Preparation and Properties of Silane Molecular Sieve Supported Composite Polyether Ionic Liquids Catalysts

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Abstract: In this work, three composite polyether imidazole ionic liquids (PIILs) supported on molecular sieve (MCM-22) with terminal hydroxyl, carboxyl and amino groups were synthesized with the help of silane coupling agent 3-chloropropyltriethoxysilane (CPTES). They were used for cycloaddition of CO$_2$ and propylene oxide (PO) in a fixed-bed reactor. The results showed that MCM-22-CPTES-HOOC-[PECH-MIM]Cl/[ZnBr$_2$] was the best catalytic properties in this reaction. The conversion rate and selectivity were 92.7% and 82.7%.

1. Introduction

As a greenhouse gas, carbon dioxide is an abundant C1 resource. If carbon dioxide can be converted into chemical products, waste can be turned into treasures and new ideas for greenhouse gas treatment can be provided[1-2]. However, carbon dioxide is chemically stable, so the choice of catalyst is especially important for the conversion of carbon dioxide[3-5]. Ionic liquids are used in the cycloaddition reaction of carbon dioxide with alkylene oxide to synthesize propylene carbonate(PC) due to their excellent catalytic properties[6-7]. However, traditional ionic liquid catalysts are difficult to separate and recover products because of their high viscous liquid state, and are limited to batch reactions in autoclave, which limits the industrial application of ionic liquids (IL)[8]. The above problems can be effectively solved by immobilizing ionic liquids onto the carrier to realize the immobilization of IL.

In this work, we reported three kinds of composite polyether imidazole ionic liquids (PIILs): MCM-22-CPTES-HO-[PECH-MIM]Cl/[ZnBr$_2$], MCM-22-CPTES-HOOC-[PECH-MIM]Cl/[ZnBr$_2$] and MCM-22-CPTES-H$_2$N-[PECH-MIM]Cl/[ZnBr$_2$] immobilized on molecular sieve (MCM-22) supporter covalently with the help of silane coupling agent 3-chloropropyltriethoxysilane (CPTES), which exhibited good chemical and thermal stability, and were applied in the preparation of PC by cycloaddition of CO$_2$ and PO as a novel heterogeneous catalyst. In addition, flexible automation, reliability process and low mechanical consumption were easily achieved in industrial continuous operation.

2. Experimental

2.1. Reagents and Instruments

Three PIILs, i.e., HO-[PECH-MIM]Cl, HOOC-[PECH-MIM]Cl and H$_2$N-[PECH-MIM]Cl, were prepared according to our published procedures. Zinc bromide (98.0%), toluene (99.5%), acetonitrile (99.0%), propylene oxide (99.5%). Above all reagents and materials (analytic grade) were purchased...
from Sinopharm Chemical Reagent Co., Ltd. (China) 3-chloropropyltriethoxysilane (CPTES, 95%) was purchased from Aladdin Chemical Co. CO₂ gas (99.95%) was offered by Petrochina Liaoyang Yifang Petrochemical Company (China). The MCM-22 was provided from Petrochina Fushun Petrochemical Company (China). All materials were used without further purification.

Instruments used in this study include MAGNA-IR750 Fourier Transform Infrared Spectrometer (FT-IR); TM3000 Scanning Electron Microscope (SEM); D/max-2400 Automatic X-ray Diffractometer (XRD); PARR4523 Catalytic Device (PARR, USA); 1790F Gas Chromatograph (GC) (Agilent Technologies, Inc.); D08-8C Carbon Dioxide Flowmeter; DF-101S Magnetic Stirrer; SFX-2L Rotary Evaporator; DZF-6050 Vacuum Drying box; 2-XZ-4 rotary vane vacuum pump. The catalytic experimental fixed bed reactor (Tianjin Pengxiang Technology Co., Ltd, China) was applied in the process of catalysis.

2.2. Preparation of MCM-22-CPTES-PIILs/(ZnBr₂)

2.2.1. Synthesis of MCM-22-CPTES. CPTES (3.5 mL) was added a flask where existed a mixture of MCM-22 (3.5 g) and toluene (50 mL) solvent slowly to prepare MCM-22-CPTES. The mixture was refluxed at 110℃ for 24 h, after that the flask was cooled to room temperature. The solvent was removed by distillation, and the solid product was washed three times with ethyl acetate and then dried at 80 °C for 12 h under vacuum to afford the MCM-22-CPTES (4.2 g).

