A short review of catalysis for CO_2 conversion

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ABSTRACT

To be the abundant natural feedstock, CO_2 chemical utilization has attracted the great interest in recent years. The key point to CO_2 conversion is the activation of either CO_2 or co-reactant at different conditions. To bear this in mind, our strategy is to activate CO_2 either with the presence of electron-rich chemicals or by hydrogen, and to convert CO_2 with a coupling reaction in some case. In this way, catalytic conversion of CO_2 has been carried out by different methodology at our lab, including CO_2 reforming of methane to syngas production over bifunctional catalysis, CO_2 hydrogenation for methanol synthesis by nano-structured catalyst, and synthesis of carbonates from sub- or super-critical CO_2 with a coupling of in situ water removal reaction or bifunctional catalyst system. Herein, this brief review presents the recent progress of catalytic CO_2 conversion and aims to shed a light into the chemical fixation of CO_2.

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CO_2 is a cheap, nontoxic and abundant C1 feedstock and its chemical utilization is a challenge and important topic. Thus, any efficient reactions using CO_2 as a reagent have positive ramifications on efforts towards carbon management. However, CO_2 is a thermodynamically stable compound, and then its reduction requires high energy substances or electroreductive processes. Such an inert property of CO_2, together with the lower reactivity in various reactions, is probably the major reasons why currently the toxic carbon monoxide, as a C1 building unit for many processes, is used mostly in industry. Although a number of organic syntheses using carbon dioxide are known, only a few were applied in industry, the main processes being the syntheses of urea and its derivatives, and the production of organic carbonates, where phosgene ($COCl_2$) is increasingly being replaced by CO_2 as the C1 building unit. Another important CO_2 consumer is the electrochemical Kolbe–Schmitt process for the production of salicylic acid.

The potential of homogeneous catalysis for CO_2 fixation has been discussed in recent reviews [1–3]. Valuable chemicals including the production of carbonates [4], carbamates [5], urethanes [6], lactones [7], pyrones [8], and formic acid and its derivatives [9] could be synthesized by homogeneous catalysts. Heterogeneous catalysis can offer several technical advantages such as stability, separation, handling and reuse of the catalyst and reactor design. Despite CO_2 activation by heterogeneous catalytic routes were still limited, efforts have been made towards the synthesis of dimethyl carbonate, cyclic carbonates, and synthetic gas (CO, H_2) as well as methanol synthesis from CO_2 hydrogena-

tion. This brief review is therefore intended to provide an overview of the research progress on those topics.

1. CO_2 reforming of CH_4

CH_4 and CO_2 are relatively inexpensive due to their natural abundance; hence, conversion of these two molecules to higher-value compounds is of great interest. The reaction between CO_2 and CH_4 to produce synthesis gas (i.e., $CO + H_2$) can be used in chemical energy transmission systems or utilized in the Fischer–Tropsch reaction to produce liquids. Reforming with CO_2, rather than H_2O, could be employed in areas where water is not available to form syngas with lower H_2/CO ratios.

$$CO_2 + CH_4 = 2CO + 2H_2, \qquad \Delta H_{298\,K} = 247.3\,kJ/mol \qquad (1)$$

Numerous researches have been devoted to the catalytic performance of noble metals such as Rh, Ru, Pd, Pt and Ir towards CO_2 reforming of CH_4 [10–15]. It is generally accepted that Rh and Ru showed both high activity and stability in CH_4 dry reforming, while Pd, Pt and Ir were less active and more prone to deactivation. Typically, the catalyst activity were in the order of: $Rh \approx Ru > Ir$, Pt and Pd. The nature of support may have some influences on the activity of noble metals. Rezaei et al. studied a series of noble metal catalysts supported on alumina-stabilized magnesia for the production of synthesis gas from methane and carbon dioxide. The catalyst activity were in the order of: $Rh \approx Ru > Ir > Pt > Pd$ [10]. Nielsen et al. found that for MgO supported catalyst, the activity for CO_2 reforming was in the order of Ru, $Rh > Ir > Ni$, Pd, Pt [11]. Erdohelyi's study indicated that the activity toward the CH_4 dissociation varied in the order of $Rh/Al_2O_3 > Rh/TiO_2 > Rh/$

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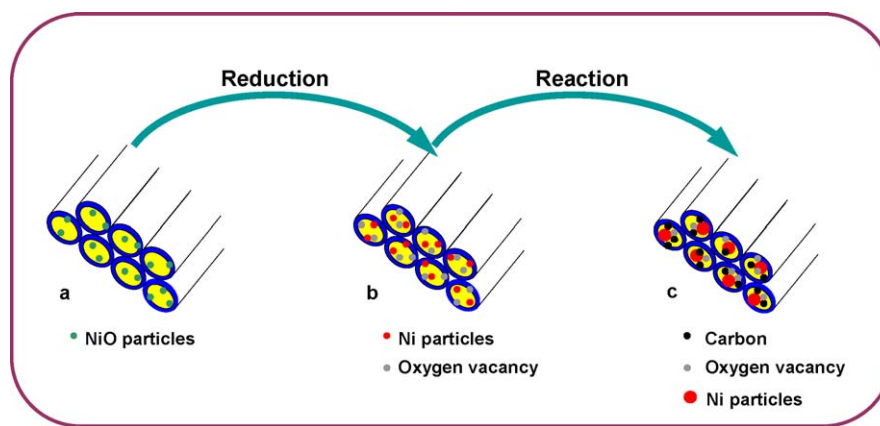
Scheme 1. Concept design of stable Ni-based catalyst.

$SiO_2 > Rh/MgO$ [13]. However, considering the aspects of high cost and limited availability of noble metals, it is more practical, from the industrial standpoint, to develop non-noble metal catalysts which exhibited both high activity and stability.

Ni-based catalysts have been widely investigated [6,16–19] due both to their similar activity and relatively low price when compared with noble metals. However, Ni-based catalysts were readily deactivated by carbon deposition and sintering. Thus, more effort were devoted towards development of a stable Ni-based catalyst with high activity. Liu et al. employed MCM-41 as support and prepared a Ni/MCM-41 catalyst by different method, it is proved that the loading amounts of Ni and preparation method have great influence on the catalytic stability [17]. Methane dry reforming was carried out by Liu et al. over 7 wt.% Ni/SiC monolithic foam catalyst. The catalyst exhibited excellent activity and stability during 100 h [18]. By using CeO_2 and ZrO_2 as modifiers, Corthals et al. improved the catalytic performance of a $Ni/MgAl_2O_4$ catalyst. The doubly promoted $NiCeO_2ZrO_2/MgAl_2O_4$ catalyst within a certain composition ranges have higher stability than singly promoted ones [19].

Al_2O_3, MgO, CaO were used as support to prepare Ni-based catalysts for CH_4 reforming reaction. It should be noticed that the support with Lewis basic site might promote the carbon-resistant ability of the catalyst for the strong adsorption capacity of CO_2. Furthermore, strong interaction might promote the dispersion of Ni on the support, while much stronger interaction would decrease the reducibility of Ni and thus the active sites Ni^0 on the catalyst surface. Besides, it was suggested that the formation of filamentous carbon was significantly influenced by the metal particle size and preceded mostly over the metal particles larger than 7 nm, which implied that the support might affect the catalytic stability of the catalyst [16].

