无机氧化物载体对催化 CO₂ 与环氧化合物合成 环状碳酸酯的促进作用

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摘要: 以一系列无机氧化物与四丁基溴化铵为双组分催化剂体系, 考察了其催化 CO₂ 和环氧化合物合成环状碳酸酯的反应性能。结果表明, 在四丁基溴化铵与这些本身并没有催化活性的无机氧化物共同作用下, 反应活性明显提高, 表现出很强的协同催化作用。另外, 通过对 SiO₂ 的表面硅烷基化, 考察了其表面羟基数量对反应活性的影响, 发现当 SiO₂ 的表面经过硅烷基化以后, 反应活性大幅度降低, 表明无机氧化物表面羟基对 CO₂ 环加成反应活性有非常显著的促进作用。

关键词: 无机氧化物; 二氧化碳; 环状碳酸酯; 二氧化硅; 羟基; 硅烷基化; 协同催化

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The Role of Inorganic Oxide Supports in Synthesis of Cyclic Carbonates from Carbon Dioxide and Epoxides

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Abstract: An inorganic oxide support coupled with a quaternary ammonium salt is an efficient catalyst for the cycloaddition of CO₂ and epoxide to produce cyclic carbonates under relatively mild reaction conditions (90 °C, 4 MPa). When tetrabutylammonium bromide (TBAB) was used alone, the activity of the cycloaddition reaction between carbon dioxide and epoxide was only moderate. When an inorganic oxide, especially one that has abundant surface hydroxyl groups was also employed, the reaction was accelerated significantly. This demonstrated that the inorganic oxide and TBAB had a strong synergetic effect for the cycloaddition reaction. Silica was chosen as a model oxide to study the role of surface hydroxyl groups in the reaction. When the surface of silica was silylated with trimethylchlorosilane or dimethyldichlorosilane, the catalytic activity decreased sharply due to surface silylation, which indicated clearly that the surface hydroxyl groups on the silica played a decisive role in influencing the catalytic activity.

Key words: inorganic oxide; carbon dioxide; cyclic carbonate; silica; hydroxyl groups; silylation; synergetic effect

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CO₂ is a major greenhouse gas in the atmosphere. There is growing awareness that anthropogenic CO₂ emission should be reduced. The chemical fixation of CO₂ into syn-

thetically beneficial compounds is of great interests for “green and sustainable chemistry” because CO₂ can then be considered a renewable carbon and it has the advantages of

being abundant, economical, and non-toxic. Therefore, if CO₂ is converted into a chemical for which there is significant demand, the chemical reutilization of CO₂ would form part of an overall strategy to reduce CO₂ emission and would also have economic benefits [1,2]. A promising methodology in this area is the cycloaddition of epoxide and carbon dioxide to afford cyclic carbonates. These carbonates can be widely used for various purposes, e.g., as organic synthetic intermediates, excellent aprotic polar solvents, pharmaceutical/fine chemical intermediates, and electrolytes for batteries [3].

For this reaction, various catalyst systems have been developed that include homogeneous and heterogeneous catalyst systems. The homogeneous catalysts include ionic liquids [4], transition metal complexes [5], ammonium salts [6], phosphonium salts [7], and alkali metal salts [8,9]. Unfortunately, they get dissolved in the phase containing the cyclic carbonates, which makes the separation of the products difficult. In order to facilitate the separation of catalyst and product, much effort have been devoted to developing heterogeneous catalysts, including zeolites [10], magnesia [11], Al-Mg mixed oxide [12], smectite [13], and lanthanide oxychloride [14]. Unfortunately, these heterogeneous catalyst systems have insufficient activity. Many of these catalysts still need an additional organic solvent and require severe reaction conditions to improve the yield and selectivity. Therefore, developing a more efficient and environmentally benign catalyst for cyclic carbonate synthesis under mild conditions still remains a challenging issue.

