



Heterogeneous cyclization of sorbitol to isosorbide catalyzed by a novel basic porous polymer-supported ionic liquid

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ARTICLE INFO

Keywords:

Isosorbide
Supported ionic liquid
Mesoporous
Solid base
Heterogeneous catalysis

ABSTRACT

In this study, heterogeneous cyclization of sorbitol to isosorbide under basic condition was realized for the first time with a novel porous polymer-supported ionic liquid as catalyst. These polymer-supported ILs were synthesized through the suspension polymerization of 4-vinylbenzyl chloride and divinylbenzene, followed by a quaternization reaction. As compared to those of non-porous, the porous polymers had high specific surface area and large number of active sites. Consequently, they exhibited excellent catalytic activity in the cyclization of sorbitol with dimethylcarbonate (DMC) to isosorbide. As a result, a high conversion of sorbitol (99%) was achieved with 83% yield of isosorbide under optimized conditions. Importantly, the catalysts could be easily separated by decantation and reused for five times without obvious loss of catalytic activity.

1. Introduction

Isosorbide is a versatile platform molecule with wide applications as a monomer or building block for biogenic polymer, functional materials, pharmaceutical molecules, and new solvents [1–8]. Various homogeneous catalysts have been developed to promote transformation of sorbitol to isosorbide, and this reaction is standing as the final step of industrial process for isosorbide from starch [9–13]. In this regard, the direct acid catalysis has dominated the field, which involves two step-wise protonation of the regioselective hydroxyl group, and each followed by cyclization with the carbon atom [14,15]. Recently, much effort has been made towards addressing the catalyst recyclability by grafting the reactive Brønsted acid into the skeleton of ionic liquids (ILs) [16]. However, serious drawbacks of environmental pollution arising from significant handling risk, corrosive nature of the catalyst and stability issues of the products are presented under this protocol. In comparison with these homogeneous catalysts, heterogeneous catalysts are industrially preferred for ease of separation and reuse. Therefore, solid acids with various structures are chosen to promote the transformation from sorbitol to isosorbide [17–23]. However, the catalytic system is still lack of practical value because of the requirement for high reaction temperature, long reaction time, abundant catalyst loading, reduced pressure condition and limited selectivity of product as well. Many studies have confirmed that neither homogeneous acid catalysts nor solid acids are ideal choices for achieving the green production of

isosorbide. Alternatively, the less explored base catalysis in the presence of stoichiometric amount of dimethyl carbonate functioning as carboxymethylating agent for hydroxyl group provides an attractive choice since it can be conducted under mild conditions with high efficiency [24]. Recently, such a conversion was achieved with a high yield in the presence of catalytic amounts of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) [25]. To the best of our knowledge, the application of basic heterogeneous system for synthesis of isosorbide has not been reported yet.

As one type of the potential and powerful supports, polymers have several advantages, such as easy preparation, structural tunability and fast recovery. The polymer-supported catalysts have been widely used in heterogeneous transition metal catalysis [26–29] and organocatalysis [30,31]. The polymers with uniform size and controlled pore structures enable themselves to be used to develop fixed-bed flow reactors for continuous flow processes [32,33]. On the other hand, supported ILs which achieve the advantages of combining the ILs and heterogeneous catalysis, have attracted growing interest [34–36]. For instance, supported acidic ILs have been employed as catalysts in the bulk and fine chemical industries [37,38]. Among these, the polymer supported acidic IL catalyst exhibits high selectivity in the dehydration of sorbitol to 1,4-anhydro-D-sorbitol [39]. Meanwhile, supported basic ILs show good catalytic activity for base-catalyzed reactions. Examples include Knoevenagel reaction [40], Henry reaction [32], transesterification reaction [41,42] and cascade reaction [43]. In most cases, the active

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<https://doi.org/10.1016/j.mcat.2018.07.019>

Received 16 March 2018; Received in revised form 19 July 2018; Accepted 19 July 2018

Available online 03 August 2018

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sites of the supported basic IL catalysts are basic anions, such as hydroxy, acetate or bicarbonate anions. The anions are introduced into the catalyst through an ion-exchange process. However, deactivation of the catalyst often occurs during the reaction imposed by the slow exchange of the catalytic anion with other less reactive anions [32].

We speculated that the nitrogen tricyclic group is more stable and efficient than the basic anion as an activator for DMC. A novel porous polymer supported IL with nitrogen tricyclic group was designed as heterogenous catalyst for the conversion of sorbitol with DMC. Compared with traditional basic anion type supported basic IL, this catalyst will be much more stable. Furthermore, the porous structure will ensure higher degree of exposure of active sites to the reactants.

In this article, we demonstrate a facile two-step synthetic method to prepare polymer-supported basic IL catalyst and the first heterogenous cyclization of sorbitol with DMC under basic condition. In the prepared catalyst, the catalytic sites were connected to catalyst matrix through covalent bond rather than basic anions such as hydroxyl. In addition, the catalyst with mesopores had much higher loading amount of active ILs moieties than nonporous one. By launching this novel basic polymer-supported IL catalyst, isosorbide could be obtained with 83% yield at 140 °C. The catalyst could be reused for five times with 7% decrease in yield of isosorbide.

2. Experimental

2.1. Materials

4-Vinylbenzyl chloride (VBC), divinylbenzene (DVB, mixtures of isomers, 78–80% grade) were purchased from Alfa Aesar Co. and distilled under vacuum before use. Azobisisobutyronitrile (AIBN), poly (vinyl alcohol) (PVA, degree of polymerization: 2080), 1,4-diazabicyclo [2.2.2]octane (DABCO), dimethyl carbonate (DMC), sorbitol were bought from Adamas Reagent, Ltd. Solvents (AR grade) were obtained from Beijing Chemical Works.

