Recent advances in the catalytic conversion of CO_2 to value added compunds

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CO_2 is a major greenhouse gas, and it can also be used as a chemical feedstock for synthesis of chemicals and fuels by passing the petrochemical source. Herein, we present the recent progress of our research work in the catalytic conversion of CO_2 to chemicals, with particular attention paid to catalytic reactivity and reaction mechanism. We also give the recommendations regarding the challenges and potential directions of the future research in this field.

CO_2 conversion, chemicals, catalysts, hydrogenation, reforming

1   Introduction

Carbon dioxide (CO_2) emission has become a global issue due to the significant and continuous rise of its atmospheric concentration from the recent accelerated growth in consumption of the petrified carbon-based energy worldwide [1]. In 2010, the global emission of CO_2 amounted at about 30000 Mt [2] and the International Panel on Climate Change (IPCC) predicted that the atmospheric CO_2 level could reach upto 590 ppm by 2100 [3]. Thus, effective strategies and technologies are required to reduce the CO_2 emission.

In principle, there are at least three routes of reducing the CO_2 content in the atmosphere, by curbing its emission, capture and storage (CCS), besides CO_2 utilization [4–6]. Among them, effective strategies in chemical conversion may play a key role in minimizing CO_2 emission [1,7]. The US government has invested over US $1 bn for the CCS research and the German government has invested €118 M

for research to utilize CO_2 as a raw material. However, CO_2 is a thermodynamically stable molecule, and it is not easy to be activated towards reaction through the use of catalysts, heat and pressure. The reactions for CO_2 can be classified into two main categories: CO_2 reduction and CO_2 insertion where there is no change in the oxidation state. While catalysts play a key role in reducing the required energy for a reaction, there is also a need to consider the supply of co-reactants and product demand, given the fact of huge quantity in current CO_2 emissions.

Our research activities focus on CO_2 catalytic conversion to methanol, syngas, linear and cyclic carbonates. Recent progress of our group research work in catalytic reactivity and reaction mechanism is summarized in this short review. An overview regarding the challenges and opportunities for the future research in this field is also proposed.
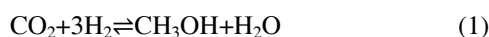
2 CO_2 hydrogenation to methanol

Catalytic conversion of CO_2 to methanol is a promising route that may offer a solution to the issues of greenhouse

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gas control and depletion of fossil fuels. Methanol is an important starting material for many valuable chemicals and can be used as a fuel additive or clean fuel. It can also be converted to high-octane gasoline, aromatics, ethylene, propylene as well as other useful petrochemicals that are currently derived from crude oil [8,9]. Furthermore, compared with state-of-the-art syngas-based methanol synthesis process, the lower byproduct content of methanol produced from CO_2 hydrogenation may allow a simplified distillation process and benefit from further chemical conversion [10]. Based on these features of CO_2 hydrogenation to methanol, a new concept of "methanol economy" was proposed by Olah *et al.* [8,11].
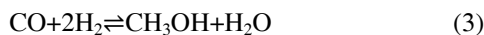
The main reactions during CO_2 hydrogenation to methanol are the synthesis of methanol (Reaction (1)) and reverse water gas shift (RWGS) reaction (Reaction (2)). There is a possibility that CO formed in Reaction (2) that undergoes further hydrogenation to form methanol (Reaction (3)) [12]. In general, at low conversions and low temperatures, the hydrogenation of CO_2 is the primary pathway because it is faster than the hydrogenation of CO [13,14]. The major product is methanol, and the main byproducts are CO and H_2O under the conventional reaction conditions [15].

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \qquad (1)$$

$$\Delta H_{298\ K,\ 5\ MPa} = -40.9\ \text{kJ/mol}$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad (2)$$

$$\Delta H_{298\ K,\ 5\ MPa} = 49.8\ \text{kJ/mol}$$

$$CO + 2H_2 \rightleftharpoons CH_3OH + H_2O \qquad (3)$$

$$\Delta H_{298\ K,\ 5\ MPa} = -90.7\ \text{kJ/mol}$$

It has been widely reported that Cu/ZnO-based catalysts exhibited high catalytic activity for methanol synthesis from CO_2 hydrogenation [16–19]. Great efforts have been made to improve the catalytic performance of Cu/ZnO-based catalysts by addition of various promoters such as Zr, Ti, Si, Al, Mg, Mn, B, Ba, Ag, and K [12,13,17,20–24]. Some rare-earth elements such as La, Ce and Y can also increase the Cu specific surface area and enhance CO_2 adsorption [25–27]. In addition, several detailed studies were devoted to the influence of Ga and Pd. It was found that the catalysis of Cu/Zn-based catalyst was improved with addition of a small amount of Ga and Pd [28,29]. Supporting noble metal (Ga, Au and Pd) catalysts have also been found to exhibit good activity and selectivity for hydrogenation of CO_2 to methanol, with improved catalysis [30–35]. However, the high cost of these noble metals hindered their practical application. In current industry, methanol is synthesized by conversion of CO_2-containing syngas over Cu/ZnO/Al$_2$O$_3$ catalysts prepared by co-precipitation [36–38]. Therefore, many researches focused on modifications of Cu/ZnO/Al$_2$O$_3$ catalysts for methanol synthesis from CO_2 [10,15,19,39,40]. Zhang *et al.* [15] studied the influences of SiO$_2$, TiO$_2$ and

SiO$_2$-TiO$_2$ promoters on the catalytic performance of Cu/ZnO/Al$_2$O$_3$ catalyst in methanol synthesis from CO_2 hydrogenation. It was found that the promoted catalysts improved performance. One promoted SiO$_2$-TiO$_2$ catalyst maximized both activity and methanol selectivity at 40.70% in CO_2 conversion and 41.17% in methanol selectivity under conditions of T=533 K, P=2.6 MPa, H$_2$:CO$_2$=3:1 and GHSV= 3600 h^{-1}. Li *et al.* [19] reported that Zr-doped Cu/ZnO/Al$_2$O$_3$ catalyst showed excellent performances for methanol synthesis from CO_2 hydrogenation under mild conditions (such as T=533 K and P=3.0 MPa) and the addition of Zr could improve the stability of Cu/ZnO/Al$_2$O$_3$ catalyst due to the promoted reduction of CuO which was formed through the oxidation by water vapor.