2.2.2. Synthesis of PIILs/(ZnBr₂). Three PIILs, i.e., HO-[PECH-MIM]Cl, HOOC-[PECH-MIM]Cl and H₂N-[PECH-MIM]Cl, were prepared according to our published procedures. Epichlorohydrin (ECH) was polymerized to form poly-epichlorohydrin (PECH) which had –OH groups, used chloroacetic acid and ammonia to reacted with PECH to achieve –COOH and –NH₂ groups respectively. Then three types of PECH with –OH, -COOH and –NH₂ reacted with imidazole to obtain three PIILs. Then, a given amount of ZnBr₂ was added into three PIILs, respectively, and resulting mixtures were stirred at reflux for 24 h. As the reaction proceeded, the mixtures became more viscous with a darker color change. When the reactions were finished, three reddish brown liquids were obtained, namely three composite PIILs, i.e., HO-[PECH-MIM]Cl/[ZnBr₂], HOOC-[PECH-MIM]Cl/[ZnBr₂], and H₂N-[PECH-MIM]Cl/[ZnBr₂].

2.2.3. Synthesis of MCM-22-CPTES-PIILs/(ZnBr₂). Then PIILs/[ZnBr₂] and MCM-22-CPTES (4.2 g) were poured into the flask with acetonitrile solvent (50 ml), the intermixture was refluxed at 80°C for another 24 h, the acetonitrile solvent was removed by rotary evaporation to obtain the immobilized catalyst, i.e., MCM-22-CPTES-PIILs/[ZnBr₂]. Among the synthesis procedure of MCM-22-CPTES-HO-[PECH-MIM]Cl/[ZnBr₂] is illustrated in Scheme 1.

![Scheme 1](image)

Scheme 1. Synthesis of the immobilized catalyst MCM-22-CPTES-HO-[PECH-MIM]Cl/[ZnBr₂]

2.2.4. Typical procedure for the synthesis of PC from PO and CO₂. A small amount of quartz sand were filled in the front and rear ends of the catalyst container, and 7.0 g of the immobilized catalyst was placed in the middle of the container of the fixed bed catalytic reactor. CO₂ was output from a high-pressure cylinder while PO was output through a pump into fixed bed reactor. PO was heated in
the preheater into the packed column to react with CO\(_2\) and there was no additional solvent would be added during the reaction. The product from the reactor was collected every 5 h after cooling, and the purity of the product propylene carbonate (PC) was tested, and the yield was calculated.

3. Results and discussion

3.1. Characterization of MCM-22-CPTES-PIILs/(ZnBr\(_2\))\(_2\)

3.1.1. FT-IR. FT-IR studies on MCM-22-CPTES and its immobilized catalysts were carried out (Figure 1). The siloxy groups of the molecular sieves in the spectrum were reflected in the four curves of 1210 cm\(^{-1}\) and 797 cm\(^{-1}\). Compared with the infrared spectrum (a) of the silane molecular sieve as it is, the spectrum (b, c, d) of the catalyst is greatly changed. For immobilized PIILs/(ZnBr\(_2\))\(_2\) catalysts, there displayed 3145 cm\(^{-1}\) and 2938 cm\(^{-1}\) characteristic peaks assigned to stretching vibrations of CH\(_3\) and CH\(_2\). The hydroxyl peak broadening in 3360 cm\(^{-1}\) as water molecules adsorbed on catalysts surface. These functional groups of PIILs/(ZnBr\(_2\))\(_2\) were removed during the preparation of immobilized catalysts, so the terminal peaks were not existed. All vibration peaks indicated the successful immobilization of PIILs/(ZnBr\(_2\))\(_2\).

3.1.2. XRD. The XRD patterns of MCM-22-CPTES and its immobilized catalysts were shown in Figure 2. It can be seen from the XRD spectrum that the diffraction peaks of the three catalysts were largely different from the crystallinity of the silane molecular sieve. In pattern (a), the high intensive peaks at 7.14°, 7.85°, 9.59°, 12.8°, 19.8°, 22.0°, 24.9° and 25.9° are the characteristic diffraction peaks of MCM-22, indicating a good crystallinity of synthesized MCM-22-CPTES.