Keep those mentioned above in mind, a novel catalyst, Ni–CaO–ZrO_2 nanocomposite, was designed for the CO_2 reforming of methane at our lab (see Scheme 1). Such a catalyst system with high surface area and high thermal stability was synthesized via a facile sol–gel process. Mesoporous ZrO_2 was employed as the substrate (see Scheme 1a), which has good oxygen storage capacity and high hydrothermal stability. In this case, Ni particle was effectively confined by the mesoporous framework and ZrO_2 was partially reduced with the formation of oxygen vacancies on the catalyst surface (see Scheme 1b). Introduction of Ca^{2+} gave rise to strong basicity of the catalyst as well as the stabilization effect to the oxygen vacancies. As a result, coke elimination capacity was improved on such a catalyst system, and the thermodynamically favored carbon deposition process during reaction was also suppressed by the small Ni particles.

In the present catalyst, most pores had a diameter of smaller than 15 nm (see Fig. 1), such a porous structure with high thermal stability showed a "confine effect" to prevent Ni particles from sintering and crystalline growth, which was very important for the catalytic stability towards CO_2 reforming of CH_4. H_2-TPR of the catalyst indicated a main reduction peak at 883 K with a shoulder at 723 K (see Fig. 2) which could be attributed to the reduction of NiO particles interacted strongly and weakly with ZrO_2, respectively. The large peak at the high temperature suggested that most of the NiO in the catalyst interacted strongly with ZrO_2 support.
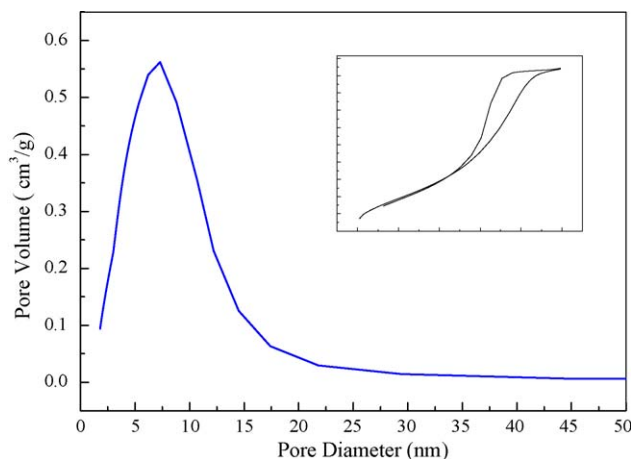

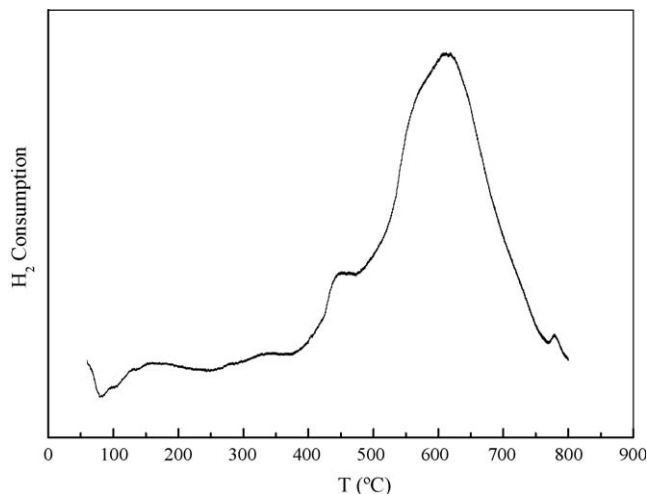**Fig. 1.** Pore distribution and absorption isotherms of Ni–CaO–ZrO_2 nanocomposites.

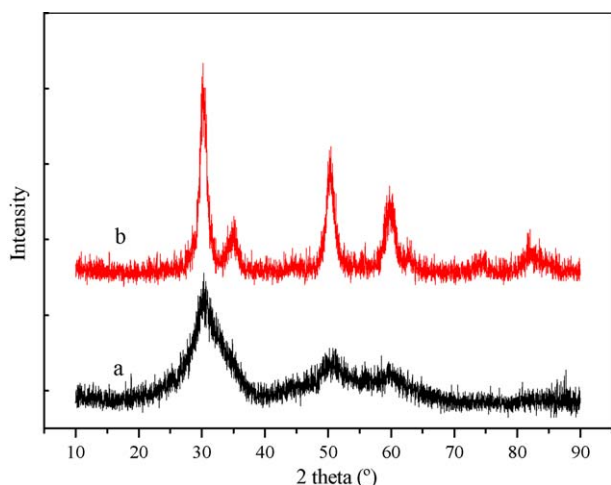**Fig. 2.** TPR pattern of Ni–CaO–ZrO_2 nanocomposites.

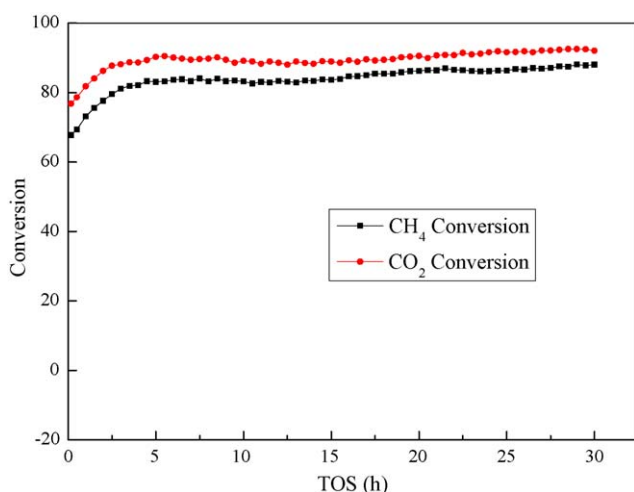**Fig. 3.** XRD patterns of fresh and used Ni–CaO–ZrO₂ catalyst.

Fig. 4. Catalytic performance of Ni–CaO–ZrO₂ catalyst (973 K GHSV = 6000 ml h⁻¹ g⁻¹ CH₄/CO₂ = 1).
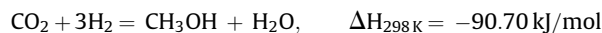
This could improve the dispersion of NiO and promoted the resistance to sintering under reaction conditions. The XRD patterns of the catalyst before and after reaction indicated no apparent change and growth in the NiO (or Ni) and CaO crystalline phase (see Fig. 3 a: Before b: after). This could be attributed to the formation of a Ni–Ca–Zr–O "nano-composite" which justified the interplanar distance of ZrO₂ lattice and consequently, responsible for the strong interactions between Ni and ZrO₂. As a result, the Ni–CaO–ZrO₂ catalyst showed both high catalytic activity and stability in CO₂ reforming of CH₄ (see Fig. 4). The conversion appeared higher for CO₂ than that of CH₄, which could be attributed to the occurrence of RWGS reaction.

2. CO₂ hydrogenation to methanol

Carbon dioxide is a kind of potential carbon raw material and also one of the air pollutants [20]. In the past decades, the potential use of CO₂, as an alternative feedstock replacing CO in the methanol production has received attention as an effective way of CO₂ utilization. Under proper conditions, methanol made from atmospheric CO₂ by its reaction with hydrogen is regarded as the "most economic way" to mitigate the greenhouse effect which is caused by the substantial rise of CO₂ concentration in the atmosphere [21,22].

