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Chemical fixation of carbon dioxide to propylene carbonate over amine-functionalized silica catalysts

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Abstract

Amine-functionalized silica catalysts (NH_2/SiO_2, $NH(CH_2)_2NH_2/SiO_2$ and 1,5,7-triazabicyclo[4,4,0]dec-5-ene/SiO_2 (TBD/SiO_2)), which were characterized by ^{29}Si NMR, elemental analysis, N_2 adsorption–desorption method and indicator dye adsorption, were prepared by ultrasonic technique under mild conditions. Such hybrid solid bases showed high catalytic activity towards CO_2 coupling with epoxide. However, it was found that the reaction conditions had a great influence on the performance. Furthermore, silanols on the surface played an important role in the chemical fixation of CO_2. Based on these, the possible reaction mechanism was proposed for CO_2 coupling with epoxide over such type of catalysts.

Keywords: Functionalized silica; Ultrasonic technique; Catalyst; Chemical fixation; CO_2; Propylene carbonate

1. Introduction

CO_2 chemical fixation is a challenging and important topic as CO_2 is an inexpensive and abundant C_1 feedstock, and therefore any efficient reactions using CO_2 as a reagent have positive ramifications on efforts towards carbon management [1,2]. A particularly studied reaction involving CO_2 is the synthesis of five-membered cyclic carbonate (propylene carbonate) via the coupling of CO_2 and propylene oxide (see Scheme 1) [3,4]. The cyclic carbonate is useful as highly polar solvent, electrolyte components for lithium batteries and chemical intermediates in polymer synthesis [5,6]. A lot of catalytic systems, including alkali metal salts [7], ammonium salts [8,9], ionic liquids [10–13], metal oxides [14,15], transition metal and main group complexes [16–19], were reported to be active for the reactions, but these catalysts usually suffered from drawbacks, such as low activity/selectivity, need for co-solvent, poor reusability and air sensitivity. The exploration of highly efficient catalysts for CO_2 coupling with epoxides still remains a challenging subject.

In the present work, amine-functionalized silica catalysts, including NH_2/SiO_2, $NH(CH_2)_2NH_2/SiO_2$ and 1,5,7-triazabicyclo[4,4,0]dec-5-ene (TBD)/SiO_2, were prepared with 3-aminopropyltrimethoxysilane (APTMS), *N*-[3-(trimethoxysilyl)propyl]ethylenediamine (EDPTMS) and 3-chloropropyltrimethoxysilane (CPTMS) as the coupling agents by ultrasonic technique under mild experimental conditions. For a comparison, NH_2/SiO_2 was also prepared by conventional method, i.e., heating, refluxing and stirring. Both their catalytic performance and mechanism understanding for CO_2 coupling with epoxides was investigated.

2. Experimental

2.1. Preparation of amine-functionalized silica

Aminopropylsilyl-functionalized SiO_2 was prepared as follows: 10.0 g SiO_2 was preheated for 12 h at 473 K in vacuo to remove all adsorbed moisture but surface OH-groups, cooled down to room temperature in vacuo and then transferred into a 250 mL conical flask. After mixing with 40.0 mL cyclohexane and 2.5 mL APTMS, the mixture in conical flask was put into the ultrasonic bath (Sheshin, Japan, operating frequency 50 kHz) for 2 h at ambient temperature. The catalyst was then obtained by extracting with toluene in a Soxhlet extractor over a period of 24 h and drying at 333 K in vacuo. The same method was used for the preparation of $NH(CH_2)_2NH_2/SiO_2$ by using 4.0 mL of EDPTMS.

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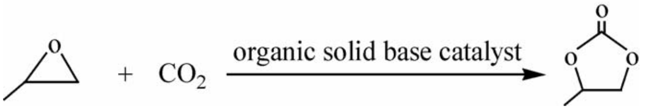


Scheme 1. Reaction between propylene oxide and carbon dioxide.