Generally, Cu/ZnO-based catalysts are prepared by co-precipitation method followed by investigating the effects of synthesis conditions and pre-treatment process such as precipitation temperature, pH, aging time, as well as calcinations and reduction temperature on the structures and properties of the catalysts [41–44]. Baltes *et al.* [43] found that the greatest methanol productivity was obtained for Cu/ZnO/Al$_2$O$_3$ catalysts with the following "preparation history": precipitation temperature of 343 K, pH of 6–8, aging time of 20–60 min, and calcination at 573 K. Other methods such as impregnation [12,45], sol-gel [46–48] and combustion method [20,25] have been developed to prepare copper-based catalysts. Bonura *et al.* investigated the influences of the conventional preparation methods (for example, coprecipitation with sodium bicarbonate, complexation with citric acid, gel-oxalate coprecipitation) on the structure and catalytic behavior of Cu/ZnO/ZrO$_2$ catalysts for methanol synthesis from CO_2 hydrogenation. The catalyst prepared via the gel-oxalate coprecipitation method showed a superior performance, attaining a CH_3OH yield of 0.305 g/(h g$_{cat}$) at 513 K, 3.0 MPa and 10000 h^{-1}. Apart from catalyst compositions and preparation methods, the nature of the precursor plays an important role in the structure and catalytic performance [43,49,50].

2.1 Cu/ZnO/Al$_2$O$_3$-based catalysts via hydrotalcite-like precursors

Hydrotalcite-like compounds (HTlcs) with the general formula of $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} and M^{3+} are the divalent and trivalent cations respectively, with a typical component of the complex phase mixture in conventionally prepared precursor materials [51,52]. The composite oxides derived from HTlcs possess homogeneous dispersion of M^{2+} and M^{3+} at atomic level, synergetic effects among the elements, large specific surface area, strong basic properties and high stability against sintering [38,53,54]. HTlcs with a wide variety of mono- to tetravalent metal cations are among the most investigated catalyst precursors for the remarkable catalytic properties. Several studies of Cu-containing hydrotalcite-like (HTl) precursors have

proven the advantages of HTl phases as precursors for Cu-based catalysts [50,52,55,56].

Hydrotalcite-like compounds were selected as the precursors for CO_2 hydrogenation catalyst preparation in our lab based on the above pioneer studies. A series of promoted Cu/ZnO/Al$_2$O$_3$ catalysts derived from hydrotalcite-like precursors were synthesized by co-precipitation method, and the effects of metal modifier (Mn, La, Ce, Zr and Y) on the physicochemical properties of Cu/ZnO/Al$_2$O$_3$ catalysts were studied [57]. From the SEM images, the precursor consisted mainly of well-developed and thin plate-shaped crystals (Figure 1(a)), and the particles of calcined sample maintained layered structure after the calcinations (Figure 1(b)). The introduction of Mn, La, Ce, Zr and Y into HTl structures could improve the physicochemical properties of catalysts, especially for the exposed Cu surface area and the surface basicity of the catalysts. It was also found that the CO_2 conversion depends on the exposed Cu surface area (Figure 2) and the CH_3OH selectivity increases linearly with the increasing proportion of strongly basic sites to the total basic sites (Figure 3). The Y- and Zr-modified Cu/ZnO/Al$_2$O$_3$ catalysts exhibit the highest CO_2 conversion and CH_3OH selectivity, respectively. A maximal CH_3OH yield of 0.52 g/(h g$_{cat}$) with the CO_2 conversion of 26.9% and the CH_3OH selectivity of 47.1% is obtained over the Cu/ZnO/Al$_2$O$_3$/Y$_2$O$_3$ catalyst. Better performance can be obtained with simultaneous incorporation of the two promoters (Y and Zr) into Cu/ZnO/Al$_2$O$_3$ catalysts via HTlcs [58]. We also investigated the influences of amount of modifier on the physicochemical properties of the precursor and final catalysts in detail [59]. The yields of hydrotalcite-like phase would decrease with increasing Zr content. The introduction of Zr could increase Cu dispersion significantly, while the Cu dispersion decreased with further increase of Zr content, which was related to the decreased amount of HTl phase in precursors. The proportion of strongly basic sites to the total basic sites showed a similar trend except for the samples with $Zr^{4+}:(Al^{3+}+Zr^{4+})$=0.7. In addition, both CO_2 conversion and CH_3OH selectivity exhibited a volcanic trend with the increase of Zr content (Figure 4). Therefore, a suitable amount of modifier was favorable for the catalytic activity and selectivity of catalysts derived from HTl precursors.

Furthermore, other parameters of synthesis conditions were optimized at our lab, and we found that the resulting Cu/ZnO/Al$_2$O$_3$/ZrO$_2$ catalyst derived from HTlcs kept a constant methanol synthesis activity over 4000 h (Figure 5). The catalyst still maintained a high productivity of 0.29 CH_3OH g/(h g$_{cat}$) with the CO_2 conversion of 25.7% after 4000 h.