Solid supported catalysts that use effective homogeneous catalysts immobilized on suitable supports have received much attention. Compared with homogeneous catalysts, such heterogeneous catalysts have the advantages of using less homogeneous catalyst and easy separation, as well as the recovery of the catalyst from the reaction mixture, which is desirable from economic, environmental, and industrial considerations. To date, many supports such as polymer [15], chitosan [16], and silica (SiO₂) materials [17,18] have been chosen as catalytic supports for fixing CO₂ to cyclic carbonate. Among these supports, silica was the most widely used [17–19]. Silica was chosen as a catalyst support due to its high surface area and pore structure. For instance, imidazolium-based ionic liquids with varied alkyl chain lengths were immobilized onto a commercial silica surface [20], and these heterogeneous catalysts exhibited high catalytic activities and selectivities in the cycloaddition of carbon dioxide and allyl glycidyl ether. When an aluminum phthalocyanine complex was covalently bonded to the silica surface of mesoporous MCM-41 molecular sieve in the presence of a quaternary ammonium salt, the catalyst exhibited good stability as well as high catalytic activity [18]. Thus, silica is a much desired solid support.

Besides the large BET surface area, the most striking feature is the surface chemistry of the various silica materials. Abundant hydroxyl groups on silica surface have made the surface chemistry of silica a very popular topic [21]. Recently, silica-supported catalysts to produce cyclic carbonates have been investigated extensively. Since the immobilization of phosphonium halides or quaternary ammonium bromides on silica dramatically increased catalytic activity as compared with the corresponding homogeneous onium salts, a synergic effect between silica and the immobilized homogeneous catalysts has been proposed [22,23]. These motivated us to consider whether the reaction can be also promoted by other inorganic oxides. Some unresolved problems are: How do these oxides affect the activity and what is their role during the reaction?

Previous researches [6] have shown that quaternary ammonium bromide is a good catalyst for the cycloaddition reaction because it is cheap, abundant, and easily recyclable. However, the single quaternary ammonium bromide showed low activity for the reaction. In this work, we used conventional inorganic materials, like SiO₂, SBA-15, Al₂O₃, and Na-Montmorillonite (MMT), in combination with tetrabutylammonium bromide (TBAB) as catalysts for the cycloaddition reaction between propylene oxide and carbon dioxide, and have examined the synergetic effects of the different inorganic materials and TBAB. Among these inorganic materials, silica gave the best catalytic performance. Here, silica was selected as a model oxide for investigating the effect of surface hydroxyl groups on the reaction. The surface of silica was modified by silylation with trimethylchlorosilane (TMCS) or dimethyldichlorosilane (DMCS) and the relationship of catalytic activity with surface hydroxyl concentration on silica is discussed and a reaction mechanism was proposed.

1 Experimental

1.1 Catalyst preparation

All chemicals were analytical grade and commercially available. They were used without further purification, unless otherwise stated. CO₂ was supplied by Shanghai Shangnong Gas Factory with a purity of >99.95%. Silica gel (HG/T2534-92 chromatography grade) was supplied by Qingdao Haiyang Chemical Reagents Co., Ltd., China. Al₂O₃ was supplied by Yangzhou Baisheng Catalyst Co., Ltd., China. MMT was supplied by Zhejiang Fenghong New Material Co., Ltd., China.

H-SiO₂ was prepared following the conventional procedure. Na₂SiO₃·9H₂O (0.02 mol, 5.7 g) was dissolved in 25 ml of water under vigorously stirring at 50 °C. Then 1 mol/L of H₂SO₄ solution was added slowly until the pH value of

the mixture was 3.5. The solution mixture was aged for 6 h at 50 °C. Then the mixture was filtered and washed with water (50 ml $\times$ 5). The white solid obtained was dried at 65 °C for 12 h, following by calcination at 550 °C for 4 h.

Layered double hydroxides (LDHs) were synthesized according to the modified method [24]. As a typical example, 0.03 mol of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.015 mol of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 50 ml of water, followed by the addition of 0.21 mol of urea while stirring. After heating to 105 °C, a white precipitate was formed. The solution was maintained at 105 °C for 10 h under stirring, and then was aged at the same temperature for another 20 h. The solids formed were collected by filtration and washed with deionized water (neutral pH) and subsequently dried at 100 °C for 12 h.