TBD/SiO_2 was prepared by two steps: silica was firstly modified by 3-chloropropyltrimethoxysilane via the same method as that of aminopropylsilyl-functionalized SiO_2, and chloropropylsilyl-functionalized SiO_2 was then reacted with TBD (1.0 g) in cyclohexane (40.0 mL). The resultant was treated by ultrasonic vibration for 2 h. Afterwards, the catalyst was obtained by extracting with toluene in a Soxhlet extractor over a period of 24 h and drying at 333 K in vacuo. In order to cap remaining free SiOH groups on the walls of silicas, TBD/SiO_2 was treated in hexamethyldisiloxane [20] by ultrasonic vibration for 1 h, yielding $TBD/Me/SiO_2$.

NH_2/SiO_2 was also prepared according to the method known from literature [21] and the experimental conditions such as dosage of raw material and reaction time were the same as that used in ultrasonic technique.

2.2. Characterization

The content of carbon, nitrogen and hydrogen in all the samples was determined using a Vario EL analyzer. For each sample, the measurements were performed with the relative error of less than 0.1%. ^{29}Si NMR spectra were recorded on a Bruker MSL-400 spectrometer at 59 MHz using zirconium oxide rotors and a rotation frequency of 4000 Hz. The specific surface area, total pore volume and average pore size were measured by N_2 adsorption–desorption method using Micromeritics ASAP-2000 instrument (Norcross, GA). The base strength of samples was detected by Hammett indicators. The samples were degassed at 373 K for 6 h before transfer into cyclohexane under N_2 for the measurement.

2.3. Catalytic test

The coupling reaction of CO_2 with propylene oxide was carried out in a 100 mL stainless steel autoclave equipped with a magnetic stirrer, in which 0.8 g catalysts and 12.45 g propylene oxide were used and then CO_2 was discharged into it. The autoclave was heated to the desired temperature. The reaction was run at 1.2–4.0 MPa CO_2 for 2–30 h and the product was then filtered and analyzed by a gas chromatograph with a flame ionization detector after centrifugal separation from the catalysts. The catalysts were washed with solvent and used for recycling test.

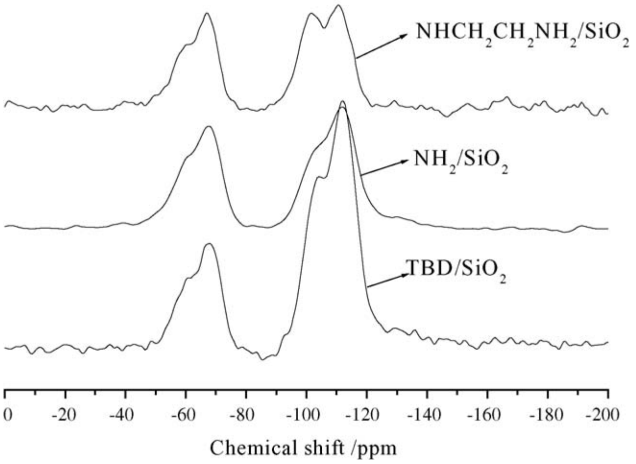


Fig. 1. Solid-state ^{29}Si NMR spectra of amine-functionalized silica.

3. Results and discussion

3.1. Amine functionalization by ultrasonic technique

The elemental analysis results showed that N% of NH_2/SiO_2 prepared by ultrasonic technic and conventional method was 1.38 and 0.59%, respectively. As a result, N_{org}% of the grafted organic groups by conventional methods known from literature [21] was 0.42 mmol/g, which was far lower than that of the sample prepared by ultrasonic technique (0.99 mmol/g) (see Table 1). Taking into account the amount of immobilized groups, it could be concluded the ultrasonic technique was indeed more efficient than the traditional method.