In order to increase the number of exposed Cu particles, we further modified the Cu/ZnO/Al$_2$O$_3$/ZrO$_2$ catalysts via hydrotalcite-containing precursors in our lab, which contained Zn/Al/Zr hydrotalcite-like phase with most Cu^{2+} located on the surface of the layered structure [50]. In particular, the effects of $Cu^{2+}:Zn^{2+}$ atomic ratios on structure and activity of the catalysts were investigated and the best $Cu^{2+}:Zn^{2+}$ atomic ratio was found to be 2. Moreover, adding the Cu^{2+} into the Zn/Al/Zr HTlcs system at different stages of Zn/Al/Zr HTlcs formation and reconstruction could greatly influence the characteristics of the resulting catalysts, such as the Cu^{2+} content located in the layer structure of precursor, the exposed Cu surface area, the Cu^+ and Cu^0 content on the reduced surface and the ratio of Cu^+/Cu^0 [60]. The catalyst prepared by adding Cu^{2+} into the precursor at the reconstructed stage exhibited the best catalytic performance due to its highest exposed Cu surface area and ratio of $Cu^+:Cu^0$.

Considering the basic nature of fluoride anion, which can promote many base-catalytic reactions [61–63], the introduction of fluoride into Cu/ZnO/Al$_2$O$_3$ catalyst via HTl precursor would modify the surface basicity of catalyst, which in turn affects the adsorption of CO_2 and influences the catalytic performance during CO_2 hydrogenation to methanol. Experimentally, the fluorine anions can be introduced into the interlayer region of HTlcs based on the so called "memory effect" [63,64]. Reconstruction of the HTl structure by the memory effect took place via rehydration of the derived mixed metal oxide formed by calcination of their HTl precursor, using aqueous solutions containing desired anions [65]. Fluorine-modified Cu/ZnO/Al$_2$O$_3$/ZrO$_2$ catalysts were prepared by calcination of the fluorine-containing HTlcs according to the literature [66]. Our results revealed that the CH_3OH selectivity was greatly improved
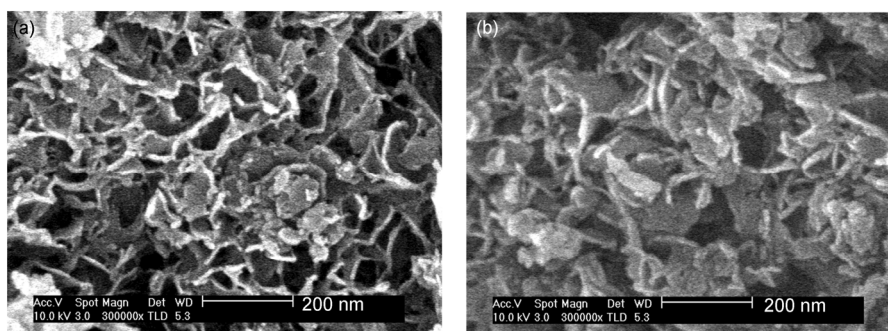

Figure 1   SEM images of (a) Cu/Zn/Al/Y precursor and (b) calcined Cu/Zn/Al/Y sample [57].
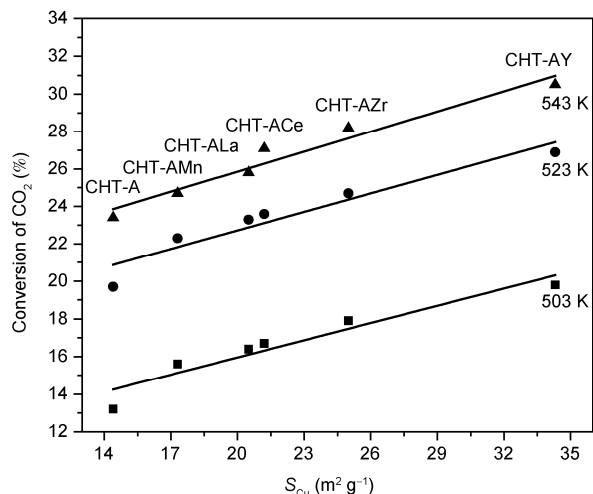
Figure 2   Correlation between CO_2 conversion and Cu surface area. Reaction conditions: T=503–543 K, P=5.0 MPa, GHSV=12000 mL/(g_{cat} h), H_2:CO_2=3:1 (molar ratio) [57].
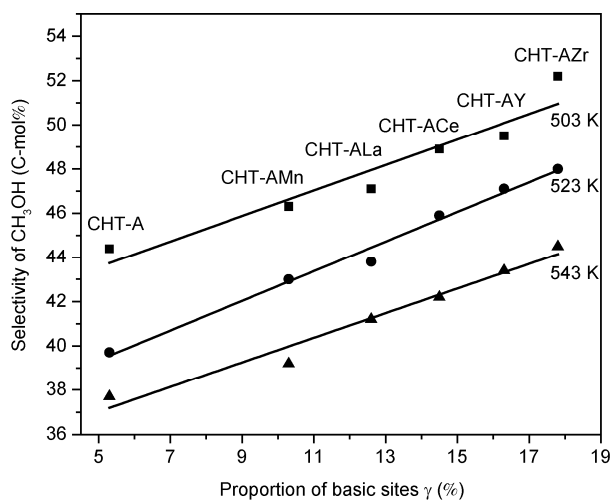

Figure 3   Correlation between CH_3OH selectivity and the proportion of strongly basic sites γ to the total basic sites. Reaction conditions: T=503–543 K, P=5.0 MPa, GHSV=12000 mL/(g_{cat} h), H_2:CO_2=3:1 (molar ratio) [57].
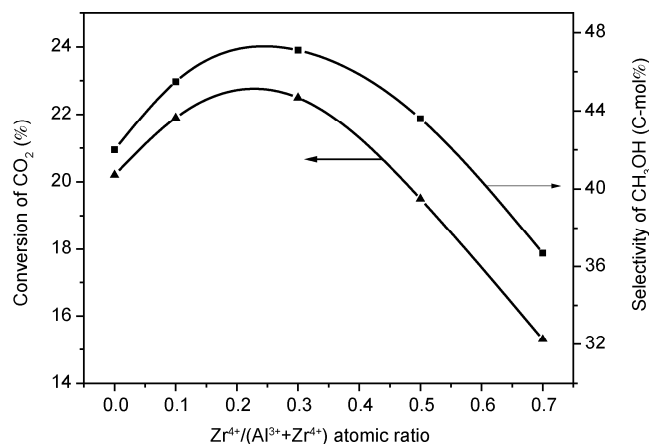

