar/SBA-15 (SAS catalysts) were characterized by various physicochemical analyses. The BET-surface area, pore size, pore volume and S content of the SAS samples are listed in Table 1. As compared to pristine SBA-15, the SAS catalysts showed lower BET surface area, pore volume and pore diameter. The changes in above parameters can be considered due to the functionalization and such parameters were decreased depending on size of organic moieties. SAS catalysts showed type IV N₂ adsorption–desorption isotherm

similar to SBA-15 characteristic of ordered mesoporous solid with average pore size ~4 nm (Fig. S1). TEM and SEM images of SAS catalysts (Fig. 1) showed long channels and morphological view of catalysts with hexagonal pore structure whereas SEM-EDX spectrum confirms the presence of Si, O, C and S in both catalysts. This suggests the incorporation of sulfonic acid organic moieties on SBA-15 surface and the functionalization did not alter the morphology and structure of SBA-15.

Powder XRD patterns of SBA-15 (Fig. 2a) showed characteristic diffraction peaks below at 2° corresponding to the (1 0 0), (1 1 0) and (2 0 0) planes which agree with its uniform hexagonal structures [20]. These diffraction peaks for SAS catalysts do not alter significantly but intensities of peaks decrease marginally confirming that the structure of SBA-15 does not collapse during surface modification. The FTIR spectra of pyridine adsorbed Ar/SBA-15 catalyst showed that the absorption bands at 1636, 1543 and 1489 cm⁻¹ were attributed to the interaction of pyridine with Brønsted acid sites which led to the formation of pyridinium ion. Another broad band at 1440 cm⁻¹ was attributed to the Lewis acid site and was originated due to the electron inductive effect of the S=O double bond [25]. The characteristic bands for acid sites were observed even at 300 °C indicating the presence of relatively strong acid sites in catalyst (Fig. 2c). The acid strengths of catalysts were determined by NH₃-TPD (Fig. S2). The acid strength of catalyst having SO₃H sites depends on its molecular environment and –SO₃H attached to an aromatic ring shows comparative high acid strength than alkyl moiety [20]. The total acid amount of catalysts was measured by acid–base titration and presented in Table 1. From the TGA profile, it can be concluded that the SAS catalysts are stable up to 300 °C (Fig. 2b).

3.2. Catalytic dehydration of sorbitol

The catalytic performances of SAS catalysts were evaluated in dehydration of sorbitol under solvent free condition. To understand the role and effect of different functional groups, the commercially available acidic resins (NR-50 and Nafion® SAC-13) and sulfated ZrO₂ were also tested for comparison purposes. The sorbitol dehydration was performed using distinct solid acids by keeping similar acid value as studied catalysts have different acid amounts (Table S1). The major dehydrated



Scheme 2. Synthesis of Ar/SBA-15 and Pr/SBA-15.

Download English Version:

<https://daneshyari.com/en/article/49382>

Download Persian Version:

<https://daneshyari.com/article/49382>

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