In the process of CO₂ hydrogenation, the major reaction is the methanol formation, while reverse water-gas-shift reaction composes of the side reactions [23]:

Methanol formation

$$CO_2 + 3H_2 = CH_3OH + H_2O, \qquad \Delta H_{298\,K} = -90.70\,kJ/mol$$

Reverse water-gas-shift reaction

$$CO_2 + H_2 = CO + H_2O, \qquad \Delta H_{298\,K} = 41.19\,kJ/mol$$

The methanol formation is an exothermal reaction with reduction of reaction molecule number. Thus, the decrease of temperature and the rise of pressure should favor for the reaction from thermodynamical analysis. However, considering the reaction rate and the chemically inert nature of CO₂, the enhancement of reaction temperature (>513 K) facilitates CO₂ activation and then the methanol formation. The reverse water-gas shift reaction causes extra consumption of hydrogen and a reduction of methanol formation. Meanwhile, the large amount of water form as a by-product, from both methanol synthesis and the reverse water-gas shift side reaction, also had an inhibitory effect on the active metal during the reaction [24,25], leading to the deactivation of the catalyst. Besides, other hydrogenated products such as higher alcohols and hydrocarbons are usually associated with methanol formation. Therefore, methanol synthesis from CO₂ hydrogenation requires a more selective catalyst to avoid the formation of undesired by-products.

Highly efficient catalyst is the key for methanol synthesis via CO₂ hydrogenation. Up to now, the exploitation of the catalyst is still not fully satisfactory for industrial application due to the lacking of the necessary knowledge in catalyst designing for the control of relevant catalytic properties and the mechanistic understanding of CO₂ hydrogenation. Although some kinetic experiments with the aid of isotope-labeled CO and spectroscopy [26–28] have demonstrated that methanol was produced by hydrogenation of CO₂ rather than CO, the commonly used ternary Cu–Zn–Al oxide catalyst at 5.0–10.0 MPa and 473–523 K for CO hydrogenation was not so active for hydrogenation of pure CO₂ [29]. Most catalyst used in CO₂ hydrogenation was the modified methanol catalyst for CO hydrogenation and the research addressed the chemical composition, supports, additives, different preparation methods/conditions and morphology.

The majority of the catalysts for CO₂ hydrogenation contained Cu and Zn as the main components together with different modifiers (Zr, Ga, Si, Al, B, Cr, Ce, V, Ti, etc.) [30–33]. Liaw and Chen [30] obtained ultrafine Cu/ZnO-based catalysts using a reduction method in which the dispersion and stability of copper could be improved by doping Cr, Zr and Th. Saito [31] reported that Al or Zr improves the dispersion of copper particles while Ga or Cr increases the specific activity per unit Cu surface area of the catalyst. And their further studies found that the Cu/ZnO-based multi-component catalysts such as Cu/ZnO/ZrO₂/Al₂O₃ and Cu/ZnO/ZrO₂/Al₂O₃/Ga₂O₃ were highly active for methanol synthesis from CO₂ and H₂. The addition of a small amount of colloidal silica to the multi-component catalysts greatly improved their long-term stability during methanol synthesis from CO₂ and H₂. Nitta et al. [32] implied that the proper addition of certain amounts of ZnO to the Cu/ZrO₂ catalyst could greatly enhance its activity. Arena [33] found that the Cu–ZnO/ZrO₂ prepared by reverse co-precipitation under ultrasound irradiation exhibited a significant improvement in the total surface area of the metal phase, and then the enhanced CO₂ conversion and methanol yield. Yang et al. [22] studied the properties of the ZrO₂-doped CuZnO catalyst prepared by precipitation method. XRD characterization confirmed that the active phase of copper in CuZnO catalyst prepared by co-

precipitation was well crystallized. The presence of ZrO_2 led to a high copper dispersion, which was distinctive from CuZnO. Though the activity for carbon monoxide hydrogenation was little lower than that of CuZnO catalyst. ZrO_2-doped CuZnO catalyst showed much higher activity and selectivity towards methanol synthesis in carbon dioxide hydrogenation.

In the noble metal-based catalysts, the supported Pd catalysts are the most commonly used catalyst, which exhibit considerable activity and selectivity for hydrogenation of CO_2 to methanol, and the supports has significant effect on the performance of the catalyst. Edwin et al. [34] investigated the effect of the supports such as SiO_2, Al_2O_3, ThO_2, La_2O_3 on the catalytic performance of the supported Pd catalysts. The experiment showed that methanol selectivity can reach above 89% at 623 K and 12 MPa on the Pd/La_2O_3, while methane was the major product when Pd supported on the acidic supports. Fan et al. [35] reported that Pd/CeO_2 possesses higher activity and longer lifetime after the catalyst was reduced by H_2 at 773 K. Recently, Liang et al. [36] developed a type of Pd–ZnO catalysts supported on multi-walled carbon nanotubes (MWCNTs), which showed the excellent performance for CO_2 hydrogenation to methanol. Under reaction conditions of 3.0 MPa and 523 K, the observed turnover-frequency of CO_2 hydrogenation reached $1.15 \times 10^{-2}\,s^{-1}$ over the 16% Pd0.1Zn1/CNTs(h-type). PtW/SiO_2 catalyst also reported to be used in CO_2 hydrogenation. Under the conditions of 473 K, 3 MPa and H_2/CO_2 ratio of 3, methanol selectivity can reach 92.2% with CO_2 conversion of 2.6% [37].

Transitional metal carbides are a type of metal-derived compounds with the incorporation of carbon in the metal lattice. They have the physico-chemical properties of high melting point and hardness, high thermal and mechanical stability as well as excellent catalytic performance for hydrogenation, which are similar to those of Pt, Rh and other noble metals [38,39]. Thus, the metal carbides can be used as potential substitutes for noble metal catalysts. Compared with metal sulfides, metal carbides possess superior hydrogen adsorption, activation and transfer capabilities, and then they have potential application in CO_2 hydrogenation reactions.

From a view of practice, a highly active, selective and poisoning-resistant catalyst for methanol synthesis is desirable. Some researchers attempted to use transition metal carbides for methanol synthesis via CO_2 hydrogenation. Different carbides were tested for CO_2 hydrogenation, the results indicated that Mo_2C and Fe_3C showed high CO_2 conversion and good methanol selectivity, while TaC and SiC were almost inactive [40]. Such results seemed that metal carbides catalysts need to be further improved for the application for methanol synthesis via CO_2 hydrogenation.

Besides the exploration of the catalyst with excellent performance, the innovation of reactor and process technology is another important aspect for obtaining the higher yield and better selectivity toward methanol with the reducing proportion of by-products in CO_2 hydrogenation. The methanol productivity is usually low using the traditional on-stage catalyst bed in the fixed-bed gas phase tubular reactor. Rahimpour [41] proposed a two-stage catalyst bed concept for conversion of carbon dioxide into methanol. Compared with a conventional single catalyst bed system, two-stage bed system showed the extremely favorable temperature profile along the reactor tube length, causing a higher level of catalyst activity and a longer catalyst life time. Also, favorable temperature profile of catalyst bed plus high level of catalyst activity in gas-cooled reactor of two-stage bed system, results in more production rate in this system. Other researchers [29] employed a novel low-temperature route in a semi-bath autoclave reactor for the efficient conversion of CO_2 into methanol. This process realized a very high catalytic activity of methanol

production with 25.9% of CO_2 conversion and 72.9% of methanol selectivity at the low temperature of 443 K and pressure of 5 MPa using alcohol as solvent. Tsubaki et al. studied a new pathway for CO_2 hydrogenation to methanol over copper catalyst. In this novel process, alcohol, acted as both solvent and a catalytic liquid medium, changed the pathway of low temperature reaction. Conversion of CO_2 reached 25.9% with a methanol selectivity of 72.9% [29].

Catalytic conversion of CO_2 hydrogenation into methanol is an attractive way to protect the global environment. Although many efforts have been made to facilitate the technology progress of methanol synthesis from CO_2 hydrogenation, the highly efficient process to enhance the CO_2 conversion is still pursued due to the thermodynamically stable nature of CO_2 molecule. The catalyst stability, catalyst sensitivities to impurities, catalyst intensity and reaction performance under scale-up conditions are needed to investigate in detail. Besides, the mechanism for methanol synthesis via CO_2 hydrogenation is not fully understood. The future shall emphasize the further developing highly efficient catalyst and integrated process technology to meet the economic efficiency for mitigation of global warming gases and sustainable development of carbon market demands.