$\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ was prepared by the procedure reported in the literature [25]. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (25 g) and Na_2CO_3 (1.45 g) were dissolved in 30 ml of water. A Na_2CO_3 solution was slowly dropped into the $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution with stirring until there was no more precipitates. The precipitate was collected by centrifugation and washed with deionized water and ethanol several times, then dried at 65 °C for 12 h.

SBA-15 was prepared by the procedure reported in the literature [26]. Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) with an average molecular weight of 5800 (P123, Aldrich) was the structure directing agent. The reaction mixture of P123 (0.25 g), TEOS (0.55 g), hydrochloric acid (1.3 ml), and deionized water (6.22 ml) was heated under stirring at 30 °C for 24 h, and then it was transferred into a Teflon autoclave and heated at 100 °C for 24 h. The resulting precipitate was filtered and washed with deionized water and ethanol, then dried at 60 °C over night. The dried precipitate was calcined at 550 °C for 5 h to remove the template.

Surface silylation of silica was carried out using TMCS and DMCS as the silylation agents. The procedures for surface modification of silica with the two silylation agents were similar to that in the literature [27]. Typically, the silica sample (0.2 g) was dried at 100 °C for 24 h, and then subsequently was soaked in a toluene solution (10 ml) of TMCS or DMCS at 80 °C with stirring. Then the solid was filtered and washed extensively with toluene and acetone, and dried overnight. The silica materials modified with silylation agents under different silylation conditions were denoted as $\text{SiO}_2\text{-TMS (or DMS)-}X\text{-}Y$, where TMS or DMS represented silylation reagent; X is the concentration of TMCS or DMCS in toluene solution for silylation and Y is the silylation time.

1.2 Typical procedure for cycloaddition

All the cycloaddition reactions were carried out in a stainless steel reactor of 50 ml equipped with a magnetic stirrer. In a typical experiment, the desired amount of TBAB, inorganic material (0.1 g), and propylene oxide (10 mmol) were added into the reactor. CO_2 was charged into the reactor to the desired pressure, and then the reactor was heated to the desired temperature. After the reaction time, the reactor was placed into ice and water and CO_2 was released slowly by passing it through a cold trap containing ethyl acetate to absorb trace amounts of reactant and product entrained in the CO_2 . After depressurization, ethyl acetate in the cold trap was added into the reactor and the catalyst was washed using ethyl acetate to remove the product. The liquid reaction mixture was obtained by centrifugation and it was analyzed by GC-MS and GC with 1-octane as internal standard. The catalyst was dried for 12 h at 60 °C. To examine the reusability of the catalyst, the recovered catalyst, combined with fresh TBAB and propylene oxide were added for the next run. The procedures for the cycloaddition of carbon dioxide with other epoxides were similar.

1.3 Catalyst characterization

FT-IR spectra were recorded from pressed KBr pellets at room temperature on a Nicolet Fourier transform infrared spectrometer (Magna550). A spectrum of dry KBr was also recorded as background. Solid-State $^{29}\text{Si}/\text{MAS}$ NMR spectra were obtained on a Varian VAMRS 400 spectrometer. The dried powdered samples were loaded into a multinuclear probe and spun at 5 kHz, and the cross-polarization (CP) contact time was 2 ms. X-ray diffraction (XRD) analyses were performed on a D/MAX 2550 VB/PC using $\text{Cu } K_\alpha$ radiation and a graphite crystal as monochromator. Surface areas (BET) were measured by N_2 adsorption at the temperature of liquid nitrogen using a NOVA 4200e Analyzer after the evacuation of the sample at 180 °C for 6 h.

2 Results and discussion

2.1 Effect of different inorganic oxides

As shown in Table 1, various inorganic materials, including silica, SBA-15, Al_2O_3 , MMT, LDHs, and $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$, were examined in the cycloaddition of CO_2 and propylene oxide. All these samples were prepared according to standard methods and characterized by XRD. The XRD patterns of these materials showed peaks that were all in accordance with the expected diffraction.

