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



Yao-Feng Wang<sup>a</sup>, Bao-Hua Xu<sup>a,b</sup>, Yi-Ran Du<sup>a,b</sup>, Suo-Jiang Zhang<sup>a,b,\*</sup>

<sup>a</sup> Beijing Key Laboratory of Ionic Liquids Clean Process, Key Laboratory of Green Process and Engineering, State Key Laboratory of Multiphase Complex Systems, Institute

of Process Engineering, Chinese Academy of Sciences, Beijing 100190, PR China

<sup>b</sup> School of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, Beijing 100049, PR China

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#### 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 stepwise 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-7ene (DBU) [25]. To the best of our knowledge, the application of basic heterogenous 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 heterogenous 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

E-mail address: sjzhang@ipe.ac.cn (S.-J. Zhang).

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<sup>\*</sup> Corresponding author.

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 (<sup>1</sup>H, 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:

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

 $Y_{isosorbide}$ % = (moles of carbon in the produced isosorbide / moles of initial sorbitol) × 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  $1 \sim 3$ ). 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



poly(VBC-DVB)

Scheme 1. Synthesis of poly(VBC-DVB)-DABCO (PVDD).

 Table 1

 Preparation of porous polymer-supported IL catalysts.

Entry	Sample	Porogen	VBC/DVB/Porogen
1 2 3	PVDD-1 PVDD-2 PVDD 3	<i>n</i> -hexane hexadecane	1/3/3.5 1/3/3.5 1/2/2.5
4 5	PVDD-4 PVDD-5	toluene –	2/3/4 1/3/0



Fig. 1. Comparisons of FT-IR spectra of PVDD-1  $\sim$  4, poly(VBC-DVB) and DABCO.

prepared (entry 4). Moreover, the PVDD-5 was synthesized without porogen as a comparison (entry 5).

#### 3.2. Characterization of catalysts

FT-IR spectra of poly(VBC-DVB) and PVDD were shown in Fig. 1. As

Table 2Porosity of the polymer-supported IL catalysts.

Entry	Sample	$S_{\rm BET}~(m^2/g)^a$	$V (\text{cm}^3/\text{g})^{\text{b}}$	$D_{\rm p}~({\rm nm})^{\rm c}$
1 2 3 4	PVDD-1 PVDD-2 PVDD-3 PVDD-4	271.1 162.6 287.2 155.9	0.44 0.53 0.29 0.17	7.1 15.6 5.1 3.8
5	PVDD-5	1.2	0.002	3.4

**PVDD** 

<sup>a</sup> BET surface area.

<sup>b</sup> Total pore volume.

<sup>c</sup> BJH mesopore diameter calculated from the adsorption branch.

compared to poly(VBC-DVB), PVDD-1~4 showed obvious bands at 1058 and 3426 cm<sup>-1</sup>, of which the former was assigned to the presence of C–N bond. These results demonstrated that the introduction of the DABCO functional group into the polymer skeleton upon quaternization was successful.

The PVDD-1~5 were further characterized by XPS technology (Fig. 2). Two characteristic peaks of N1*s* were observed (Fig. 2A). The peak at 399.6 eV is ascribed to the tertiary amine N and the peak at 402.3 eV is attributed to the quaternary ammonium N. The assignment of amino groups was in good agreement with previous studies [44]. The Cl2*p* spectrum is the expected doublet due to the spin orbit coupling (Fig. 2B). The Cl2*p*<sub>1/2</sub> peak is found at 198.7 eV, and the Cl2*p*<sub>3/2</sub> is found at 197.2 eV. This doublet was assigned to the Cl<sup>-1</sup> of IL moieties on PVDDs according to literature [45,46]. No chlorine signals due to covalent C-Cl bonds identified by XPS were detectable in any PVDDs. The XPS spectra further confirmed the successful quaternization of DABCO with benzyl chloride moiety on poly(VBC-DVB).

The specific surface area and porosity of the polymer-supported ILs were characterized by nitrogen adsorption isotherms. The results were listed in Table 2. There was significant difference in specific surface areas between non-porous (PVDD-5) and porous (PVDD-1 ~ 4) polymer-supported ILs. The pore structure of PVDD was significantly affected by the types of porogen used, with the  $S_{\text{BET}}$  value decreasing in the following order: toluene > *n*-hexane > hexadecane. The highest  $S_{\text{BET}}$ 



Fig. 2. XPS spectra of N1s (A) and Cl2p (B) for PVDD-1 (a), PVDD-2 (b), PVDD-3 (c), PVDD-4 (d) and PVDD-5 (e).



