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Short Communication

Basic ionic liquid supported on mesoporous SBA-15: An efficient heterogeneous catalyst for epoxidation of olefins with H_2O_2 as oxidant

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1. Introduction

The epoxidation of olefins is of great interest due to the importance of epoxides in the manufacture of fine chemicals [1,2]. For the economic and environmental reasons, hydrogen peroxide (H_2O_2) is an ideal oxidant for epoxidation of olefins because of its ease of handling and high active oxygen content, as well as the fact that water is the only byproduct [3–5]. Epoxidation of olefins with H₂O₂ has been extensively studied over the last two decades using various of catalysts such as Ti [6], Mn [7], W [8], and Re [9]. A major drawback of the processes mentioned above is the using transition metals as catalytically active components. Alternatively, epoxidation of olefins is usually performed under strongly alkaline conditions using bases such as NaOH, Na₂CO₃ or KOH with H₂O₂ as the oxidant. However, using these strong bases has numerous disadvantages such as large production of industrial waste, severe corrosion and difficulty in catalyst recovery [10]. To solve the problems mentioned above, various solid basic catalysts such as hydrotalcites [11-13], hydroxyapatites [14,15] and basic metal oxides [16] have been used for epoxidation of olefins using H₂O₂.

In recent years, ionic liquids (IL) have received increasing interest in the area of green chemistry [17]. Initially, ionic liquids were usually used as alternative reaction solvents, but today they have been employed as catalysts for different reactions [18–21]. Among them, basic ionic liquids have attracted unprecedented attention, because compared to the combination of inorganic base and ionic liquid they

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ABSTRACT

Basic ionic liquid functionalized mesoporous silica SBA-15 was prepared and characterized by XRD, N₂ adsorptiondesorption, FT-IR and TEM. The catalyst demonstrated to be an efficient heterogeneous catalyst for olefin epoxidation using H_2O_2 as oxidant. The catalyst could be recycled at least five times without appreciable loss of catalytic activity.

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exhibited more advantages such as high catalytic efficiency and easy catalyst recycling for some base-catalyzed processes [22–24]. Up to now, basic ionic liquids have been successfully introduced as catalysts to catalyze various reactions such as Heck reaction [25], Michael addition [26] and Markovnikov addition [27].

Although the catalytic ability of basic IL has been successfully demonstrated in many reactions, the chemical industry still prefers to use heterogeneous catalysts due to the easy separation. Furthermore, it has been reported that supported ILs led to more improvements in efficiency than homogenous ionic liquids [28,29]. Therefore, it is highly desirable to supported basic ILs onto solid supports. Our group has successfully used supported basic ILs to catalyze hydrolysis of propylene carbonate reaction [30] and Knoevenagel condensation reaction [31].

Herein, we report a catalytic system based on SBA-15 molecular sieves supported basic ILs, which proved to be efficient for epoxidation of olefins using H_2O_2 as oxidant.

2. Experimental

2.1. Catalysts preparation

Mesoporous SBA-15 was prepared according to the reported method [32]. The preparation of chloropropyltriethoxysilane modified SBA-15 molecular sieves was carried out as follows. 2.0 g of SBA-15 was dispersed in 50 ml dry toluene and to this suspension 3 ml chloropropyltriethoxysilane (CPTES) was added. The resulting mixture was refluxed under N₂ protection for 24 h. After cooling to room temperature, the solid was separated by filtration and washed in a Soxhlet apparatus with dichloromethane for 24 h. After filtration, the solid was dried at 60 °C under reduced pressure to give the

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Scheme 1. Preparation of the SBA-15 supported basic ionic liquid.



Fig. 1. Small angle XRD patterns of (a) SBA-15 and (b) SBIL.

product of CPTES/SBA-15 (Scheme 1 step I). Grafting IL of 1-methyl-3-(chloropropyltriethoxysilane) imidazolium chloride (CIL) on SBA-15 was as follow: a mixture of CPTES/SBA-15 (2.0 g) and 1-methyl imidazole in 50 ml dry toluene was refluxed for 24 h under N₂ protection. After cooling to room temperature, the reaction mixture was filtered, and the resulting solid was washed with toluene and methanol, followed by drying at 60 °C under reduced pressure for 24 h. The obtained product was designated SCIL (Scheme 1 step II). The loading of the IL was obtained to be 0.39 mmol/g according to the results of elementary analysis. Finally, basic IL of 1-methyl-3-(chloropropyltriethoxysilane) imidazolium hydrogen carbonate (BIL) was supported on SBA-15 by ion exchange. Solid potassium hydrogen carbonate and SCIL were added to 50 ml distilled water, and the mixture was stirred vigorously at room temperature for 24 h. Then the mixture was filtrated and washed with distilled water until neutral, followed by drying at 70 °C under reduced pressure for 24 h to give the product which was designated SBIL (Scheme 1 step III).