2.2. Preparation of catalysts

Step 1 : Synthesis of mesoporous copolymers

In a typical synthesis process of mesoporous copolymers of poly (VBC-DVB), AIBN (122 mg, 0.65 mmol, 0.1 equiv.) were charged into a 125 ml three-necked flask with a mechanical stirrer and reflux condenser. Then VBC (1.0 g, 6.5 mmol, 1 equiv.), DVB (2.5 g, 19.5 mmol, 3 equiv.) and porogen (3.5 mL) were added successively and stirred regularly until the mixture became uniform, followed by addition of PVA (1 wt.%, 20 mL). The polymerization was conducted at 70 °C under 300 rpm for another 12 h. The raw product poly(VBC-DVB) was collected and washed for five times with water and methanol to remove the dispersant. The PVB beads were obtained upon drying under vacuum at 60 °C for 12 h.

Step 2 : Synthesis of poly(VBC-DVB)-DABCO (PVDD)

The target catalyst was obtained by grafting DABCO on the polymer beads through quaternization reaction. In a 100 ml three-necked flask equipped with a reflux condenser and magnetic stir bar, the poly(VBC-DVB) beads (3 g) were reacted with DABCO (1.45 g, 13 mmol, 2.0 equiv.) in 1,4-dioxane (50 mL) at 100 °C for 24 h. Then the suspension was filtered and washed with 1,4-dioxane and methanol until the DABCO could not be detected in the final elution. Finally, the PVDD was obtained upon drying at 60 °C for 12 h.

2.3. Characterization

Elemental analysis was performed for carbon, hydrogen and nitrogen by using an Elemental vario EL cube. The nitrogen sorption isotherms at the temperature of liquid nitrogen were measured using a Micromeritics ASAP2460 system. The specific surface area and the pore size distribution were calculated using the Brunauer-Emmett-Teller

(BET) equation and the Barrett-Joyner-Halenda (BJH) model. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet380 FT-IR. The thermal decomposition of catalysts was analyzed by thermogravimetry/differential thermal analysis (TG/DTA, DTG-60H, Shimadzu, Japan). The experiment was performed at a temperature ramp rate of 10 °C/min in a nitrogen atmosphere. Transmission electron microscopy (TEM) was performed on a HT-7700 electron microscope (Hitachi, Japan) with an acceleration voltage of 80 kV. The cross-sectional specimen for TEM observation was prepared by Leica EM UC7 Ultramicrotome. Scanning electron microscope (SEM) experiments were performed on a SU-8020 microscope (Hitachi, Japan). Surface morphology of catalysts was characterized by a scanning electron microscope (SEM). X-ray photoelectron spectroscopy (XPS) was conducted using an ESCALAB 250Xi spectrometer. The charging effect was corrected by referencing the binding energy of C1s at 284.8 eV. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ASCEND spectrometer (¹H, 600 MHz). Chemical shifts were given with reference to the solvent resonance.

2.4. Catalyst performance evaluation and product analysis

The reaction was carried out in a sealed glass tube. Sorbitol (200 mg, 1.1 mmol, 1 equiv.), PVDD (50 mg), DMC (0.79 mL, 8.78 mmol, 8 equiv.) and methanol (0.4 mL) were added in a glass tube with a stir bar. The mixture was heated to 140 °C and reacted for 14 h. After that, the reaction was cooled to room temperature and the mixture was filtered to recover the catalyst. The filtrate was condensed and analyzed by high performance liquid chromatography (HPLC; ThermoFisher UltiMate3000) equipped with UV and refractive index (RI) detectors and a Rezex RCM-Monosaccharide column (300 × 7.8 mm). The column was operated at 80 °C by a column heater and the operating temperature of detectors was 40 °C. Distilled water was used as the eluent at a flow rate of 0.6 mL/min. Sorbitol conversion and isosorbide yield were calculated according to the following formula:

$$C_{\text{sorbitol}}\% = (\text{moles of reacted sorbitol} / \text{moles of initial sorbitol}) \times 100\%$$

$$Y_{\text{isosorbide}}\% = (\text{moles of carbon in the produced isosorbide} / \text{moles of initial sorbitol}) \times 100\%$$

The crude product was purified by recrystallization from ethyl acetate. The NMR spectra was shown in Figure S1 and the NMR data correspond to the reported values [25].

2.5. Procedure for recycling the catalyst

The reactions were repeatedly conducted under identical experimental conditions as mentioned above. After each run, the resulted solution of products could be separated easily by decantation. The catalyst was washed with methanol and then dried in the oven at 60 °C for 1 h, then used directly without regeneration for next cycle.

3. Results and discussion

3.1. Preparation of porous polymer-supported IL catalysts

The basic polymer-supported IL catalysts were prepared through suspension polymerization between VBC and DVB, followed by nucleophilic addition reaction involving the resulting polymeric beads and DABCO as shown in Scheme 1. A variety of solvents that are insensitive to polymerization conditions, such as *n*-hexane, hexadecane and toluene, were employed as the porogen to synthesize poly(VBC-DVB) beads, thereby the influences on the pore structure of poly(VBC-DVB) were investigated (Table 1, entries 1–3). It is well known that toluene is a thermo-dynamically good solvent for linear polystyrene during the polymerization. However, alkanes can dissolve the mixture of monomers but not the copolymer that was generated *in situ*. In addition, poly(VBC-DVB) with a high ratio of VBC and DVB was also

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