Fig. 3. Nitrogen adsorption-desorption isotherms (A) and pore size distribution curves (B) of basic porous polymer-supported IL catalysts.



Fig. 4. TEM images of the sliced specimen: PVDD-1 (A), PVDD-2 (B), PVDD-3 (C), PVDD-4 (D).

Table 3 The loading of basic site in PVDD-1~5.

Samples N element content		Loading amount
	(wt.70)	(mmor/g)
PVDD-1	3.00	1.07
PVDD-2	2.68	0.96
PVDD-3	3.74	1.33
PVDD-4	5.44	1.94
PVDD-5	0.80	0.28

value was  $287.2 \text{ m}^2/\text{g}$  denoted as PVDD-**3** when toluene was used as the porogen. In comparison, the largest pore volume was  $0.53 \text{ cm}^3/\text{g}$  found in PVDD-**2** when hexadecane was used as the porogen. Besides, nitrogen (N<sub>2</sub>) adsorption/desorption isotherm of PVDD-**1** ~ **3** showed the type IV, III and II isotherms, respectively, with hysteresis loops in the relative pressure between 0.45 and 0.9, indicating the formation of mesopores [47–49] (Fig. 3). On the other hand, the N<sub>2</sub> adsorption/desorption isotherms of PVDD-**1** and PVDD-**3** in the high relative pressure between 0.9 and 1.0 become flat and close themselves, suggesting no macropore existence in the catalysts. As for PVDD-**2** with largest pore volume, the sharp uptake at high relative pressure between 0.9 and 1.0, together with the pore size distribution, suggested that its pore structure was dominated by large mesopores and macropores

[49,50]. As the IL units were the active species, large amount of loading of the reactive site for quaternization in porous polymer was tested, by increasing the molar ratio of VBC (PVDD-4). The adsorption/desorption isotherms of PVDD-4 were similar to PVDD-3, which suggested the same porogen (toluene) in the polymerization. However, higher VBC/DVB ratio led to a decrease of pore volume  $(0.17 \text{ cm}^3/\text{g vs}. 0.29 \text{ cm}^3/\text{g})$ . In addition, the  $S_{\text{BET}}$  value decreased from 287.2 to 155.9 m<sup>2</sup>/g, which was attributed to a lower concentration of DVB incorporated into the poly(VBC-DVB). This result is consistent with the observation in the synthesis of mesoporous poly(ionic liquid)-based copolymer reported by Yuan and co-workers [51].

In order to further analyze the porosity inside the porous polymersupported ILs, the sliced specimen of PVDD was observed by TEM (Fig. 4). The TEM images with scale bar 500 nm and 50 nm confirmed the pores were well distributed in PS/IL networks. Furthermore, TEM images were in good agreement with the results of BET analysis. PVDD-1, PVDD-3 and PVDD-4 possessed mesopores. And pore structure of PVDD-2 was dominated by large mesopores and macropores.

To quantify the loading of active ILs moieties that were introduced into the resulted PVDD, the PVDD- $1 \sim 5$  were analyzed by elemental analysis (Table S1). The results revealed that the nitrogen mass fraction in porous PVDD- $1 \sim 4$  were 3.00%, 2.68%, 3.74%, 5.44%, indicating that the loading of basic site in PVDD- $1 \sim 4$  were 1.07 mmol/g, 0.96 mmol/g, 1.33 mmol/g and 1.94 mmol/g, respectively (Table 3).



Fig. 5. The whole and magnified SEM images of PVDD-1 (A), PVDD-2 (B), PVDD-3 (C), PVDD-4 (D), PVDD-5 (E).



Fig. 6. Thermogravimetric curves of PVDDs.

However, the nitrogen mass fraction in non-porous PVDD-5 was 0.8% and the basic site loading which only distribute over the surface is 0.28 mmol/g.

The morphology of the synthesized PVDD-1  $\sim$  5 was characterized by SEM as shown in Fig. 5. All of them exhibited spherical structures with the diameters in the range of  $250 \sim 400 \,\mu$ m. At high



Scheme 2. The cyclization of sorbitol with DMC catalyzed by PVDD. Reaction conditions: sorbitol (200 mg, 1.1 mmol, 1 equiv.), PVDD- $1 \sim 5$  (50 mg), DMC (0.79 mL, 8.78 mmol, 8 equiv.) and methanol (0.4 mL).

magnifications, the surfaces of PVDD-1 and PVDD-2 were much rougher compared to PVDD- $3 \sim 5$ .