2.2. Catalysts characterization

X-ray powder diffraction (XRD) experiments were carried out on a PANalytical X'pert Pro diffractometer. The N_2 adsorption/desorption isotherms were measured using a Micromeritics ASAP 2010 instrument at liquid N_2 temperature. Fourier transform infrared (FT-IR) measurements were carried out using a Bruker IFS 120HR FT-IR sepectrometer and KBr pellets. Transmission electron microscopy (TEM) images were obtained on a Hitachi H-600 electron microscope.

2.3. Catalytic performance

A typical procedure of the epoxidation of cyclohexene was as follow: A mixture of cyclohexene (4 mmol), SBIL (100 mg), benzonitrile (10 mmol), 30% aq. H_2O_2 (2.4 ml, 24 mmol) and MeOH (10 ml) was stirred at 60 °C for 24 h. The catalysts were separated by filtration and the filtrate was treated with MnO₂ and anhydrous MgSO₄ for GC analyses. The used catalysts were washed with MeOH and then dried under reduced pressure for recycle. Qualitative analysis was conducted with a HP 6890/5973 GCMS with chemstation containing a NIST Mass Spectral Database. Quantitative analysis was conducted with an Agilent 6820 GC equipped with a FID using an internal standard method.

3. Results and discussion

3.1. Catalysts characterization

Low-angle powder X-ray diffraction patterns of SBA-15 and SBIL are depicted in Fig. 1. SBA-15 patterns showed an intense peak assigned to reflections at (100) and two low-intensity peaks at (110) and (200), indicating a significant degree of long-range ordering in the structure and a well-formed hexagonal lattice [32]. The sample of SBIL also exhibited three clear diffraction peaks in low angle region, which indicated that the mesoporous structure of the support remained intact under the conditions used for functionalization. Compared with pure SBA-15, the intensity of reflections of (100)



Fig. 2. N2 adsorption-desorption isotherms and pore diameter distributions of (a) SBA-15 and (b) SBIL.



Fig. 3. FT-IR spectra of (a) SBA-15, (b) CPTES/SBA-15 and (c) SBIL.

peak of SBIL was slightly decreased, which could be mainly attributed to the effect of pore-filling of organic components that reduced scattering contrast between the pores and the framework of SBA-15 [33]. Furthermore, the (100) peak of SBIL shifted toward higher 20 values, implying the reduction of pore size due to the introduction of organic components into the pore channel of SBA-15 [34].

Fig. 2 shows the N₂ adsorption–desorption isotherms and pore diameter distributions of SBA-15 and SBIL. BET surface areas and BJH distributions were calculated using N₂ adsorption at 77 K. Both of samples displayed a type IV isotherm with HI hysteresis loop and a sharp increase in pore volume adsorbed above P/P₀~0.7, which is typical characteristic of highly ordered mesoporous materials [35]. The textural properties of SBA-15 were substantially maintained over basic ionic liquid functionalization. Functionalization of basic ionic liquid significantly affected the surface area and pore distribution of the modified samples. The parent SBA-15 sample showed a maximum pore diameter at 8.7 nm and surface area of 574 m²/g. After functionalization of basic IL, the maximum pore diameter and surface area of the sample SBIL decreased to 6.3 nm and 361 m²/g, respectively.

In order to warrant the successful functionalization SBA-15 with basic IL, FT-IR is employed to give detailed investigation of the obtained SBIL (Fig. 3). For all samples, the bands at 1630 and 3430 cm⁻¹ can be assigned to the O–H vibration of physisorbed water. The bands due to Si–O–Si stretching of SBA-15 framework were observed at 804 and 1080 cm⁻¹. A band was seen at 960 cm⁻¹ aroused by O–H vibration of surface silanols. After functionalization with CPTES and basic IL, the intensity of this band for the samples of CPTES/SBA-15 and SBIL decreased significantly which was caused by the occupation of surface O–H by CPTES and basic IL [36], indicating the successful supporting of CPTES and basic IL. In

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Epoxidation of cyclohexene under various reaction conditions ^a.

| Entry | Catalyst | Conversion (%) ^b | Yield (%) ^c |
|-------|------------------|-----------------------------|------------------------|
| 1 | None | 18 | 14 ^d |
| 2 | SBA-15 | 18 | 13 ^d |
| 3 | CIL ^e | 19 | 16 ^d |
| 4 | BIL ^e | 65 | 53 ^d |
| 5 | SCIL | 20 | 17 ^d |
| 6 | SBIL | 87 | 87 |
| 7 | SBIL | No reaction ^f | - |

^a Reaction conditions: cyclohexene (4 mmol), benzonitrile (10 mmol), catalyst (100 mg), MeOH (10 ml), 30% aq. H₂O₂ (2.4 ml, 24 mmol H₂O₂), 60 °C, 24 h. ^b Conversion determined by GC.