3. Synthesis of dimethyl carbonate from CO_2 and methanol

$$CO_2 \;+\; 2CH_3OH \longrightarrow H_3C \diagdown_O \diagup^{\displaystyle \overset{O}{\underset{|}{C}}} \diagdown_O \diagup CH_3 \;+\; H_2O$$
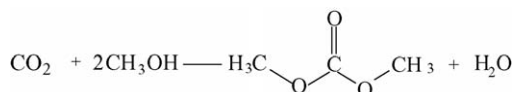
Dimethyl carbonate (DMC) was widely used in industry [42–44]. Synthesis of DMC directly from CO_2 and methanol was favorable not only for reduction of greenhouse gas emissions but also for development of new carbon resource. Typically, synthesis of DMC from CO_2 and methanol was conducted in an autoclave. Lee et al. investigated the catalytic performance of supported copper catalyst and found that the reaction temperature and pressure had great influence on the DMC yield [45]. Kizlink et al. found that Sn(IV) and Ti(IV) alkoxides was effective for DMC synthesis from CO_2 and methanol using metal acetates as support [46–48]. Fang et al. reported that MCO_3 (Here, the letter M means alkaline metal) was superior for DMC formation, moreover, CH_3I played a key role in the reaction [49]. Fang et al. found that Mg powder showed better performance than Ca powder, while Al powder showed no activity toward the reaction. The DMC yield reached to the maximum at the reaction pressure of 7.5 MPa which was related with the supercritical state of CO_2 [50]. Cao et al. also found DMC yield reached to the maximum near the critical pressure of CO_2 over K_2CO_3 and CH_3I. The possible reaction mechanism was as follows: methanol was decomposed to CH_3O- and $H+$ by K_2CO_3 followed by CO_2 insertion to form $[CH_3O–(CO)O]–$, which reacted with CH_3I and H^+ to form DMC and HI. CH_3I was recovered via reaction of HI and methanol [51]. The catalytic activities of the organotin alkoxides were very low due to the decomposition of the catalysts by the side-product water. Toshiyasu et al. indicated that the yield and selectivity of DMC enhanced by the increase of CO_2 pressure taking $R_2Sn(OMe)_2$ as the homogenous catalyst under the critic condition. However, $R_2Sn(OMe)_2$ was unstable in the moist environment, which could hydrolyze with the by-product water. Thus, some typical dehydrating agents, such as dimethyl acetal and trimethyl ortho ester, to consume the water were used in this reaction system. And the DMC yield could reach as high as 70% [52,53]. Furthermore, the reaction mechanism and structure of $R_2Sn(OMe)_2$ were also discussed in detail [54].

Bell et al. deduced the adsorption configuration of CO_2, DMC and methanol through Raman spectra. The mechanism for the reaction of methanol and CO_2 was elucidated in Scheme 2 [55,56].
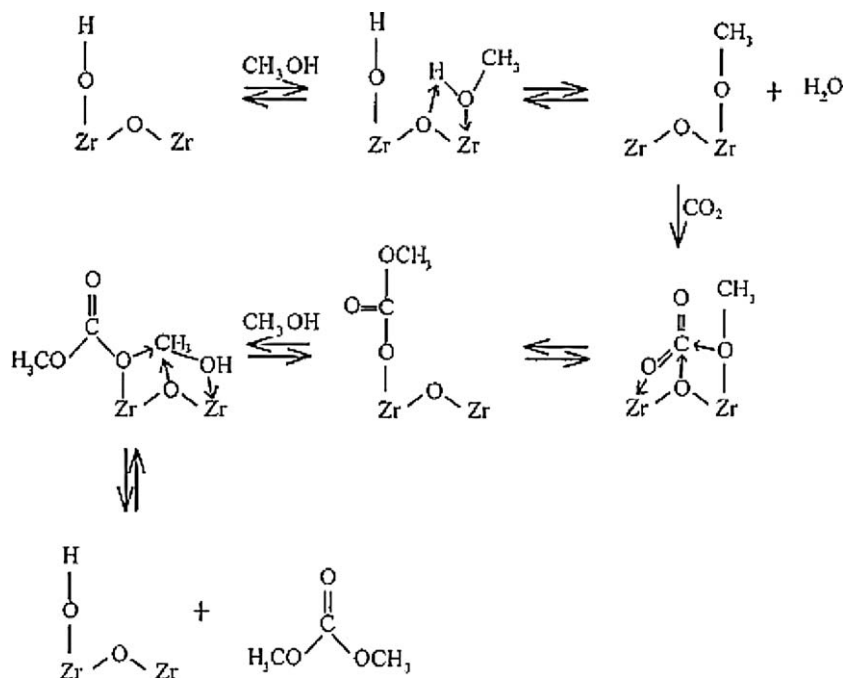
Scheme 2. Mechanism for the reaction of methanol and CO_2.

Jiang et al. has reported the zirconia supported Kiggin unit 12-tungstophosphoric acid/zirconia ($H_3PW_{12}O_{40}/ZrO_2$), which was prepared via sol–gel technique, promoted the formation of DMC from CO_2 and methanol effectively under mild condition. The results shown that with the amount of $H_3PW_{12}O_{40}$ on the catalysts in the range of 0–50 mg the DMC formation increased almost linearly. And the mechanistic studies indicated that acid–base bifunctional catalysis is essential in selective DMC synthesis. Compared with ZrO_2, the $H_3PW_{12}O_{40}/ZrO_2$ catalysts has weak Brønsted acid sites, uniquely, which were more effective than Lewis acid sites for CH_3OH activation [57].

Wu has reported direct synthesis DMC from gaseous methanol and CO_2 over the modified V_2O_5 catalysts, such as H_3PO_4/V_2O_5 and Cu–Ni/VSO. In the H_3PO_4/V_2O_5 catalysts, the direct interaction between V and P formed weak Brønsted acid sites, which were more effective for the CH_3OH activation. The crystal phase of H_3PO_4/V_2O_5 was influenced by the composition of P/V, significantly, and with $P/V = 0.15$–0.50 it was in bicrystal phase (orthorhombic/tetragonal) showed effective activation of both CO_2 and CH_3OH [58].

At our lab, direct synthesis of dimethyl carbonate from CO_2 and methanol was carried out at near supercritical conditions using nickel acetate as the catalyst. It was demonstrated that DMC could be produced as the unique product at such low temperature as 305 K and the yield was 12 times higher than that at non-supercritical conditions. The synthesis was sensitive to the

reaction pressure and showed a maximum for DMC yield at the pressure of 9.3 MPa. The concentration of methanol showed an obvious influence on both the yield and selectivity of DMC. Nickel acetate appeared to be the precursor of the catalyst. The formation mechanism of dimethyl carbonate in supercritical phase was proposed in Scheme 3 [59].