The thermal stability of PVDDs was investigated by thermogravimetric analysis (Fig. 6). The thermogravimetric curves showed that the degradation temperature of PVDD-1~2 and PVDD-3~4 were about 200 °C and 250 °C, respectively. In addition, the weight loss percentages of PVDD-1~4 were about 10%, 9%, 13% and 22%, respectively, at the first stage of weight loss. It was caused mainly by the loss of DABCO group accompanied with breakup of C–N bond. According to the results, it could be deduced that the loading of ILs moieties in PVDD-1~4 were 0.89 mmol/g, 0.80 mmol/g, 1.16 mmol/g and 1.96 mmol/g, respectively. These loading of ILs obtained from TG analysis were found to be in good agreement with those from elemental analysis.



Fig. 7. The catalytic performance of PVDD-1  $\sim$  5. Reaction conditions: sorbitol (200 mg, 1.1 mmol, 1 equiv.), PVDD-1  $\sim$  5 (50 mg), DMC (0.79 mL, 8.78 mmol, 8 equiv.) and methanol (0.4 mL), 120 °C, 12 h.



**Fig. 8.** The influence of reaction temperature. Reaction conditions: sorbitol (200 mg, 1.1 mmol, 1 equiv.), PVDD-4 (50 mg), DMC (0.79 mL, 8.78 mmol, 8 equiv.) and methanol (0.4 mL), 12 h.



Fig. 9. The effect of reaction time on the yield of isosorbide. Reaction conditions: sorbitol (200 mg, 1.1 mmol, 1 equiv.), PVDD-4 (50 mg), DMC (0.79 mL, 8.78 mmol, 8 equiv.) and methanol (0.4 mL), 140  $^\circ$ C.



**Fig. 10.** Conversion of sorbitol and yield of isosorbide in recycle tests under optimized conditions: sorbitol (200 mg, 1.1 mmol, 1 equiv.), PVDD-4 (50 mg), DMC (0.79 mL, 8.78 mmol, 8 equiv.) and methanol (0.4 mL), 140 °C, 14 h.

#### 3.3. Catalytic performance

The formation of isosorbide from sorbitol with PVDD-1 as the catalyst was initially conducted in refluxing DMC under atmospheric pressure in the reactor with a condenser. However, the conversion of sorbitol was less than 5% after 24 h. It was speculated that the starting materials did not contact efficiently with the solid catalyst since the melting point of sorbitol (95 °C) was higher than the specific reaction temperature (90 °C/1 atm). Consequently, the reaction was moved into a sealed reactor and the temperature was increased to 120 °C, thereby providing isosorbide with 26% yield in 36 h. To our delight, the yield was increased to 43% when methanol (0.4 mL) was used as an additive. The by-product in the absence of methanol was isolated and the effect of methanol will be discussed later. After the initial examination, the reaction of sorbitol and DMC catalyzed by PVDD in presence of methanol was chosen as the model reaction for further optimization (Scheme 2).

The catalytic performance of PVDD- $1 \sim 5$  were evaluated by using the catalytic cyclization of sorbitol as shown in Fig. 7. Sorbitol was reacted with DMC (8 equiv.) in the presence of methanol (0.4 mL) over the catalysts (25 wt.%) for 12 h under 120 °C. Evidently, sorbitol was significantly converted (more than 89%) in the presence of porous PVDD- $1 \sim 4$ , but most sorbitol retained with PVDD-5 under identical conditions. Moreover, various kinds of intermediates rather than the desired isosorbide were obtained with PVDD-1 and PVDD-2. In comparison, the yield of isosorbide was obviously improved in the case of either PVDD-3 (yield: 37%) or 4 (yield: 58%). The result suggested that the yield of isosorbide increased with the increasing of the basic site loading of ILs moieties in PVDD-1~5 which was determined by elemental analysis. An approximated linear positive correlation between catalytic activities of PVDD and their quantity of basic sites was shown in Figure S2. Therefore, the PVDD-4 was selected as the optimal catalyst for subsequent experiments.