The ^{29}Si NMR spectra in solid state indicated that the covalent bond formed between silylating agents and silanol groups on the silica surface (see Fig. 1). Two resonances at -109 and -99 ppm could be attributed to ^{29}Si nuclei having four Si–O–Si linkages (Q^4) and ^{29}Si nuclei having three Si–O–Si linkages and one –OH (Q^3) [22,23], respectively, while the resonances at -58 and -67 ppm were assigned to $RSi(O\text{-}Si)(OH)_2$ and $RSi(OSi)_3$ [24–26], respectively. These illustrated the successful organofunctionalization of porous silica by the organic groups via covalent bonds. C/N value (molar ratio)

Table 1
Elemental analysis results and structural parameters

Sample	Element analysis					Structural parameters		
	N% (wt%)	C% (wt%)	H% (wt%)	N_{org} (mmol/g)	C/N (number ratio)	BET surface area (m^2/g)	V_p (cm^3/g)	d_p (nm)
Porous silica	0	0	0.73	0	0	347	0.9	10.1
$NH(CH_2)_2NH_2/SiO_2$	3.03	7.61	2.02	1.08	2.9	267	0.7	10.0
NH_2/SiO_2[a]	1.38	3.96	1.03	0.99	3.0	266	0.6	9.7
NH_2/SiO_2[b]	0.59	1.70	0.45	0.42	3.0	–	–	–
TBD/SiO_2	4.20	12.79	1.68	1.00	3.3	258	0.6	8.3

[a] Prepared by ultrasonic technique.
[b] Prepared by heating, refluxing and stirring.

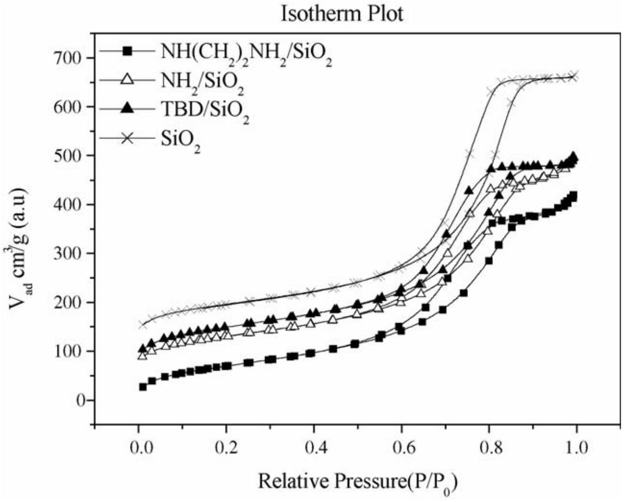


Fig. 2. Nitrogen adsorption–desorption isotherms of the samples.

could also reflect the degree of grafting reaction between silanol groups and organosilanes [21]. NH_2/SiO_2, $NH(CH_2)_2NH_2/SiO_2$ and TBD/SiO_2 showed the C/N = 3–3.5, 2.5–3.0 and 3.3–3.6 (see Table 1), respectively. This suggested the anchorage of $–(CH_2)_3NH_2$, $–(CH_2)_3NH(CH_2)_2NH_2$ and $–(CH_2)_3TBD$ by almost three Si–O–Si bonds. This agreed with that of the ^{29}Si NMR spectra.

3.2. Textural structure and basicity

Fig. 2 shows N_2 adsorption isotherms of the samples. The functionalized samples displayed type IV isotherms with clear hysteresis loops associated with capillary condensation. This indicated that the materials remained mesoporous before and after the functionalization, but the BET surface area and pore volume decreased due to the presence of functional groups (see Table 1). The effect of the organic groups on the pore size was slight for the samples NH_2/SiO_2 and $NH(CH_2)_2NH_2/SiO_2$, but for the sample TBD/SiO_2, perhaps due to the big framework of $–(CH_2)_3TBD$ groups, the pore size decreased to 8.3 nm.