After the three composite PIILs were immobilized, the XRD spectrum changed greatly. The strong and sharp diffraction peak of the original molecular sieve became a very weak peak, and some peaks were not observed. This indicated that during the PIILs immobilization process, the hydrogen on the terminal group was condensed with the chlorine at the end of the silane molecular sieve, and the released strong acid HCl gas destroys the crystallinity of the molecular sieve. The XRD analysis resulted further demonstrate the successful preparation of the silane molecular sieve supported PIILs catalyst.
Figure 2. XRD of the silane molecular sieve MCM-22-CPTES and immobilized catalysts (a) MCM-22-CPTES; (b) MCM-22-CPTES-HO-[PECH-MIM]Cl/[ZnBr₂]; (c) MCM-22-CPTES-HOOC-[PECH-MIM]Cl/[ZnBr₂]; (d) MCM-22-CPTES-H₂N-[PECH-MIM]Cl/[ZnBr₂]

3.1.3. SEM. SEM images of MCM-22-CPTES and its immobilized catalysts were provided in Figure 3. Compared with the original MCM-22-CPTES(a) of silane molecular sieve, the surface of the immobilized catalyst was covered with a thin but less pronounced material. This means that only a small amount of complex PIILs was immobilized on the surface of the molecular sieve, and most of it was retained in the pores. SEM results further suggested the successful immobilization of PIILs/(ZnBr₂)₂ catalysts on MCM-22-CPTES and the solid state of obtained immobilized catalysts.

Figure 3. SEM of the silane molecular sieve MCM-22-CPTES and immobilized catalysts (a) MCM-22-CPTES; (b) MCM-22-CPTES-HO-[PECH-MIM]Cl/[ZnBr₂]; (c) MCM-22-CPTES-HOOC-[PECH-MIM]Cl/[ZnBr₂]; (d) MCM-22-CPTES-H₂N-[PECH-MIM]Cl/[ZnBr₂]

3.2. Effect of Different Catalyst on Catalytic Performance
The catalytic performance of the above-mentioned three immobilized catalysts for synthesizing PC with CO₂ and PO was investigated and the results were shown in Table 1.
Table 1. Effects of different catalysts on the catalytic performance

| Catalyst                        | Conversion rate (%) | Selectivity (%) | Yield (%) |
|---------------------------------|---------------------|----------------|-----------|
| MCM-22-CPTES-HO-[PECH-MIM]Cl/[ZnBr₂] | 91.3                | 81.8           | 74.7      |
| MCM-22-CPTES-HOOC-[PECH-MIM]Cl/[ZnBr₂] | 93.2                | 83.6           | 77.9      |
| MCM-22-CPTES-H₂N-[PECH-MIM]Cl/[ZnBr₂] | 92.8                | 82.7           | 76.7      |

1Reaction condition: catalyst, 2.5% (wt%); temperature, 120 °C; pressure, 3.0 MPa; time, 5 h.

It can be seen from the results in the table that the type of the composite PIILs still affected the cycloaddition reaction. Among which MCM-22-CPTES-[PECH-MIM]Cl/[ZnBr₂] has better catalytic activity than the other two immobilized catalysts, because there was still a small portion of HOOC-[PECH-MIM]Cl/[ZnBr₂] physical adsorbed on the surface of MCM-22-CPTES still had acidity which was good for ring opening[9-10]. The conversion rate and selectivity were 92.7% and 82.7%.

4. Conclusions
In conclusion, three composite PIILs that MCM-22 was immobilized with CPTES catalysts were prepared successfully and used in the cycloaddition reaction of CO₂ and PO. Among the three catalysts investigated, MCM-22-CPTES-HOOC-[PECH-MIM]Cl/[ZnBr₂] exhibited excellent catalytic performance in fixed bed reactor. MCM-22-CPTES-HOOC-[PECH-MIM]Cl/[ZnBr₂] exhibited the highest catalytic activity in the synthesis of PC under the optimized condition: the reaction temperature of 120 °C, the pressure of 3 MPa and the time of 5 h, the conversion rate was 93.2% and selectivity was 83.6%.

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