^c Yields of epoxides were determined by GC analysis using internal standards (toluene), based on the olefins.

^d The byproduct of cyclohexane-1, 2-diol was found.

^e The amount was equivalent to the amount of basic IL on the surface of SBIL.

Benzonitrile was not added.

comparison with the naked SBA-15, the bands at 2978 cm⁻¹ and 2928 cm⁻¹ for CPTES/SBA-15 and SBIL were due to C–H stretching of CPTES. Additional band at 1574 cm⁻¹ due to the C–C and C–N stretching vibrations of imidazole ring [37] was observed for the sample of SBIL, confirming the functionalization of basic IL into the material.

Fig. 4 shows TEM images of SBIL. It can be clearly seen that the uniform mesoporous structure of SBA-15 was not destroyed after functionalization with basic IL, which was in good agreement with the results obtained from XRD and N_2 adsorption–desorption.

3.2. Catalytic activity

Table 1 shows results of epoxidation of cyclohexene under various reaction conditions. As it has been found, in the absence of a catalyst, the cyclohexene conversion and epoxide yield were very low with formation of byproduct of cyclohexane-1, 2-diol (entry 1). Since SBA-15 and ionic liquid of CIL exhibited similar low catalytic activity as that of no catalyst, SBA-15 and CIL were not active component of the catalyst (entries 2 and 3). Using SCIL as catalyst did not increase cyclohexene conversion and epoxide yield remarkably (entry 5), indicating that SCIL was not effective. When only addition of ionic liquid of BIL, the conversion and epoxide yield increased remarkably, demonstrating that BIL was active for our epoxidation system (entry 4). Compared with BIL, SBIL exhibited much higher catalytic activity (entry 6). The cyclohexene conversion increased to 87%, and no byproduct was detected so epoxide yield was also 87%. It has been reported that basic reaction medium could effectively prevent ring opening reaction in olefin epoxidation [38], so the excellent epoxide



Fig. 4. TEM pictures of SBIL.







Fig. 5. Reuse of the SBIL catalyst.

yield was probably due to the basicity provided by SBIL. Furthermore, we found that no reaction happened without addition of benzonitrile (entry 7), so benzonitrile was indispensable for our epoxidation system. It has been reported that base-catalyzed epoxidation reaction using H₂O₂ required the addition of nitrile [39]. The possible mechanism is depicted in Scheme 2. In first step (StepI), a hydroperoxide anion is formed from hydrogen peroxide in basic condition provided by the catalyst of SBIL [39]. In the second Step (StepII), nitrile is oxidated to peroxicarboximidic acid by hydroperoxide anion. Finally, in the third step (StepIII), the peroxicarboximidic acid transfers oxygen to the olefin to form epoxide.

Table 2

The epoxidation of various olefins catalyzed by SBIL using H_2O_2 ^a.



 a Reaction conditions: olefin (4 mmol), benzonitrile (10 mmol), SBIL(100 mg), MeOH (10 ml), 30% aq. $\rm H_2O_2$ (2.4 ml, 24 mmol $\rm H_2O_2$), and 60 °C, 24 h.

^b Conversion determined by GC.
 ^c Yields of epoxides were determined by GC analysis using internal standards (toluene),

^d Reaction temperature was 50 °C.

^e Byproduct of benzaldehyde was formed.

A series of catalytic cycles were run to investigate the constancy of the catalyst activity. As it is displayed in Fig. 5, this catalyst can be reusable for at least five times with slight loss of activity.

The SBIL catalyst can be used for the epoxidation of a wide range of cyclic, linear and aromatic olefins, the results are summarized in Table 2. Cyclic and aromatic olefins such as cyclopentene (entry 1), cyclooctene (entry 2) and indene (entry 4) gave the corresponding epoxides with good conversion and epoxide yield, respectively. Besides epoxide product, byproduct of benzaldehyde was found for epoxidation of styrene (entry 3). Compared with cyclic and aromatic olefins, linear olefins such as 1-heptene and 1-dodecene showed lower conversions and epoxide yields (entries 5 and 6).

4. Conclusions

In summary, mesoporous SBA-15 functionalized with basic IL was synthesized, and used as an efficient heterogeneous catalyst for epoxidation reaction of various olefins using a combined oxidant of aqueous hydrogen peroxide and benzonitrile. The cyclic and aromatic olefins were oxidized to corresponding epoxides with good yields, whereas linear olefins were less reactive. The catalyst could be facilely separated from the reaction mixture by filtration and could be reused at least five times without significant degradation in activity.

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