The influence of reaction temperature was also examined by using PVDD-4 as the catalyst (Fig. 8). The variation in the conversion of sorbitol PVDD was found less than 5% within the range of temperature scope, with a higher temperature being slightly favorable. The yield of isosorbide was less than 20% at relatively lower temperatures, such as 100 °C and 110 °C. Instead, intermediate of unrecognized structure was mainly obtained under these conditions. In contrast, the yield was greatly improved at relatively higher temperatures. It was increased from 58% to 73% with the increase of temperature from 120 to 140 °C. The suitable temperature was set as 140 °C.

The effect of reaction time was also examined with PVDD-4 at



Scheme 3. Proposed mechanism of cyclization of sorbitol catalyzed over the PVDD catalyst.



Fig. 11. Structure of the cyclic carbonates byproduct A.

140 °C. As shown in Fig. 9, almost full conversion of sorbitol was achieved after reaction for 12 h. A 83% yield of isosorbide was obtained after reaction for additional 2 h. With prolonging the reaction time, the yield was decreased owing to the increase of by-products, which were observed by HPLC. Indeed, the use of catalyst PVDD-4 with methanol (0.4 mL) as an additive at 140 °C within 14 h provided isosorbide with 83% yield, which was also established as the optimal conditions.

#### 3.4. Recycling experiments

The experiments on catalyst recycling using the PVDD-4 have also

been carried out for five times at 140 °C for 14 h (Fig. 10). The PVDD-4 showed good recyclability and stability after recycling for five times under the optimized reaction conditions. The reaction required 5 h to reach almost full conversion of sorbide (95%–98%) for each cycle. Complete conversion was observed at 6 h in each cycle. In particular, the yield of isosorbide decreased from 83% to 77% after five cycles. In addition, there was almost no difference in FT-IR spectra before and after reuse (Figure S3). Herein, it could be concluded that the porous polymer-supported ILs could serve as stable and efficient catalysts for the cyclization of sorbitol to isosorbide.

#### 3.5. Mechanism of cyclization reaction

In the previous homogeneous cyclization, reaction of diols with DMC in a stoichiometric excess of a strong base or catalyzed by basic catalyst led to the formation of related 5-membered cyclic ethers [24,25]. This transformation encompasses both methoxycarbonylation via BAc2 mechanism, i.e., formation of the intermediate, and cyclization via the BA12 mechanism, i.e., alkylation reaction. The basic reagent or catalyst was capable of enhancing the reactivity of DMC and hydroxyl group. In the present work, the catalytic reaction path of cyclization over basic polymer-supported IL was consistent with the reported homogenous reactions. As shown in Scheme 3, DMC was activated by PVDD and adduct I was formed. Sorbitol reacted with adduct I via BAc2 mechanism resulting carbonate intermediate II. The intermediate II could also be activated by PVDD forming the adduct III. The methoxide group served as a base deprotonated the 4-hydroxyl group of the intermediate III. And then subsequent intramolecular cyclization by BA12 mechanism leading to the formation of 1,4-sorbitan IV. The 1,4-sorbitan underwent another similar cyclization progress affording the



**Scheme 4.** Reversible reaction in the presence of methanol.

#### product isosorbide.

The promotion of methanol to this transformation was also explored. To achieve this goal, the byproduct from the reaction in absence of methanol was collected. Then it was isolated by recrystallization for purification. The single crystal structure was determined by the X-ray single crystal diffraction (Fig. 11) [52]. It was indicated that the byproduct **A** was formed during the cyclization in absence of methanol. This cyclic carbonate **A** could further transform to isosorbide in the presence of methanol. Thus, a reversible reaction existed (Scheme 4).

## 4. Conclusions

A series of novel basic porous polymer-supported ILs catalysts with uniform size, high surface area and good stability were synthesized through a concise method. Basic ILs were successfully supported on the internal surface of the mesoporous polymer by covalent bond. The porous catalysts have more active sites than the nonporous one and showed higher catalytic activity. Such porous supported ILs polymer were successfully applied as solid basic catalysts for the synthesis of isosorbide from sorbitol and DMC. Furthermore, this catalyst could be separated by simple decantation and reused for five times without significant loss of activity. Therefore, this novel basic porous polymersupported ILs were good recyclable basic catalysts for the production of isosorbide.

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#### Appendix A. Supplementary data

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  [52] CCDC-1820201 contains the supplementary crystallographic data of the byproduct

  A. These data can be obtained free of charge from The Cambridge Crystallographic

Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.