4. Reaction of CO_2 and propylene glycol (PG)

Cyclic carbonate can be used to produce chain carbonate via transesterification which is a widely used method for carbonate synthesis [60,61]. In particular, five-membered ring carbonate, propylene carbonate (PC) are used as the feed of one of the main process for dimethyl carbonate (DMC) synthesis, with 1,2-propanediol (1,2-PG) as by-product. Thus, if 1,2-PG could be further used to produce PC with CO_2, not only 1,2-PG but also CO_2 would be recycled, which could be considered as a new green technology.
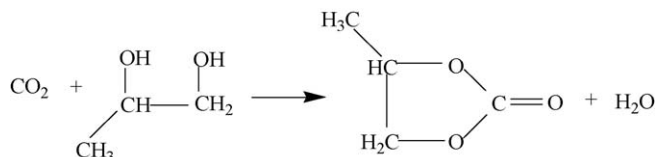
Tomishige et al. [62,63] found that over CeO_2–ZrO_2 catalysts, cyclic carbonates such as ethylene carbonate (EC) and 1,2-PC were selectively synthesized via the reactions of CO_2 with ethylene glycol and PG, respectively. No polycarbonate and ethers (diethylene glycol and dipropylene glycol) were detected under the optimum reaction conditions. The 1,2-PG conversion was 2%, and was much dependent on the composition and calcination temperature of the catalysts. On the basis of the catalyst characterization, it was suggested that the active sites could be weak acid–base sites which were present on the plain surface of the catalysts calcined at high temperatures. On the other hand, catalyst calcined at high temperature exhibited low activity due to very low surface area. Du et al. [64] evaluated the catalytic performance of Sn compound in this reaction and found that the
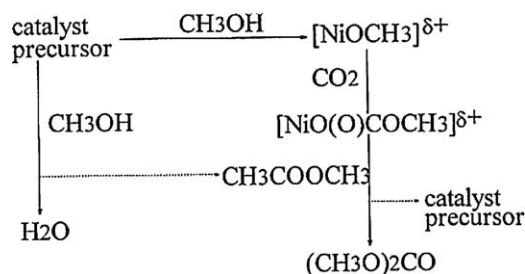
Scheme 3. Plausible mechanisms of dimethyl carbonate formation.

$$CH_3CN \xrightleftharpoons{+H_2O} CH_3CONH_2 \xrightleftharpoons{+H_2O} CH_3COOH + NH_3$$
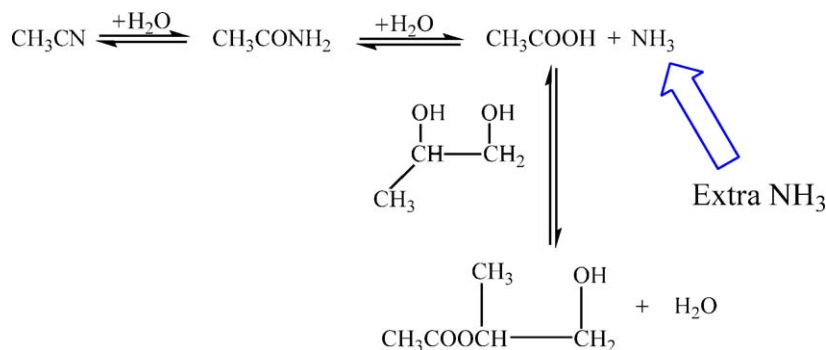
Scheme 4. Possible mechanism of ammonium carbonate formation.

selectivity of PC was 99.9%, but the yield of PC was only 3.4%. They presumed that dibutyltin oxide reacted with 1,2-PG to give 4-methyl-2,2-dibutyl-1,3,2-dioxastannolane, then the Sn–O bond in 4-methyl-2,2-dibutyl-1,3,2-dioxastannolane was easily inserted by CO_2 to form a cyclic tin carbonate, and finally a subsequent intramolecular nucleophilic attack of alkoxy group on the carbonyl carbon atom caused the formation of PC and regeneration of dibutyltin oxide.

Although the selectivity of PC was high, the conversion of 1,2-PG was less over the above mentioned catalysts. Water, the by-product, was concluded to limit the equilibrium. More recently, CH_3CN was reported as an available dehydrater in the carbonylation of 1,2-PG. Wang et al. utilized zinc acetate [65] to catalyze the reaction of CO_2 and 1,2-PG to synthesis PC in the presence of acetonitrile. With the acetonitrile hydrolysis, the conversion of 1,2-PG and the yield of PC increased obviously. They suggested that for zinc acetate, it turned to ZnO by the reaction with PG and then ZnO reacted with both CO_2 and NH_3 to form $(NH_3)ZnCO_3$, and a possible mechanism for the synthesis of PC from CO_2 and PG over zinc acetate catalyst was elucidated [66].

However, in this reaction system acetic acid from the hydrolysis of CH_3CN could react with 1,2-PG to produce PG-2-acetate, which resulted in the drop of the selectivity. At our lab, ammonia and different amido compounds were chosen as the source of ammonia to balance the side reactions for the improvement of PC selectivity [67]. And the results showed ammonium carbonate was probably the best reagents according to the following mechanism (see Scheme 4).

We also reported different catalysts for the carbonylation of 1,2-PG with carbon dioxide in the present of CH_3CN. For alkali carbonates catalysts, with the strengthening of alkaline the catalyst activity was enhanced, and Cs_2CO_3 possessed the best catalytic activity than other alkali carbonates [67]. For organic bases, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) showed best catalytic effects than others [68]. In the reaction PG was activated via being looted one hydroxyl H by the N atom of TBD, followed by the electrophilic attack of CO_2 on the hydroxyl O atom giving rise to an "ion pair". Then, with the proton migrated to the other hydroxyl group of PG, the oxygen of the bonded CO_2 nucleophilicly attacked the hydroxyl-losing carbon in PG to afford PC and water, and the catalyst TBD was recovered. The essence of TBD catalysis lay in its capability to act as a proton bridge with the synergistic action of its N atoms. Further studies showed the catalytic activity of zinc salts [69] catalysts were higher than those of organic base and inorganic base mentioned above. It was found that zinc salts and transition metal halides were only the precursor of catalysts. The real catalysts were coordination compounds, which was generated by the coordination of transition metal atom with acetamide molecules. Zinc oxide modified with potassium salt as catalysts were prepared and used to effectively synthesis PC via the reaction of 1,2-PG with CO_2 in the presence of acetonitrile [70]. Among the catalysts, KI/ZnO showed the highest catalytic activity for PC

synthesis. Moreover, the reaction mechanisms were studied and proposed over different catalysts.

5. Synthesis of cyclic carbonate from CO_2 and epoxide

The synthesis of cyclic carbonate via cycloaddition of CO_2 to epoxide is one of effective routes of CO_2 chemical fixation. Cyclic carbonates were widely used as excellent aprotic polar solvents, electrolytes in secondary batteries, precursors for polycarbonates and other polymeric materials, and intermediates in the production of pharmaceuticals and fine chemicals like dialkyl carbonates, glycols, carbamates, pyrimidines, purines, etc. The catalysts development as well as the reaction mechanisms had been reported over alkali metal halides [71–74], organic bases [75–77], metal oxides [78–81], zeolite [82,83], titanosilicates [84], smectites [85,86], and metal complexes [87–96] for synthesis of cyclic carbonates from CO_2 and epoxides. The synthesis of cyclic carbonates from CO_2 and epoxides has been applied in industrial scales; however, the activity, stability and recovery of the catalysts still remain to be improved.

In recent years, significant progress has been made in the application of ionic liquids as catalysts and alternative solvents in organic synthesis due to their unique advantages of negligible vapor pressure. The use of ionic liquid as reaction media and/or catalysts for clean catalytic transformations would indicate profound effects on the reaction rate and product selectivity. It was also reported that CO_2 could significantly dissolve into the ionic liquid phase, which therefore made the reactions of CO_2 possible and suitable [97,98]. Under these circumstances, the use of ionic liquids would be attractive for synthesis of cyclic carbonate from CO_2 and epoxide.