Figure 4   Effect of the Zr content on the CO_2 conversion and the methanol selectivity over Cu/Zn/Al/Zr catalysts. Reaction conditions: T=523 K, P=5.0 MPa, GHSV=4000 h^{-1}, H_2:CO_2=3:1 (molar ratio).
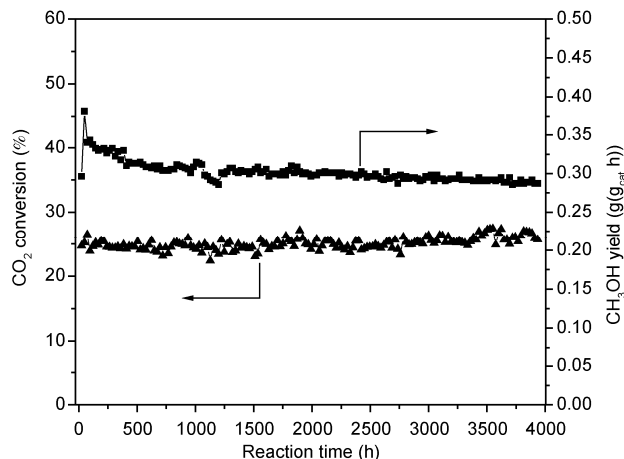

Figure 5   Change of CO_2 conversion (triangles) and methanol yield (rectangles) over reaction time on the Cu/ZnO/Al$_2$O$_3$/ZrO$_2$ catalysts via HTlcs. Reaction conditions: T=523 K, P=5.0 MPa, GHSV=4000 h^{-1}, H_2/CO_2/N_2=73:24:3 (molar ratio).

by the remarkable increase of proportion of strongly basic sites, while CO_2 conversion decreased slightly due to the decrease of the exposed copper surface area [67]. CH_3OH yield for the fluorine-modified Cu/ZnO/Al$_2$O$_3$/ZrO$_2$ catalysts was higher than that for the fluorine-free catalysts, thus the introduction of fluorine favored the methanol formation.

2.2   Cu/ZnO-based catalysts via perovskite-type precursors

Recently, perovskite-type oxides as catalysts have gained increasing attention due to their high activity and thermal stability. With the general formula of ABO$_3$ (A-site is a larger rare earth and/or alkaline earth cation and B-site is a smaller transition metal cation), the high dispersion of "metal-on-oxide" catalysts can be realized by reduction of perovskite-type precursors [68]. The metallic elements are stable in the perovskite structure when the radii meet the tolerance factor $t=(r_A+r_B)/2(r_B+r_O)$ ($0.75<t<1$), so it is possible to prepare multi-component perovskite-oxides by partial substitution of A-site and/or B-site cations. With this defined structure, the A-site keeps the structure and the B-site provides the catalytic activity site. B-site cations could be reduced to well disperse metallic species supported on the A-site cations oxide, which leads to ideal catalyst precursors for many reactions that involve metal as active sites [69]. Moreover, A$_2$BO$_4$ mixed oxides belong to perovskite-type oxides, with alternating layers of ABO$_3$ perovskite and AO rock salt, which exhibit variable oxygen stoichiometry. However, little work on the application of Cu-based perovskite-type oxides for CO_2 hydrogenation has been reported. In our lab, La-M-Cu-Zn-O (M=Y, Ce, Mg, Zr) based perovskite-type catalysts were prepared and tested for CO_2 hydrogenation to methanol, and the influence of the fourth elements on the perovskite structure, the relationship

between physic-chemical property and catalytic performance of as-prepared catalyst were discussed [70]. The catalysts exhibited La_2CuO_4 perovskite structure and showed high selectivity for methanol, which was correlated with the $Cu^{\alpha+}$ species that existed in the catalysts.

2.3   Reaction mechanism for CO_2 hydrogenation to methanol

To better understand and design the highly active catalysts for CO_2 hydrogenation to methanol, the reaction mechanism has been thoroughly investigated. For the Cu/ZrO_2 or $Cu/ZnO/ZrO_2$ catalyst, a bifunctional (dual-site) mechanism of CO_2 hydrogenation is currently accepted which assumes that the adsorption and dissociation of hydrogen occur on the Cu sites, while the adsorption of CO_2 takes place over the ZrO_2 or $ZnO\text{-}ZrO_2$ sites. The atomic hydrogen transports from the surface of Cu onto the surface of $ZnO\text{-}ZrO_2$ sites via spillover and hydrogenates the adsorbed carbon-containing species to form methanol [16,25,59,71,72]. Some researchers proposed that formaldehyde (H_2CO) was a key intermediate species in the reaction pathway, which can be produced by both dioxomethylene ($H_2COO^{**}+H^{\#}\rightarrow H_2COOH^{**}\rightarrow OH^*+H_2CO^*$, * and ** represent the monodentate and the bidentate species, respectively; # represents the adsorption site on Cu) via the formate pathway and formyl (HCO) hydrogenation via the RWGS+CO–Hydro pathway [71,73–75]. Hong and Liu [71] suggested that CO_2 molecules adsorbed on the catalytic surface produced the formate (HCOO) intermediate which then dissociated to formaldehyde (H_2CO) that either reacted with surface hydrogen to methanol or dehydrogenated to CO. A similar reaction mechanism for CO_2 hydrogenation to methanol over $YBa_2Cu_3O_7$ was proposed by Gao and Au [74]. Recently, Guo *et al.* [25] suggested that both methanol and CO might be produced via the same intermediate species and compared with the intermediate species adsorbed on moderately basic sites (basic sites β), with those adsorbed on strongly basic sites (basic sites γ) that prefer to be hydrogenated into methanol rather than to dissociate to form CO. Moreover, it is generally accepted that the rate limiting step is the formation and hydrogenation of the reactive intermediates such as formate and formaldehyde present on the basic sites [17,25,76]. We also proposed a possible reaction mechanism for CO_2 hydrogenation to methanol over

