



Isosorbide production from sorbitol over porous zirconium phosphate catalyst



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ABSTRACT

A porous zirconium phosphate catalyst prepared by hydrothermal method was studied for the dehydration of sorbitol to isosorbide under water-free conditions. Various characterization techniques such as XRD, Raman, SEM, NH₃-TPD and Pyridine adsorption etc were conducted to determine the textural and acidic properties of the catalyst so as to build the relationship between catalytic performance and catalyst structure. In screening tests with other solid acids, the as-prepared ZrP sample exhibited the promising catalytic behavior for isosorbide production probably assigned to its high surface area, porous structure and the adequate Brønsted acid sites. Full sorbitol conversion with as high as 73% isosorbide selectivity could be obtained at mild conditions (210 °C, 2 h). Noticeably, the ZrP catalyst could be repeatedly used without any obvious deactivation. Generally, the ZrP catalyst studied in this work possessed a great potentiality as an efficient heterogeneous solid acid catalyst for isosorbide production to diminish the application of homogeneous mineral acid.

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1. Introduction

Recently, great efforts have been devoted to the catalytic conversion of renewable biomass and/or biomass-derived feedstocks to fine chemicals and liquid fuels to fulfill the sustainable development [1–5]. In particular, sorbitol, known as one of the top twelve platform chemicals, has achieved considerable attention and has a special application in chemicals, fuels, commodity to partially replace conventional fossil fuels [6–9]. Meanwhile, sorbitol as an important biomass-derived material could be readily produced from enormous cellulose or lignocellulose [10,11]. Among the various sorbitol-derived chemicals, isosorbide(1,4:3,6-di-anhydrohexitol), a product of sorbitol dehydration, is regarded as one of the most promising derivatives considering its typical application in the polymer and medicine field because of its rigid molecular structure and chiral centers [12,13]. Notably, incorporation of isosorbide monomer into the poly(ethyleneterephthalate) polymer (PET) might greatly enhance its glass transition temperature. Currently, isosorbide also acted as an promising alternative

of bisphenol A in the synthesis process of epoxy resins or polycarbonate to eliminate environmental pollution [14–16].

Up to date, many research has been conducted on the sorbitol dehydration to isosorbide in order to develop an efficient catalyst [17]. From the standpoint of environmentally-benign, Yamaguchi et al. studied the dehydration of sorbitol in high temperature liquid water without the addition of any acid catalysts and the maximum isosorbide yield was ca.57% at 317 °C for 1 h [18]. In contrast, the results were still not satisfactory for the industrial application due to high temperature and pressure. Similarly, Almeida et al. selected a molten ZnCl₂ hydrate medium as both solvent and catalyst and 100% sorbitol conversion with ca.85% selectivity of isosorbide was obtained at 200 °C. It is noteworthy that this process possessed several drawbacks such as solvent recover and remarkable salt formation [19]. Otherwise, mineral acids like HCl and H₂SO₄ as homogeneous catalysts showed a satisfied performance. Fleche et al. revealed that 77% isosorbide yield could be achieved at 135 °C over liquid H₂SO₄ catalyst [20]. Moreover, major obstacles for the process using the liquid acids were difficult separation of isosorbide from reaction system, equipment corrosion and environmental pollution caused by any discharge of acids. Hence, a great interest has been arisen on the development of heterogeneous solid acid catalyst to replace conventional min-

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eral acids because of their environmentally friendly nature with respect to easy separation, less corrosiveness and waste [21–23]. Consequently, several solid acid catalysts such as sulfated copper oxide [24], supported heteropolyacid [25], zeolites [26,27], super-hydrophobic mesoporous acid (P-SO₃H) [28], Amberlyst-15 [29] and metal phosphates [30,31] have been selected in the catalytic dehydration of sorbitol. Nevertheless, the process using heterogeneous catalysts still has not been commercialized. Most of the studied solid acid samples normally need higher reaction temperature and more reaction time to achieve satisfactory isosorbide yield leading to high operation cost. Additionally, zeolite based catalysts suffered from the readily deactivation because of the structure distortion during the reaction process [32]. Some catalysts also exhibited less stability due to serious leaching of acid sites and several other ones were toxic like tin phosphate [33,34]. Therefore, it is desirable to development an efficient catalyst for the dehydration of sorbitol that could be operated at moderate conditions.

Generally, zirconium phosphate is one of the most promising solid acids for dehydration reactions. Much efforts have been conducted on zirconium phosphate, considering its several merits such as nontoxicity, thermal stability, eco-friendly, strong acidity, recycling etc [35–37]. Moreover, many literatures have described the synthesis of high-valued chemicals from biomass-derived feedstocks over zirconium phosphate [38,39]. Meanwhile, the incorporation of enormous nanopores in solid acid catalysts might remarkably improve the mass transfer of reactants and facilitate the exposure of acid sites leading to better catalytic behavior in various reactions like isomerisation, dehydration, esterification etc. To the best of our knowledge, the application of zirconium phosphate with porous structure for the catalytic dehydration of sorbitol has still been in its infancy. Rusu et al. [40] investigated the isosorbide production using trivalent and quadrivalent phosphate as solid acid catalysts and the best catalytic performance was obtained over boron phosphate sample.