Deng et al. firstly reported the synthesis of cyclic carbonate over ionic liquids 1-butyl-3-imidazolium tetrafluoroborate ([C4-mim]BF$_4$) [99]. They also found that either cation or anion affects the activity of the ionic liquid. The activity for propylene carbonate synthesis decreased in the order of imidazolium > pyridinium and of $BF^{4-} > Cl^- > PF^{6-}$. Kawanami et al. [100] investigated the cyclic carbonates synthesis over various 1-alkyl-3-methylimidazolium salts ([Cn-mim]X) under scCO$_2$ and found that both anion and the length of alkyl chain in the cation were important for the catalytic performance. The carbonate yield increased with the increasing of the alkyl chain length (from C2 to C8) which might be attributed to the higher solubility of both the epoxide and CO_2 in the ionic liquid having longer alkyl chain under the same pressure and temperature. Moreover, influence of CO_2 pressure on the yield also depended on the alkyl chain length, e.g. for [C8-mim]BF$_4$, with the CO_2 pressure reduced from 14 MPa to a subcritical pressure of 6 MPa, a remarkable decrease of the yield was also observed.

It was also found that the presence of Lewis acidic compounds as cocatalysts greatly enhanced the activity of ionic liquid for the cyclic carbonate synthesis. Kim et al. [101] showed that with the addition of ZnBr$_2$, the catalytic activities of ionic liquid [C4-

mimi]Cl or [C4-mim]Br for the reactions of CO_2 with ethylene oxide and propylene oxide can surprisingly be improved, although zinc bromide alone showed no activity for the reactions. It might be due to the in situ formation of bis(1-butyl-3-methylimidazolium) zinc tetrahalides from $ZnBr_2$ and [C4-mim]Cl or [C4-mim]Br.

For conversion of styrene oxide to styrene carbonate, high reaction temperature, long reaction time, high CO_2 pressure, and/or solvent were required to obtain satisfied styrene carbonate yield due to the less reactivity of b-carbon atom compared with propylene oxide and ethylene oxide. Recently, Arai et al. found that the catalyst system comprised of $ZnBr_2$ and an ionic liquid [C4-mim]Cl, could afford 93% yield with 100% selectivity for styrene carbonate at 353 K for 1 h [102] instead of the lower activity for $ZnBr_2$ and [C4-mim]Cl. They also found that the type of metal cations in metal halides which acted as co-catalyst had strong effect on the carbonate yield. The type of anion as well as the length of alkyl chain on the imidazolium cation had strong effects on the conversion and selectivity. Besides, the [C4-mim]Cl/$ZnBr_2$ ratio also affected the carbonate yield.

Several research groups studied the reaction mechanisms for the synthesis of cyclic carbonate from epoxide and CO_2 and proposed that both Lewis base for the activation of CO_2 and Lewis acid for the activation of epoxide were demanded in the reaction despite the different catalyst systems [79,80,92,94,97,103]. Ionic liquids could also act as solvents in the reaction of CO_2 and epoxide, e.g. Garcia et al. [104] have reported that [C4-mim]PF_6 was a suitable reaction media for the CO_2 cycloaddition to epoxide catalyzed over chromium salen complex. The catalyst could be recovered and reused by liquid–liquid extraction of the substrate and the products after the reaction. Zhang et al. prepared a series of hydroxyl-functionalized ionic liquids (HFILs) which showed efficient reactivity and reusability toward the coupling of epoxide and CO_2 without any additional co-catalyst and organic solvent. OH groups in the catalyst or reaction media were crucial for the reaction to proceed smoothly due to its cooperation function of ring-opening of epoxide. Highest activity and selectivity were achieved in the presence of 1-(2-hydroxyl-ethyl)-3-methylimidazolium bromide (HEMIMB) [105].

Although ionic liquid had showed a high performance for the reaction of carbon dioxide and epoxide, the heterogeneous catalyst system still remained a challenge due to the ease of separation and the possibility to use a fixed-bed reactor. Recently, a novel method to immobilize ionic liquid onto solid supports was proposed and used for the hydroformylation [106], hydrogenation [107] and Friedel–Crafts alkylation reaction [108]. Xiao et al. found that the supported [C3-mim]Br/SiO_2-zinc chloride catalyst system exhibited a high activity and selectivity for the synthesis of cyclic carbonates from carbon dioxide and epoxides under mild conditions in a high TOF without any additional co-solvents [109]. Takahashi et al. demonstrated that phosphonium halides covalently bound to SiO_2 exhibit excellent catalytic activities for synthesizing propylene carbonate from propylene oxide and CO_2. The pseudo-first order rate constant of the catalyst normalized to phosphorus atom is about 300 times larger than that of the corresponding homogeneous catalyst [110]. Wang et al. prepared silica-supported [C4-mim]$^+$[BF4]$^-$ and found that the as-prepared catalyst was effective for cyclic carbonate synthesis under supercritical carbon dioxide conditions. High cyclic carbonate yield together with excellent selectivity was achieved [111]. Zhu et al. prepared the ionic liquid choline chloride/urea supported on molecular sieves for the reactions of CO_2 and epoxides and found that this biodegradable and green catalyst was very active and selective, and choline chloride and urea showed a synergetic effect in promoting these reactions [112].

In our work, a series of new catalysts grafted ionic liquid 1-butyl-3-methylimidazolium hydroxide [Bmim]X/SiO_2 were prepared for CO_2 cycloaddition (see Scheme 5).
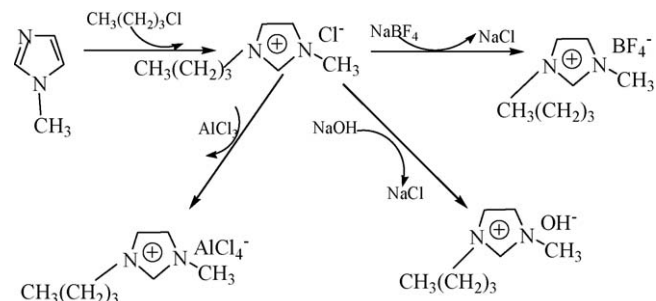
Scheme 5. The preparation of [Amim]OH/SiO_2.

A mixture of [Bmim]OH (30 mmol)and silica powder (20 g, pretreated at 300 °C for 6 h) in toluene (100 ml) was refluxed for 16 h at 90 °C. After being fully stirred, the volatile components of the mixture were removed on a rotary evaporator. Then, the resulting material was dried in vacuum at 80 °C for 12 h. Finally, a red powder was obtained which was denoted as [Bmim]OH/SiO_2.

As the same way, the GILs [Bmim]BF_4/SiO_2, [Bmim]Cl–$AlCl_3$/SiO_2, [Bmim]Cl–$ZnCl_2$/SiO_2 were also prepared, respectively.

The structure of the grafted ionic liquids (GILs) characterized by various physico-chemical measurements such as element analysis, BET, FTIR.

The content of nitrogen, carbon, and hydrogen for porous silica support and the GILs were measured by elemental analysis (Table 1). The results showed that there was no nitrogen and carbon in the porous silica which suggested that nitrogen and carbon in grafted sample came from the ionic liquids instead of the support. Considering that only [Bmim]OH contained N element, so the weight percent of [Bmim]OH could be obtained according to that of N. The grafted amount of [Bmim]OH was about 11.2%, which was equivalent to 1.4 mmol of imidazolium salt per gram of catalyst.