It was found that propylene carbonate synthesis can be catalyzed by conventional inorganic oxides, especially when these were used in combination with TBAB. The products

besides propylene carbonate contained a trace of 1,2-propanediol, which could be from the hydration of propylene oxide. No halogenated organic compounds were detected by GC-MS. It was worth noting that all these inorganic materials were inactive for this cycloaddition reaction alone, while when TBAB (0.08 g) was used alone, the conversion was also only 57% (Table 1, entry 1). However, the combination of any of these inorganic materials with a small amount of TBAB improve catalytic activity significantly (Table 1, entries 2–7). Even when the amount of TBAB used was decreased to one-fourth its initial amount, the catalytic performance of the binary systems were still much better than that when TBAB was used alone (Table 1, entries 1 vs 2–8). These materials are all common, cheap, and easily available, and none need a special modified process, but they played an important role in the coupling reaction of CO₂ and propylene oxide. To understand the role of these inorganic oxides, the BET surface areas of these materials were determined. The comparison of the surface area of these materials clearly showed that there was no close relationship between the BET surface area and catalytic activity. Previous works [29,30] have demonstrated that it is the hydroxyl groups on these inorganic material surface that had the crucial effect on the enhanced catalytic performance. Because the commercially available silica afforded the best catalytic performance among these materials (Table 1, entry 3), the combination of silica and TBAB was selected as the model catalytic system for the following investigation. The present work focused on the effect of the surface hydroxyl groups on the reaction.

Table 1 Effect of inorganic oxides on cycloaddition activity between propylene oxide and carbon dioxide

Entry	Inorganic oxide	A_{BET} (m ² /g)	Conversion ^a (%)	Selectivity (%)
1	none	—	57 (38)	>99
2	H-SiO ₂ ^b	408	99 (94)	99
3	SiO ₂	550	99 (97)	99
4	SBA-15	582	99 (97)	99
5	Al ₂ O ₃	190	98 (92)	99
6	Zn ₅ (OH) ₆ (CO ₃) ₂	12.8	98 (94)	98
7	MMT	26.7	92 (51)	98
8	LDH	44.0	92 (55)	98

Reaction conditions: 0.1 g inorganic oxides, 0.08 g TBAB, 10 mmol propylene oxide, 4 MPa CO₂, 90 °C, 4 h.

^aValues in parentheses referred to the conversion of propylene oxide when 0.02 g of TBAB was added.

^bThis sample with a lower surface area was prepared in our lab for comparison.

2.2 Effect of the amount of TBAB

The effect of the amount of TBAB on the cycloaddition

of propylene oxide and CO₂ to produce propylene carbonate (PC) was examined. The results are summarized in Table 2. The conversion of propylene oxide was negligible when only silica oxide was used to catalyze the reaction. However, even the addition of a very small amount of TBAB can promote the reaction significantly (Table 2, entry 2). When the amount of TBAB was increased to 0.02 g, the conversion of propylene oxide was already 97% (Table 2, entry 3). Since the conversion of propylene oxide was 57% when only TBAB was used, this indicated the excellent synergetic effect of SiO₂ and TBAB for catalyzing the coupling reaction.

Table 2 Effect of the amount of TBAB on the reaction

Entry	Catalyst (g)		Conversion (%)	Selectivity (%)
	SiO ₂	TBAB		
1	0.1	0	trace	—
2	0.1	0.01	82	99
3	0.1	0.02	97	99
4	0.1	0.04	98	99
5	0.1	0.08	98	99

Reaction conditions: 10 mmol propylene oxide, 4 MPa CO₂, 90 °C, 4 h.