$Cu/ZnO/Al_2O_3$-based catalysts via HTl precursors as described in Scheme 1. The linear relationship between the physicochemical properties, especially the exposed Cu surface area and the surface basicity of the catalysts, and the catalytic performance provided an evidence for the proposed bi- functional mechanism. Based on the above discussion, we proposed a possible reaction mechanism for CO_2 hydrogenation to methanol over $Cu/ZnO/Al_2O_3$-based catalysts via HTl precursors which is described in Scheme 1. Therefore, a highly exposed Cu surface area and appropriate adsorption amount and adsorption strength of CO_2 are favorable for the hydrogenation of CO_2.

It is noteworthy that the major part of the studies concerning the CO_2 hydrogenation to methanol has been focused on the reaction performed at high temperatures (>493 K) which experiences severe thermodynamic limitation. An important challenge in CO_2 reduction is the necessity of carrying out the reaction at low temperature in order to improve the flexibility of the operation and to ameliorate the energetic efficiency of the process. In addition, high CO_2 conversion becomes available at low temperature [77]. Nevertheless, the knowledge of the influence of the experimental parameters at low temperatures (<453 K) is very limited in the literature. One major problem that restrains their low-temperature behavior is the deactivation of Cu-based catalysts due to the high activation energy of hydrogen dissociation. Arena *et al.* [78] reported that the CO_2 conversion was only 5.7% and CH_3OH selectivity was 90% over the $Cu/ZnO/ZrO_2$ catalyst at 453 K, 5.0 MPa and 80 mL/min. It has been reported that the high activity for CO_2 hydrogenation was generated by the presence of surface defects of metallic Cu surface which can reduce the activation energy of hydrogen dissociation [79,80]. In addition, largely enhanced surface defects can be achieved by decreasing the Cu particles into the nano-scale with a simultaneous high dispersion. On the other hand, low temperature methanol synthesis from CO_2 hydrogenation in a liquid medium using the slurry-phase reactor is another solution to this. Liu *et al.* [48] employed a new low-temperature process for methanol synthesis such that high activity of methanol production from CO_2 hydrogenation could be achieved at 443 K and 5 MPa in a slurry-phase reactor. It was found that a maximum CO_2 conversion of 25.9% with the CH_3OH selectivity of 72.9% was obtained over the copper catalysts prepared by an oxalate-gel coprecipitation method. Further-
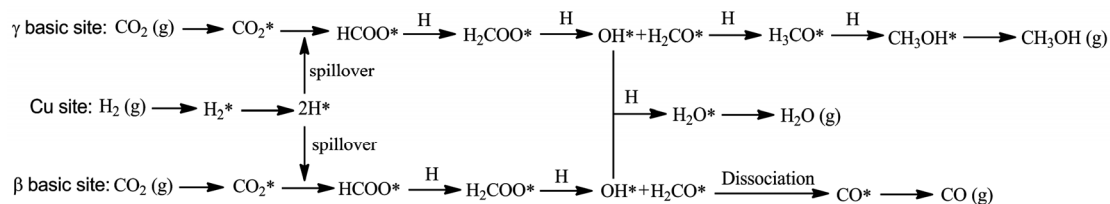

Scheme 1   Proposed reaction mechanism for CO_2 hydrogenation to methanol over Cu/Zn/Al/Zr catalysts via HTl precursors (X^* stands for an adsorbed species on the surface).

more, the methanol synthesis from CO_2 hydrogenation can be achieved by using electrochemical techniques under mild conditions. Although many electrochemical investigations of CO_2 reduction have been undertaken, to the best of our knowledge, there are little reports of CO_2 reduction selectively to methanol in an aqueous photoelectrochemical cell occurring at potentials where light energy solely drives the reaction [81].

3 CO_2 reforming of methane to synthesis gas

CO_2 (dry) reforming of methane for synthesis gas, which converts the two main greenhouse gases to value-added syngas (CO and H_2), is receiving progressive attentions from both energy and environmental protection aspects [82–84].

$$CO_2 + CH_4 \rightleftharpoons 2CO + H_2 \quad \Delta H_{298K} = 247.3 \text{ kJ/mol} \qquad (4)$$
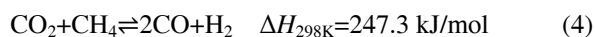
Because of the high endothermicity of dry reforming, this reaction easily proceeds at higher temperature which means catalysts with high activity and stability play a significant role.

In the past decades, a lot of researchers have been devoted to develop the catalysts with high performance for CO_2 and CH_4 reforming reaction. Noble metals, such as Ru, Rh and Pt [85,86], exhibited both high activity and carbon resistance properties. A detailed review by Devendra and James [87] had addressed the kinetics, mechanism and deactivation of these noble catalysts. Compared with noble metals, Ni-based catalysts have been widely investigated because of their high activity and relatively low price [88,89]. Unfortunately, Ni-based catalysts deactivate easily due to carbon deposition and/or catalyst sintering [90,91]. It has been suggested that Ni with smaller particle size had a higher resistance towards the formation of inactive carbon [92,93] and basic supporters or promoters can decrease the carbon deposition on the surface of catalysts [94,95]. Therefore, considerable effort has been focused on confining the Ni particle size and the minimizing of inactive carbon formation by alteration of the nature of the supporter, addition of promoters and selection of preparation method.