In this work, a zirconium phosphate catalyst with porous structure was successfully synthesized by a sol-gel process using P123 as a sacrifice template and elaborately investigated to design an effective, environmental-benign catalyst for isosorbide production. Catalytic parameters (reaction temperature, reaction time, catalyst amounts etc) were studied in detail and the results were compared to other solid acid catalyst. Additionally, a systematic characterization of the as-prepared catalyst (XRD, SEM, TEM, FTIR, pyridine adsorption, NH₃-TPD, BET etc) were conducted to establish a relationship between catalyst textural properties and catalytic behavior.

2. Experimental

2.1. Catalyst preparation

Zirconium phosphate catalyst was synthesized by a sol-gel self-assembly process [41]. Typically, aqueous H₃PO₄ was slowly added into a solution of ZrOCl₂ (P/Zr = 2/1, molar ratio) under magnetic stirring (800 rpm). Another ammonia solution was then dropped into the mixture until the pH value was at around 5.0. The precipitate was thoroughly filtered and washed with hot deionized (DI) water until no chloride ions were detected. Under continuous stirring, the obtained precipitate was then added into an aqueous solution of Pluronic P123 (PEG-PPG-PEG triblock copolymer) which was employed as the structural directing agent. Finally, aqueous H₃PO₄ was dropwise under stirring and the resultant gel was poured into a Teflon-lined stainless steel autoclave at 40 °C for 24 h and at 75 °C for another 24 h. After filtration and thorough washing with hot DI water, the precipitate was dried at 90 °C overnight and calcined at 450 °C for 6 h in static air. The as-prepared zirconium

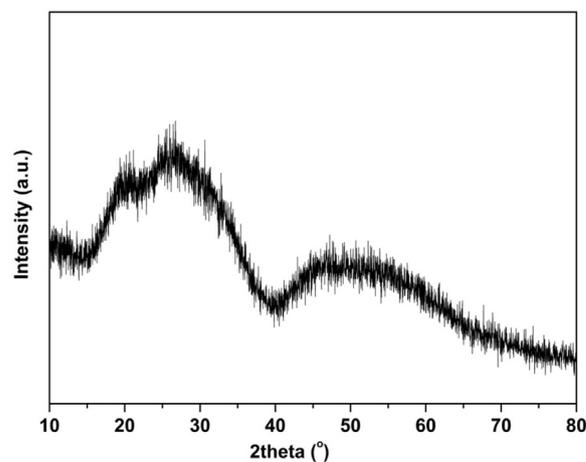


Fig. 1. XRD pattern of the ZrP catalyst.

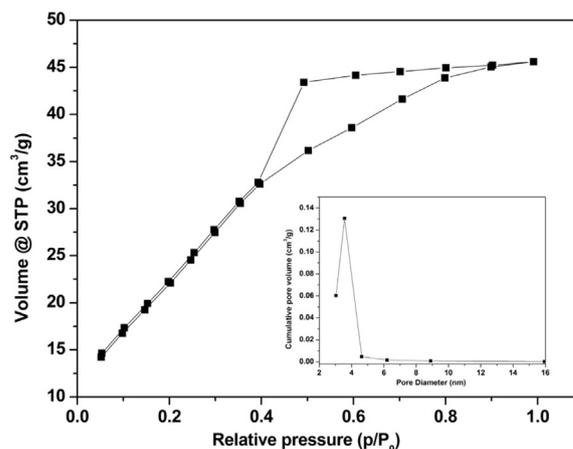


Fig. 2. Nitrogen adsorption-desorption isotherm of the ZrP catalyst.

ium phosphate was denoted in a general form ZrP in the following discussion.

2.2. Catalyst characterization

X-Ray diffraction patterns (XRD) were recorded in the 2θ range of 10–80° on a Rigaku X-3B diffractor with Cu K_α radiation source operating at 40 kV and 60 mA.

The surface area and porous structure was measured by Nitrogen adsorption-desorption at –196 °C on an ASAP2010 Micro-metrics apparatus. Before analysis, the catalyst was outgased at 300 °C for 3 h under N₂ flow (50 mL/min) to remove the adsorbed impurities on the catalyst surface.

Fourier transform infrared (FT-IR) spectra was conducted on a Digilab FTS 3100 FTIR spectrometer. Prior to measurement, the investigated ZrP sample was dried at 100 °C over night and then pressed into a wafer by diluting the catalyst with KBr (spectroscopic grade).

Infrared (IR) spectra of pyridine adsorption was also operated on a same Digilab FTS 3100 FTIR spectrometer to explore the acid types of ZrP catalyst. Firstly self-supported wafers of the catalysts were placed into an IR cell and then the disk was heated at 300 °C for 1 h under vacuum conditions to remove adsorbed impurities over the catalyst surface. After quenching down to room temperature, IR spectrum was recorded as background and pyridine vapor was then added until equilibrium was achieved. Subsequent evacuation was performed at 150 °C under vacuum conditions followed by spectral

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