2.3 Effect of reaction pressure and reaction temperature

A significant drawback associated with using carbon dioxide as a reagent in organic synthesis is the potential danger due to the high pressures on raising the reaction temperature, especially in heterogeneous catalytic system [31]. Therefore, we first investigated the dependence of the conversion of propylene oxide on the reaction pressure. The effect of the CO₂ pressure on the catalytic activity was examined at 90 °C. The results are shown in Fig. 1. The selectivity for PC was more than 99% in all cases. The conversion increased with the CO₂ pressure from 1 MPa to 4 MPa, but the conversion decreased slightly as the pressure was

Fig. 1. Effect of CO₂ pressure on PO conversion. Reaction conditions: 0.1 g SiO₂, 0.02 g TBAB, 10 mmol propylene oxide, 90 °C, 4 h.

further increased from 4 to 6 MPa. This can be explained qualitatively by the effect of the pressure on mass transfer. The concentrations of CO₂ and propylene oxide in the two phases changed with the pressure. When the pressure was relatively low (1–4 MPa), the solubility of CO₂ in the propylene oxide phase increased with increasing pressure, which increased the rate of the reaction because CO₂ is a reactant. But when the pressure was higher, the solvent power of CO₂ became stronger, which was unfavorable for the adsorption of the reactants on the surface of the catalyst and this reduced the catalytic activity. The competition of the two factors resulted in an optimum reaction pressure of 4 MPa.

It is highly desirable that the reaction can be performed at mild conditions. The dependence of the conversion of propylene oxide on temperature is plotted in Fig. 2. It can be seen that the reaction is temperature dependent at low temperature. As the temperature increased from 70 to 90 °C, the conversion of propylene oxide changed from 75.4% to 97.5%, but the further increase in temperature beyond 90 °C up to 110 °C only increased the conversion slightly.

Fig. 2. Effect of reaction temperature on PO conversion. Reaction conditions: 0.1 g SiO₂, 0.02 g TBAB, 10 mmol propylene oxide, 4 MPa CO₂, 4 h.

2.4 Effect of surface silylation of the silica

It is well known that surface silylation of SiO₂ can be carried out through the reaction between silylation agents (such as TMCS and DMCS) and surface Si–OH groups [32]. This is shown in Scheme 1.

The degree of surface silylation is affected by many factors, such as type of solvent, concentration of silylation agent, time and temperature of silylation [33]. Here, in order to obtain different concentrations of surface hydroxyl groups on the silica, the degree of silylation was manipulated by tuning the concentration of silylation agent and reaction time.

The different silylated SiO₂ materials were further char-

Scheme 1. Surface silylation of the silica with TMDS or DMCS.

acterized by FT-IR. The spectra are shown in Fig. 3. The bands around 1100, 800, and 450 cm⁻¹ were due to the Si–O–Si bond [34]. A broad absorption band at 3430 cm⁻¹ can be assigned to hydrogen-bonded surface –OH groups perturbed by adsorbed water. A small band observed at 1650 cm⁻¹ was due to absorbed water [35]. There were marked differences between fresh SiO₂ and the silylated ones. A well defined band appeared at 2960 cm⁻¹ after silylation, which was due to C–H stretching vibration in surface –CH₃ groups [36]. This showed that the silylation reaction between the silylation agents and the silanol groups had succeeded. It should be noted that the absorption from the Si–OH bond is at 960 cm⁻¹ [37,38]. It can be observed from the FT-IR spectra of SiO₂, SiO₂-TMC-4.8-1, and SiO₂-TMC-4.8-12 that there was a corresponding decrease in the Si–OH bond band and the broad absorption –OH

Fig. 3. FT-IR spectra of the silica silylated with TMCS or DMCS.

band (3430 cm^{-1}) with longer silylation time. Simultaneously, the intensity of the band at 960 cm^{-1} was reduced after silylation. This band became much weaker with DMCS as silylating reagent because the silylation was completed within 1 h in this case (Fig. 3). This is because silylation with DMCS was a quick process, but a slow process with TMCS due to high steric hindrance. Therefore, the degree of silylation with TMCS can be tuned by varying the silylation condition, as indicated in a previous work [39].