The base strength $H\_$ of a solid surface is defined as the ability of the surface to convert an adsorbed electrically neutral acid into its conjugate base, i.e., the ability of the surface to donate an electron pair to an adsorbed acid. When an electrically neutral acid indicator is adsorbed on a solid base from a non-polar solution, the color of the acid indicator is changed to that of its conjugate base, provided that the solid has the necessary base strength to impart electron pairs to the acid. Thus, it was generally possible to determine the basic strength by observing the color changes of acid indicators over a range of $pK_a = H\_$ values [27]. As a result, the indicators can only used to determine the base strength of light color solid. A solid with a large positive $H\_$ has strong basic sites. Grafting with different functional groups resulted in different base strengths. As shown in Table 2, TBD/SiO_2 had the highest base strength of $H\_ \approx 15.0$, while NH_2/SiO_2 and $NH(CH_2)_2NH_2/SiO_2$ only had a weak basicity of $H\_ \approx 9.3$ and $9.3 < H\_ < 15.0$, respectively. Thus, the base strength of the samples was in the order of $TBD/SiO_2 > NH(CH_2)_2NH_2/SiO_2 > NH_2/SiO_2$.

3.3. Catalytic performance

Obviously, TBD/SiO_2, which had the highest base strength, showed the highest catalytic activity among amine-functionalized silica (see Table 2). However, the reaction conditions such as reaction time, temperature and CO_2 pressure were shown to have an influence on the catalytic activity (see Fig. 3). The propylene oxide hardly reached the total conversion until time up to 20 h, CO_2 pressure up to 1.5–2.0 MPa or temperature up to 413–423 K. Both high conversion (99.5%) and selectivity (99.8%) could be obtained over the TBD/SiO_2 catalyst. For NH_2/SiO_2 and $NH(CH_2)_2NH_2/SiO_2$ catalysts, the conversion of propylene oxide to propylene carbonate increased in the same order as the basic strength (see Table 2). The catalytic activity of NH_2/SiO_2 was lower than that of $NH(CH_2)_2NH_2/SiO_2$ at the same conditions. This suggested that the catalyst basicity played an important role in the reaction, as previously reported for solid base catalysts [28]. Furthermore, both TBD/SiO_2 and $NH(CH_2)_2NH_2/SiO_2$ were recovered by filtration, and were subjected to utilization for five cycles (see Fig. 4). $NH(CH_2)_2NH_2/SiO_2$ showed better reusability than TBD/SiO_2.

3.4. Possible mechanism

Bifunctional catalysts have been extensively used for the CO_2/epoxide coupling reaction to achieve high yields. The cooperative actions of base and acid sites for the cyclic carbonate synthesis were proposed [16–19], in which, the epoxide was activated via binding to a Lewis acidic metal center followed by nucleophilic ring-opening resulting from attack of Lewis base towards epoxide. These interactions had synergistic effect on each other. The activation of CO_2 was

Table 2
Base strengths and CO_2 coupling with propylene oxide

Catalysts	pK_a values of the indicators			Reaction results	
	7.2	9.3	15.0	Conversion of propylene oxide (%)	Selectivity towards propylene carbonate (%)
SiO_2	−	−	−	0	0
NH_2/SiO_2	+	±	−	6.1	90.3
$NH(CH_2)_2NH_2/SiO_2$	+	+	−	86.4	99.7
TBD/SiO_2	+	+	±	99.5	99.8
$TBD/Me/SiO_2$	+	+	±	0.2	99.3

(+) Clear color changes; (−) color does not change; (±) uncertain color changes. Reaction conditions: 423 K; initial CO_2 pressure, 2.0 MPa at 293 K; amount of propylene oxide and catalyst was 12.45 and 0.8 g, respectively; reaction time, 20 h.