It has been reported that the small size of Ni can be stabilized by the fabrication of well-defined structure, such as solid solution [96], spinel [97] or perovskite [98]. Hu [96] has summarized the characteristics of the solid solution catalysts for CO_2 reforming. The excellent performance of the solid solution catalysts was because of the very small nickel particles. Choi and Moon [98] prepared a Ce-substituted $LaFe_{0.7}Ni_{0.3}O_3$ for steam reforming of methane. The Ce-substitution enhances the methane conversion and hydrogen selectivity by increasing both the catalyst surface area and the nickel dispersion. The coke resistance is also improved. The higher stability can be attributed to that nickel particles highly dispersing in the precursor and strong interaction

between nickel and the support, but the role of strong metal support interaction would also induce great difficulties in the reduction process.

The basic promoter/supports (such as MgO, CaO, K_2O, etc.) can enhance the adsorption and activation of CO_2 and accelerate the gasification of the surface reaction with carbon and retard the formation of inactive carbon [99–101]. At the same time, the redox supports/promoters (such as CeO_2, ZrO_2, La_2O_3, etc.) can also reduce carbon deposition on catalysts by the reaction between carbon and the lattice oxygen formed in these redox oxides [102–104]. Apparently, the catalyst has a basic promoter, redox support, smaller Ni particles and strong metal-support interaction together, and may present a high activity and stability for CO_2-CH_4 reformation.

3.1   Ni-CaO-ZrO_2 nano-catalyst

In our lab, a novel catalyst, Ni-CaO-ZrO_2 nanocomposite, was designed for the CO_2 reforming of methane. Mesoporous ZrO_2 was employed as the support, which has good oxygen storage capacity and high hydrothermal stability. Nickel particle size was effectively confined by the mesoporous framework. CaO was introduced to give rise to the basicity of the catalyst and for stabilizing 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 [105–108]. Thus, the activity and stability was enhanced as shown in Figure 6, with 90% in CO_2 conversion and 98% CH_4 conversion under conditions of T=850 °C, CO_2/CH_4=1.2, GHSV=79000 mL/(h g) and the catalyst still maintained a high performance during 800 h.

The method of preparation is believed to be an important factor in the performance and structure of the catalyst. Ni-CaO-ZrO_2 catalysts with different pore structures were prepared by coprecipitation method [109,110]. The Ni-CaO-ZrO_2 catalysts with different pore structures were
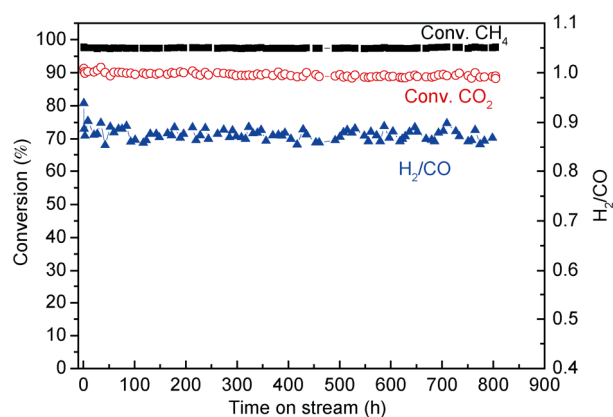

Figure 6   Long time activity curves of the Ni-CaO-ZrO_2 catalysts (reaction temperature: 850 °C, CO_2/CH_4=1.2, GHSV=79000 mL/(h g)) [108].

prepared and denoted as M-NiCaZr (mesoporous) and N-NiCaZr (non-mesoporous), respectively. It was found that the mesopores in the MNiCaZr catalyst had a "confine effect" which limited the growth of Ni crystals during the reaction, and thus sintering of Ni particles was avoided. For the N-NiCaZr catalyst without such a pore structure, however, Ni particles easily sintered during the reforming reaction at high temperatures. Thus the mesoporous structure of the catalyst was the critical factor to stabilize nano-sized Ni particles via the "confine effect" during the reaction, thereby providing high stability for the catalyst. It also be founded that reflux-digestion treatment plays a key role in the formation of a catalyst with high activity and less coke formation [109]. A simple reflux digestion in hot water for certain time led to the formation of smaller particle size of NiO and ZrO_2, thus increasing the interface between Ni and ZrO_2 [109]. As given in Figure 7, the catalyst without reflux-digestion treatment (NC-0-C) had a relative low conversion of methane and poor stability. As the reflux time increased, both activity and stability were evidently improved. There was no deactivation for the NC-100°C-24h-C sample during a period of about 150 h and a relatively stable Ni-CaO-ZrO_2 composite catalyst was obtained for CO_2 reforming of CH_4.