The silylation of the silica was also characterized by ^{29}Si CP/MAS NMR spectra. Figure 4 shows the ^{29}Si CP/MAS NMR spectra for fresh silica and the silylated sample SiO₂-TMS-4.8-12. The two resonances, Q⁴ (about $\delta = -110$) and Q³ (about $\delta = -101$) were assigned to Si bonded to four siloxane bonds $[(\text{-OSi})_4]$ and Si bonded to three siloxane bonds and one silanol group $[(\text{-SiO})_3\text{SiOH}]$, respectively. For the silylated sample, a new resonance at 9.5 was observed, which was assigned to the O-Si(CH₃)₃ [40]. Simultaneously, the intensity of the Q³ silicon resonance was significantly decreased. These observations clearly showed that the silylation agent (TMCS) had reacted with the silanol groups. The intensities of the Q³ and Q⁴ components were estimated by calculating the integrated area of each peak. The decrease of the relative area of the Q³ component in the silylated samples with respect to the non-silylated one was a consequence of the disappearance of surface Si-OH groups by chemical reaction with the silylation agent to form Si-O-Si(CH₃)₃ moieties. The extent of sample silylation can be estimated by calculating the ratio between the peak areas of the Q³ and Q⁴ components. In the fresh silica sample, the ratio of Q³ to Q⁴ was 0.22, while the ratio decreased to 0.18 after the silylation, which illustrated clearly that the surface of the silica has been successfully modified by trimethylsilylation (Fig. 4).

The materials with different degrees of silylation were tested for the CO₂ cycloaddition reaction. The results are

Fig. 4. ^{29}Si CP-MAS NMR spectra of the fresh silica and SiO₂-TMS-4.8-12.

shown in Table 3. The catalytic activity decreased sharply with increasing degree of silylation (Table 3, entries 1–3), which was confirmed by the FT-IR spectra and ^{29}Si NMR spectra (Figs. 3 and 4). The fresh silica afforded the best catalytic activity (57.8%, Table 3, entry 1), while partly silylated SiO₂-TMC-4.8-1 had a lower catalytic activity (43.2%, Table 2, entry 2) and the fully silylated SiO₂-TMC-4.8-12 had the lowest activity (23%, Table 3, entry 3). In addition, the same catalytic activities of both SiO₂-DMC-4.8-1 and SiO₂-DMC-4.8-12 proved that the silylation with DMCS was almost completed within 1 h (Table 3, entries 4 and 5), which was also in agreement with the FT-IR spectra.

Table 3 Effect of silylation on catalytic activity

Entry	Silylated silica	Conversion (%)	Selectivity (%)
1	SiO ₂ ^a	57.8	99
2	SiO ₂ -TMC-4.8-1	43.2	99
3	SiO ₂ -TMC-4.8-12	23	99
4	SiO ₂ -DMC-4.8-1	25	99
5	SiO ₂ -DMC-4.8-12	24	99

Reaction conditions: 0.1 g silylated silica, 0.08 g TBAB, 10 mmol propylene oxide, 4 MPa CO₂, 60 °C, 2 h.

^aWithout silylation.

Figure 5 showed typical conversion/time profiles obtained for the fresh SiO₂ vs the silylated sample SiO₂-TMC-4.8-12. This comparison revealed that the silica modified with silylation afforded a lower reaction rate than the fresh silica. This was attributed to the decreased number of the surface Si-OH groups caused by the silylation. This demonstrated that the catalytic activity decreased when there was a lower concentration of surface hydroxyl groups. Conversely, silica which is rich in hydroxyl groups in combination with TBAB can facilitate the reaction significantly.

Fig. 5. Effect of time on conversion of the cycloaddition reaction between carbon dioxide and propylene oxide by fresh silica and silylated silica. Reaction conditions: 0.1 g the silica or the silylated silica materials, 0.08 g TBAB, 10 mmol propylene oxide, 4 MPa CO₂, 60 °C.