IR is known to be useful for detecting functional group in the molecular. The FTIR spectrums for the novel hydroxyl ionic liquid [Bmim]Cl–$AlCl_3$/SiO_2, [Bmim]Cl–$ZnCl_2$/SiO_2, [Bmim]BF_4/SiO_2 and [Bmim]OH/SiO_2 were recorded in KBr disks and paraffin oil coats because paraffin oil coats could exclude the influence of hydrophilic character and IR absorption of KBr (see Fig. 5). The peaks in the region 3000–2700 cm^{-1} were account for aliphatic C–H stretching frequency and the peak at 3200 and 3800 cm^{-1} were assigned to the hydroxyl band, respectively. In addition, methylic C–H transmutative peak at 1398 cm^{-1} and 1468 cm^{-1}, as well as the peak at 1570 cm^{-1} and 1647 cm^{-1} ascribed to imidazole absorbs and C=N stretching vibration were observed. These bands indicated that ionic liquid groups had been successfully grafted on the support of silica gel.

N_2 adsorption–desorption isotherms for the [Bmim]OH/SiO_2 and SiO_2 (Fig. 6) displayed type IV isotherms with clear hysteresis loops according to the IUPAC. This indicated that the samples kept the mesoporous nature after grafting of ionic liquid groups. The specific surface areas of the samples were also calculated by BET method. It was found that the surface area and pore volume of the grafted samples decreased in comparison with pure silica (see Table 2). This could be attributed to the grafting of ionic liquid groups into the mesopore. The N_2 adsorption–desorption iso-

Table 1
The element analysis of the samples.

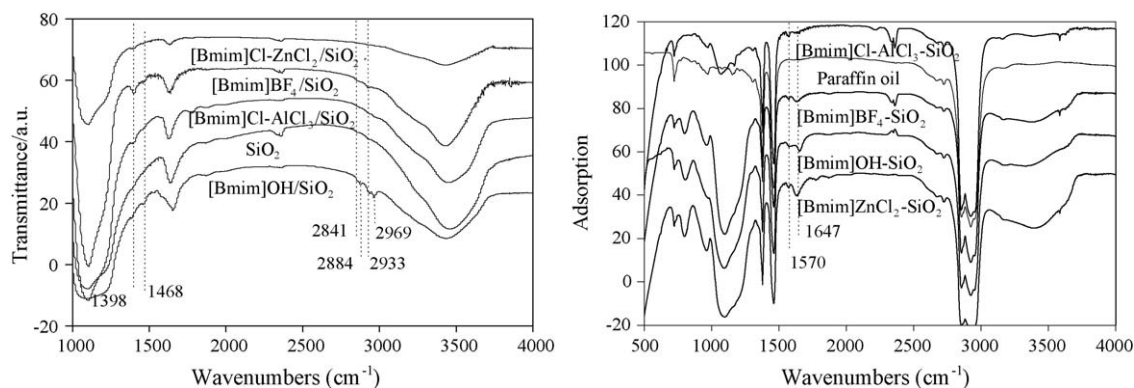| Sample	wt.%			n_C/n_N	Norg (mmol g^{-1})
	N	C	H		
Silica gel	–	–	0.73		
[Bmim]OH/SiO_2	1.96	5.83	1.14	2.97	1.4

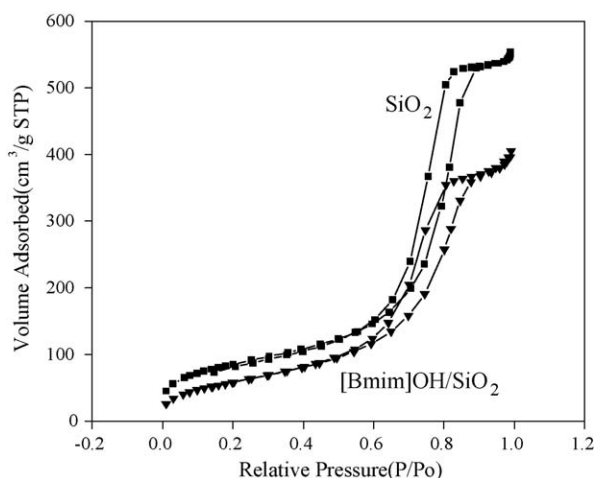**Fig. 5.** The infrared spectra of GILs with different [Bmim]OH immobilized on silica gel.

Fig. 6. Nitrogen adsorption–desorption isotherms of the samples.

therms of all the samples all showed a large break of relative pressure in 0.6–0.9 which indicating that the ordered pore was kept after the grafting of ILs.

Thermogravimetry (TG) and differential thermal analysis (DTA) of the sample were employed to clarify the thermal stability of the grafted ionic liquid. As shown in Fig. 7, gradual weight loss was observed from about 50 °C to approximately 600 °C, with three main loss weight peaks. The first peak involved in the outer layer water desorption; the second peak accounted for decomposition of GILs; and the last one could be assigned to condensation of silanol group. It can be seen that the sample was stable under 250 °C.

In the present work, the catalytic performance of catalysts was investigated under the identical conditions (see Table 3). Grafted ionic liquids [Amim]OH/SiO2 possessed the best catalytic performance.

A series of catalytic cycles were conducted to investigate the reusability of the catalyst. In each cycle, the catalyst was separated by simple filtration and then used for the next reaction directly. The results listed in Table 4 indicated that the catalyst could be reused for up to four times.

6. Synthesis of cyclic carbonate in the presence of ammonium salt

Quaternary ammonium salts may also catalyze CO_2 fixation into cyclic carbonate. It was reported that inactive substrate styrene oxide and polymerization sensitive oxirane glycidyl methacrylate oxirane could convert to the corresponding cyclic carbonates with satisfied yields by using molten tert-butylammonium bromide (TBAB) and/or tetrabutylammonium iodide (TBAI) as solvent and catalyst [113]. TBAI showed higher activity than TBAB because of the difference in the nucleophilicity of the halide ions. The reaction rate depended greatly on the structure of the cation as well as the nucleophilicity of anion. Significant difference on reactivity among imidazolium, thiazole, pyridinium and tetraalkyl ammonium salts were observed. The effective activity of the tetraalkylammonium salt might come from the bulkiness of the tetrahedral ammonium ion, which forces the halide ion away from the cation easier, resulting in less electrostatic interaction between anion and cation and consequently in more nucleophilicity of the anion. Lewis acid could enhance the activity of ammonium salt. Kossev et al. [114] observed that calcium chloride promoted the reaction between CO_2 and epoxides catalyzed over tetraalkylammonium or phosphonium halides. Arai et al. also found that a catalyst system consisting of $ZnBr_2$/TBAB is active for the CO_2 cycloaddition [115], which quantitatively produces styrene carbonate from styrene oxide at 353 K for 1 h. Such synergistic effect also occurs by the combination of metal complex

Table 2
The BET results of the samples.

Sample	$S_{BET}/(m^2\,g^{-1})$	$V_p/(cm^3\,g^{-1})$	d_p/nm
Porous silica	310.88	0.86	11.38
[Bmim]Cl–AlCl3/SiO2	254.62	0.73	10.76
[Bmim]Cl–ZnCl2/SiO2	277.46	0.84	11.20
[Bmim]BF4/SiO2	254.46	0.81	11.31
[Bmim]OH/SiO2	240.82	0.67	10.70

Table 3
Catalytic performance of the samples.

Catalysts	PO conversion (%)	PC selectivity (%)
Silica gel	–	–
[Bmim]Cl	99.8	98.2
[Bmim]Cl/SiO2	97.2	98.6
[Bmim]Cl–AlCl3/SiO2	90.1	99.7
[Bmim]Cl–ZnCl2/SiO2	98.0	98.6
[Bmim]BF4	94.9	97.5
[Bmim]BF4/SiO2	93.2	99.0
[Bmim]OH	100	99.9
[Bmim]OH/SiO2	99.1	100

Table 4
Catalyst recycle studies in cycloaddition of CO_2.