In our following work, some interesting results were obtained by investigating the formation of carbon residuals on the catalysts prepared by different producers. It was found that the most active and stable sample had the highest carbon accumulating rate and carbon depositing amount among all the samples [111], which means that the catalyst deactivation may not necessarily relate to the amounts of deposited carbon and the morphology of carbon residuals was also a critical factor that influenced the catalyst performance. Four types of carbon residuals were identified on the used Ni-CaO-ZrO_2 catalysts as shown in Figure 8, namely, amorphous carbon, encapsulating carbon, whisker carbon, and graphite. Among them, amorphous carbon was recognized as an active carbon residual, which participated in the reaction as the precursor of other kinds of carbon deposition. However, encapsulating carbon or graphite could cover the
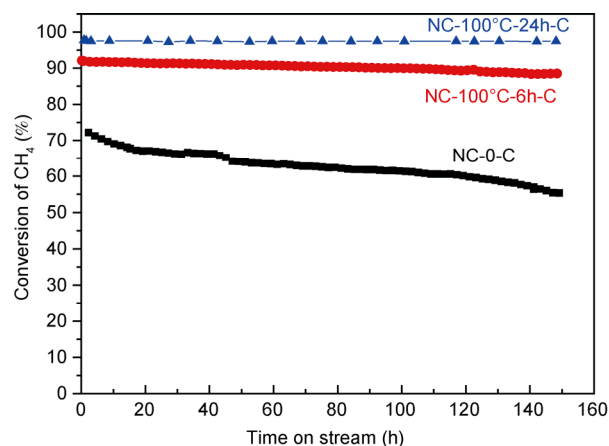
Figure 7 Effect of reflux conditions on the activity and stability of the Ni-CaO-ZrO_2 catalysts. Reaction conditions: T=850 °C, CO_2/CH_4=1.2, GHSV=79000 mL/(h g). (NC-0-C: catalyst without reflux-digestion treatment; NC-100°C−6h-C: catalyst refluxed at 100 °C for 6 h; NC-100°C−24h-C: catalyst refluxed at 100 °C for 24 h) [109].

active sites and inhibit the surface reaction.

3.2 Reaction mechanism for CO_2 dry reforming to synthesis gas

Difference reaction mechanisms were assumed based on the various catalysts and reaction conditions. Based on our experimental study, a bi-functional mechanism for dry reforming on Ni-CaO-ZrO_2 catalyst was proposed [111]. CH_4 was firstly activated on the Ni sites and subsequently converted to H_2 and the hydro-carbonaceous species CH_x. During this stage, CH_4 decomposition was assumed as a slow step while its adsorption was at equilibrium state. Some of the formed H_2 could be adsorbed on the Ni sites via a dissociated way; CO_2 adsorbed on the oxygen vacancies to form adsorbed CO_2 species. The activated CH_4 and CO_2 then reacted at the interface forming CO and H_2, meanwhile, a RWGS occurs as a side reaction between the adsorbed CO_2 and H atom.

The further theoretical understanding of reaction mechanisms and carbon formation will lead to design and synthesis of other novel Ni-based catalysts.
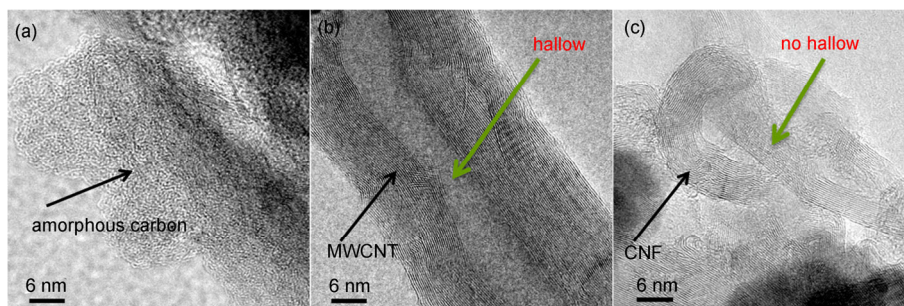
Figure 8 High-resolution TEM images of different type of carbon species. (a) Amorphous carbon; (b) whisker carbon; (c) encapsulating carbon [111].

4 Catalytic conversion CO_2 to dimethyl carbonate

The CO_2 catalytic conversion to cyclic and linear carbonate illustrates atom efficiency. Linear organic carbonates are useful as solvent and cyclic carbonate can be used as a solvent and an intermediate in organic and polymer synthesis, which have a substantial potential market. Catalytic conversion CO_2 to cyclic carbonate has been summarized in detail in our previous review [112–114]. Herein, we present the advances in the direct and indirect synthesis of dimethyl carbonate from CO_2. Dimethyl carbonate (DMC) is an environmentally benign chemical product and versatile intermediate [115–117]. It finds extensive uses as a precursor for polycarbonate resins as well as a starting material for organic synthesis via carbonylation and methylation, replacing poisonous phosgene and dimethyl sulfate [118–121]. It is also considered to be a promising gasoline octane enhancer and an electrolytic solution in a secondary lithium battery. The traditional industrial synthesis of DMC uses phosgene as reagent, which suffers from the shortcomings as corrosive gases of chlorine, treating with large amounts of pyridine and removing the by-product NaCl salts. DMC can be synthesized from CO_2 directly or indirectly via phosgene-free methods.

## 4.1 Synthesis of DMC directly from CO_2 and methanol

The direct synthesis of DMC from CO_2 and methanol is considered to be a promising route for DMC production based on economical and environmental issues (Reaction 5) [122]. However, the yield of DMC based on methanol is far from satisfactory because of equilibrium limitations. The reaction is slightly exothermic, with a heat of reaction of 23 kJ/mol [123]. Higher DMC yields will be obtained by lowering the reaction temperature as well as by removing coproduced H_2O.

$$2CH_3OH + CO_2 \rightleftharpoons (CH_3O)_2CO + H_2O \qquad (5)$$
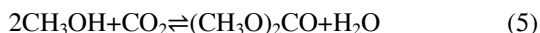
Both homogeneous [124] and heterogeneous catalysts [125] can catalyze this reaction. Organometallic complexes, in particular dibutyltin dimethoxy ($Bu_2Sn(OMe)_2$), show high selectivity for DMC synthesis [126], however, these catalysts have low activity and stability mainly due to the deactivation in presence of water. Heterogeneous catalysts are more environmentally-friendly. ZrO_2 catalyst was first reported to be active for the direct synthesis of DMC from CO_2 and methanol by Tomishige *et al.* [127]. When the catalyst was modified by H_3PO_4, the conversion rate of methanol increased up to about 4.5% [128]. However, the activity remained low and needs to be improved.