2.5 Generality and reusability of the catalyst

The use of different substrates was also investigated. Various epoxides were chosen as substrates and the reaction results are summarized in Table 4. The catalyst system was found to be applicable to the cycloaddition reaction of CO₂ with different epoxides (Table 4, entries 1–6). Excellent conversion and selectivity were obtained for most of the epoxides except for cyclohexene oxide (Table 4, entry 6). This could be due to the higher hindrance resulting from the two rings in the cyclohexene oxide molecule. The conversion of cyclohexene oxide was only 73%, but the selectivity to the corresponding carbonate was still quite high.

The recyclability of the catalyst was also examined. The silica material can be reused at least six times without decreasing the catalytic activity (Table 4, entries 1 and 2). The catalyst after the sixth recycle was characterized by XRD and IR (Figs. 6 and 7). In Fig. 7, the band appeared at 2960 cm⁻¹ can be assigned to C–H asymmetrical stretching vibration and 2880 cm⁻¹ C–H symmetrical stretching vibration, which indicated the presence of TBAB on the silica. The results indicated that the catalyst did not show any obvious change after reuse. The advantages of the current catalyst system are not only its cost effectiveness, but also it was efficient and stable. These benefits have great potential for applications in the fixation of carbon dioxide.

2.6 Reaction mechanism

Inorganic oxides (SiO₂, Al₂O₃, etc.) in combination with TBAB were found to accelerate significantly the cycloaddi-

Fig. 6. XRD patterns of the fresh SiO₂ and the recovered SiO₂.

Fig. 7. FT-IR spectra of the fresh SiO₂ and the recovered SiO₂.

tion reaction of epoxides and CO₂. Since these inorganic oxides generally contained hydroxyl groups on their sur-

Table 4 Cycloaddition reactions between carbon dioxide and various substrates

Entry	Epoxide	Product	Reaction time (h)	Conversion (%)	Selectivity (%)
1			4	98	> 99
2 ^a			4	96	> 99
3			6	97	96
4			6	97	97
5			8	97	98
6			14	73	97

Reaction conditions: 0.1 g SiO₂, 0.02 g TBAB, 10 mmol epoxides, 4 MPa CO₂, 90 °C.

^a Sixth catalytic recycle.

face, the hydroxyl groups play a main role in promoting the reaction. A hydrogen bond is formed as a A—H···B bond where A and B are electronegative elements, like fluorine, oxygen and nitrogen [41]. In the present binary system, A and B are oxygen atoms from the inorganic oxide and epoxide. As a result, hydrogen bonding between Si—OH groups and the epoxides formed, which would decentralize the electron cloud and weaken C—O bond in the epoxide molecule, leading to activation of the epoxy ring. Hydrogen bonding between isolated silanol species at the surface of amorphous silica and furan derivatives or carbonyl compounds has been observed in previous works [42,43].

Based on the discussion above, it can be suggested that the inorganic oxide and TBAB has a synergetic effect. A possible mechanism of the cycloaddition reaction catalyzed by the inorganic oxide and TBAB can be proposed with silica as an example (Scheme 2). The O atom in the epoxide has two pairs of lone electrons, so that surface silanol groups can form hydrogen bond with the O atom of the epoxide, cause the polarization of the epoxide and activate the epoxy ring. Second, Br[−] from TBAB attacks the less hindered carbon atom of the epoxide, which is followed by the ring opening step. Then, the oxygen anion of the opened epoxy ring interacts with CO₂ to form an alkylcarbonate anion, which is transformed into a cyclic carbonate through a ring closing step, while the catalyst is regenerated. Other inorganic oxides containing —OH groups would also play a similar role in the cycloaddition reaction.

Scheme 2. Proposed mechanism for the cycloaddition reaction.

3 Conclusions

An inorganic oxide, which contains —OH groups, in combination with TBAB can facilitate the cycloaddition reaction of CO₂ and epoxides. Binary silica-TBAB is a highly active, stable and selective catalytic system for the reaction, which

was ascribed to a synergetic effect of surface —OH groups and TBAB. A decreased catalytic activity from surface silylation of the silica demonstrated clearly the important role of the surface —OH groups on the silica. This simple and cheap catalytic system has great potential for applications in the fixation of carbon dioxide.

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