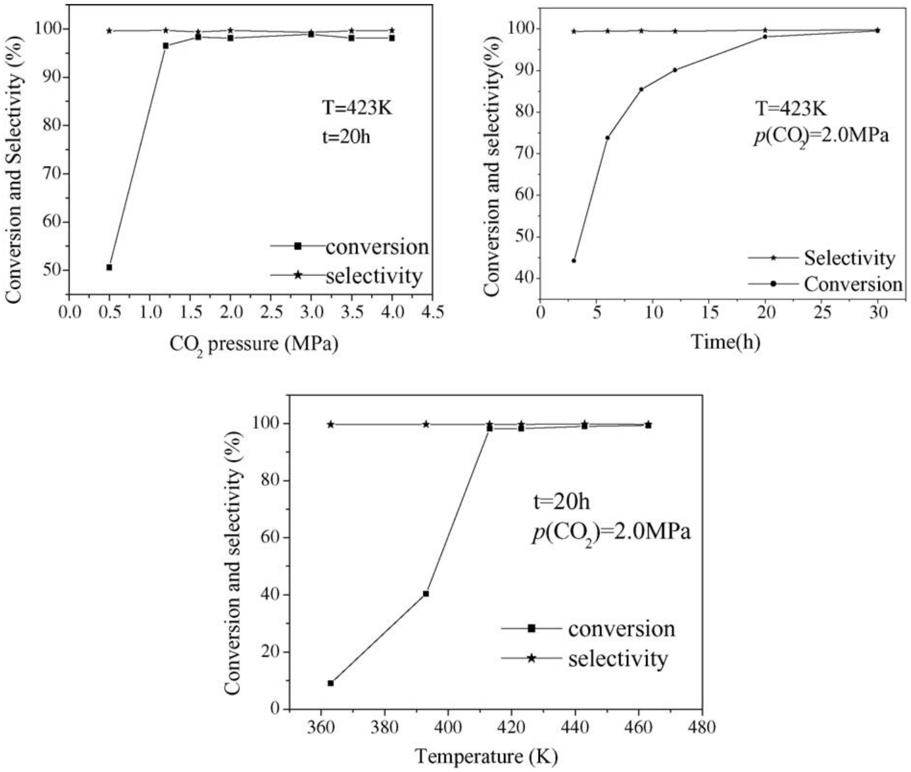


Fig. 3. Conversion and selectivity as a function of time, temperature and CO_2 pressure with TBD/SiO_2 catalyst.

generally initiated by nucleophilic attack of the alcoholate at the carbon atom of CO_2 and the ring-opening of epoxides was described in terms of two pathways, i.e., an acid-catalyzed cleavage and a base-catalyzed cleavage [29]. In the present case, however, the samples used for the coupling reaction were characteristic of single site, i.e., the catalyst with unique basic site similar to the homogeneous base. As there was no Lewis acidic site on the catalysts, the mechanism should be different from those involving bifunctional catalysts.

With amine-functionalized silica, CO_2 could be activated by amine groups, which might be beneficial for the insertion of CO_2 into the C–O bond of epoxides via nucleophilic attack, as previously reported for solid basic catalysts [14,28]. On the other hand, high CO_2 concentration hardly reduced the conversion of propylene oxide (see Fig. 3), which was different from the conventional mechanism reported in literature [30]. Thus, the activation of propylene oxide seemed different from the pathway of the conventional mechanism, and the hydroxyls such as the silanols on the support surface perhaps are involved in the activation of epoxide by H-bond formation (see Scheme 2). On condition that such hypothesis is reasonable, the epoxides activated by H-bond formation were readily ring-opened in view of nucleophilic attack of even poorly nucleophilic reagents. The synergistic effect was sufficient to promote the insertion of CO_2 to epoxides to form linear carbonates, which were transformed into cyclic carbonates by intramolecular substitution. In order to understand the role of the silanols on the silica surface, the surface of TBD/SiO_2 was modified by methyl groups to remove