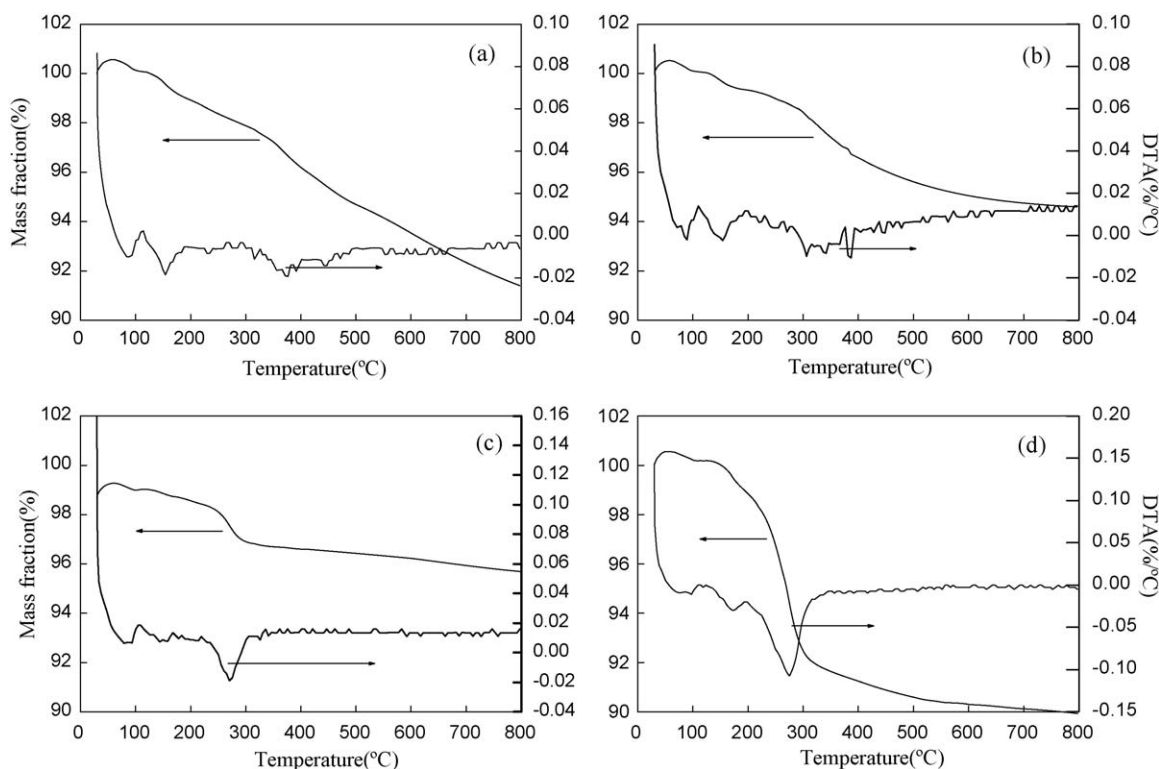| Reused no.	PO conversion (%)
1	99.1
2	97.3
3	94.6
4	89.0

Fig. 7. TGA for the [Bmim]Cl–AlCl$_3$/SiO$_2$, [Bmim]Cl–ZnCl$_2$/SiO$_2$, [Bmim]BF$_4$/SiO$_2$ and [Bmim]OH/SiO$_2$.

and onium salt. Researches [115–119] also found that a coupled catalyst system of the tetradentate Schiff base aluminium complex (SalenAlCl) and tetraalkylammonium halide were active toward the reaction of CO$_2$ and epoxide. Various cyclic carbonates could be produced from corresponding epoxides even at room temperature with good yields, although the long reaction time was needed [117]. The possible mechanism might involve the ring-opening insertion of epoxide into Al–Cl bond followed by insertion of CO$_2$ into Al–O bond of the resulting alkoxy complex. The ammonium halide was supposed to contribute to the activation of epoxide.

At our lab, amine-functionalized silica catalysts (NH$_2$/SiO$_2$, NH(CH$_2$)$_2$NH$_2$/SiO$_2$ and 1,5,7-triazabicyclo[4,4,0]dec-5-ene/SiO$_2$ (TBD/SiO$_2$)) were prepared by ultrasonic technique under mild conditions. Such hybrid solid bases showed high catalytic activity towards CO$_2$ coupling with propylene oxide. The reaction conditions had a great influence on the performance. 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. On the other hand, high CO$_2$ concentration hardly reduced the conversion of propylene oxide which was different from the conventional mechanism reported in literature. 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 involved in the activation of epoxide by H-bond formation On condition that such hypothesis was 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,
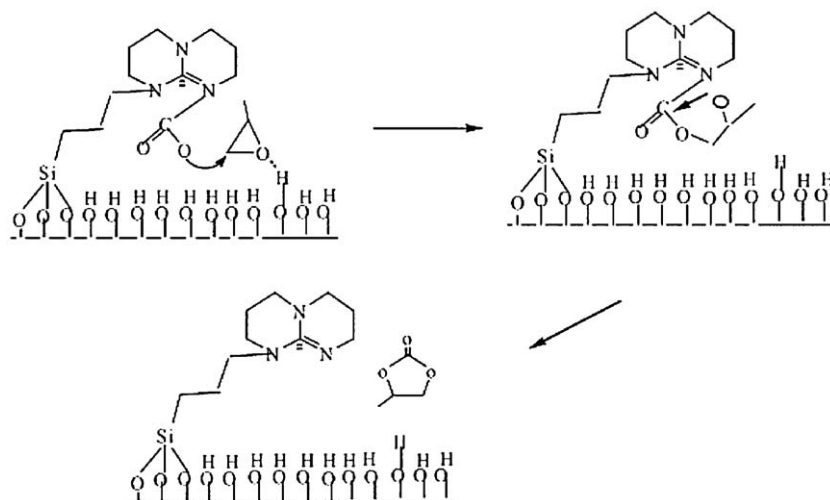
Scheme 6. Possible mechanism for cycloaddition of CO$_2$ to an epoxide on TBD/SiO$_2$.

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/SiO₂ was modified by methyl groups to remove the surface hydroxyls. The resultant was named as TBD/Me/SiO₂. It was interesting that the conversion of propylene oxide to propylene carbonate decreased to 0.2% for TBD/Me/SiO₂. 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 (Scheme 6) [120].

7. Summary

One of the routes for CO_2 mitigation is the utilization of CO_2 as the abundant natural feedstock, which has been a hot topic in catalysis for chemicals synthesis. Considering that CO_2 is chemically inert molecule, the activation of CO_2 has been carried out at our lab either with the presence of electron-rich chemicals or by hydrogen, and even with a coupling reaction in some case. Based on those in mind, nano-structured Cu/ZrO₂ catalyst was made for the selective production of methanol via CO_2 hydrogenation, and bifunctional Ni catalyst with high catalytic activity and stability was developed for CO_2 reforming of CH_4 in term of the formation of a Ni–Ca–Zr–O "nano-composite" which justified both methane decomposition and coke elimination. Furthermore, dimethyl carbonate and cyclic carbonate were synthesized from methanol and glycol in supercritical CO_2, respectively, which could be improved with a coupling of in situ water removal reaction, and cyclic carbonate was produced via cycloaddition of CO_2 to epoxide with bifunctional catalyst system. Obviously, these results evidenced that the key to CO_2 conversion was the activation of either CO_2 or co-reactant at different conditions. In order for the practical CO_2 utilization, however, the mechanisms need a deep understanding along with the development of high performance catalysts in the future.

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