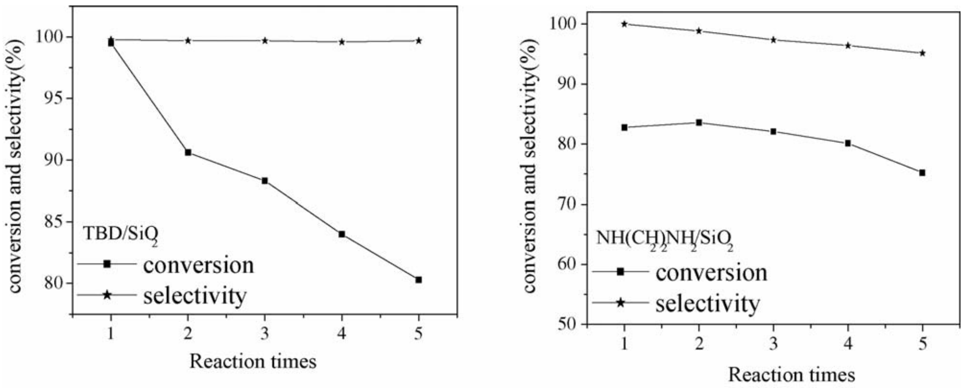
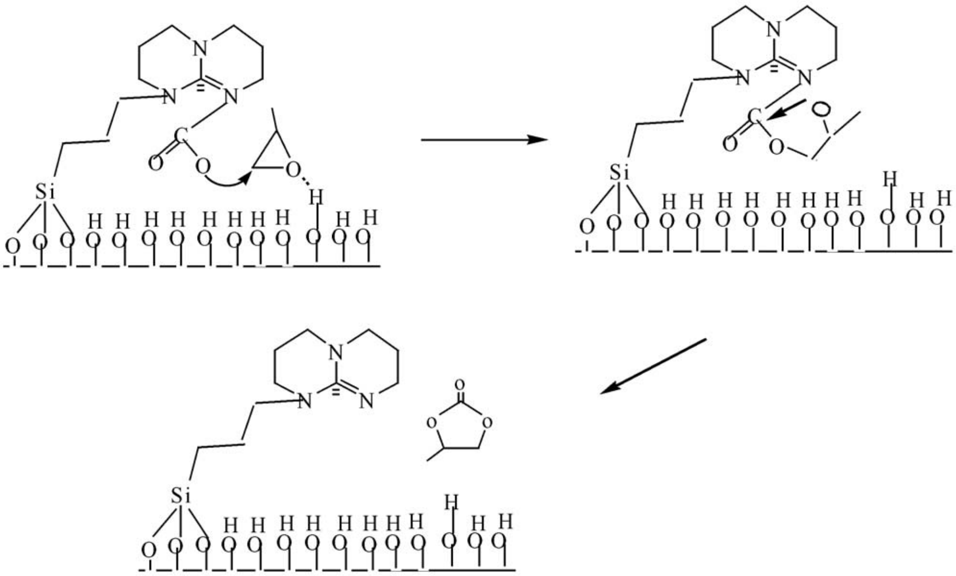


Fig. 4. The reusability of $NH(CH_2)_2NH_2/SiO_2$ and TBD/SiO_2 for the cycloaddition of carbon dioxide and propylene oxide. Reaction conditions: 423 K; initial CO_2 pressure 2.0 MPa at 293 K; amount of propylene oxide and catalyst were 12.45 and 0.8 g, respectively; reaction time = 20 h.



Scheme 2. Possible mechanism for cycloaddition of CO_2 to an epoxide on TBD/SiO_2.

the surface hydroxyls. The resultant was named as TBD/Me/SiO_2. It was interesting that the conversion of propylene oxide to propylene carbonate decreased to 0.2% for TBD/Me/SiO_2 (see Table 2). This strongly suggested the importance of the silanol groups in the reaction, i.e., the silanol-free surface was inactive towards CO_2 coupling with epoxides. A deeper understanding of this mechanism is underway.

4. Conclusions

The efficient ultrasonic technique was used for the preparation of amine-functionalized porous catalysts for CO_2 coupling with epoxide. The characterization indicated that the amine groups were grafted onto the silica surface by covalent bond. Such hybrid solid bases showed high catalytic activity towards CO_2 coupling with epoxide. Besides catalyst basicity, the reaction time, reaction temperature and CO_2 pressure was found to have a great influence on the catalytic performance. The catalysts could be recovered by filtration and were subjected to utilization for several cycles. Furthermore, silanols on the surface were found to play an important role in the coupling reaction.

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