Direct synthesis of DMC from CO_2 and methanol over nickel acetate catalyst at near supercritical condition was studied in our lab. It was demonstrated that DMC could be produced as the unique product at such a low temperature as 305 K, and the yield was 12 times higher than that at non-supercritical conditions. The reaction 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. The formation mechanism of DMC in supercritical phase was proposed [129].

4.2 Synthesis of DMC via transesterification

Transesterification of cyclic carbonate and methanol is a green process that there is no waste and corrosions as shown in Scheme 2, in which a cyclic carbonate is formed from epoxide and carbon dioxide, and subsequently transesterified to form DMC and alkylene glycol.

Basic catalyst was regarded to be more effective than acidic ones [130]. Homogeneous basic catalysts, such as alkali metal compounds and quaternary ammonium salt with high activities, however, give rise to the problems of product separation and catalyst reuse. Consequently, heterogeneous basic catalysts have gained much more interest. CaO showed unique catalytic activity for the transesterification of propylene carbonate (PC) with methanol with high PC conversion and DMC selectivity [131]. However, when CaO based catalyst was employed in the continuous synthesis of DMC, its activity gradually decayed with time-on-stream due to leaching of calcium [132]. For supported catalysts, perfectly stable anchored active species on carries are employed to overcome the leaching problem. For instance, active species were grafted in mesoporous materials, encapsulated by ship-in-a-bottle techniques, and ion exchanged in layered structure [133]. Feng *et al.* [134] used amino-functionalized MCM-41 as a catalyst in the continuous transesterification of EC to DMC. Dhuri and Mahajani [135] reported that the basic anion-exchange resin exhibited good catalytic performance for DMC synthesis of EC with methanol. Dharman *et al.* [136] employed IL as a catalyst through microwave heating, and the coproduction of an equimolar amount of DMC was obtained in high yield and better selectivity.

In our work, CaO-ZrO_2 solid solution was prepared by co-precipitation that prevented the leaching of calcium via the strong interaction between CaO and ZrO_2 in the solid

Scheme 2 Synthesis of DMC by transesterification.

solution [137]. The newly-produced solid base showed high stability and was subjected to continuous synthesis of DMC on reactive distillation reactor for 250 h without any obvious change of activity. Further study indicated the activity and stability depend greatly on the Ca/(Ca+Zr) ratios. The activity of catalysts increased with the increase of CaO content, which is ascribed to the improvement of the base strength of catalysts. But the high stability is only obtained for the catalysts with Ca/(Ca+Zr) ratio from 0.1 to 0.3 (Figure 9). This is due to the formation of homogeneous CaO-ZrO$_2$ solid solution [137]. The influence of preparation methods on the structure and performance of CaO-ZrO$_2$ catalyst was also performed by Wang *et al.*. It was found that both catalytic activity and stability are strongly influenced by the structure of CaO-ZrO$_2$. The aggregated CaO on the support as well as highly dispersed CaO shows poor catalytic stability, while Ca^{2+} ion substituted Zr^{4+} ions in the host lattice to form homogeneous CaO-ZrO$_2$ solid solution leading to high stability [138]. Nevertheless, although CaO-ZrO$_2$ solid base mentioned above exhibits remarkable stability, the specific surface area of this catalyst is only 10–50 m^2/g. Thus, mesoporous Na-ZrO$_2$ and CaO-ZrO$_2$ catalysts were prepared via appropriate sol-gel process. The specific surface area of mesoporous Na-ZrO$_2$ was increased to 247 m^2/g and mesoporous CaO-ZrO$_2$ exhibited the specific area as high as 243 m^2/g. Both the mesoporous solid bases exhibited remarkable activity and durability in the synthesis of DMC from PC and methanol [139,140].

4.3   Synthesis of DMC via urea alcoholysis

The synthesis of DMC by urea methanolysis is economic and facilitates facile separation of products [141]. Another advantage for this process was that ammonia and the co-product can be used as a precursor for the urea production. In urea methanolysis, DMC is synthesized via a two-step reaction (Scheme 3). The first step is to form methyl

Scheme 3   Synthesis of DMC by the urea methanolysis method.

carbamate (MC) from urea and methanol usually with a high yield [142]. The second step, that produces DMC using MC as the building material [143,144], is the rate limiting step. Thermodynamic analysis of this reaction shows that Reaction (1) is thermodynamically favorable unlike Reaction (2) which is unfavorable. The kinetics can be used to shift the reaction equilibrium as well as to increase the rate. Therefore, the key point is to develop the novel catalysts for effectively promotion of the second reaction and continuous elimination of product to shift the equilibrium.

4.3.1   ZnO-based catalysts

Various catalysts for the DMC synthesis by urea alcoholysis have been reported. Cho *et al.* [145] revealed bases, such as K$_2$CO$_3$ and CH$_3$ONa, could be used as catalysts for this process, but the DMC yield based on urea was < 5%. Saleh *et al.* [146] tried to use polyphosphoric acid (PPA) to promote the reaction between urea and methanol. A desirable DMC yield of 67.4% was obtained at 413 K for 4 h with added 0.8 MPa CO$_2$. Researchers disclosed that organotin derivatives, such as Bu$_2$Sn–(OMe)$_2$ and SnOBu$_2$, were active catalysts with high selectivity, but the homogeneous nature of the organotin posed separation and deactivation problems [147–149]. Currently, zinc has been proved to be the active component toward the DMC synthesis because its weak acidity/basicity effectively promotes the activation of urea and methanol [150]. In our previous work, the highest DMC yield was measured about 35% over a ZnO catalyst in the batch process. ZnO-CaO and ZnO-Al$_2$O$_3$ bi-functional catalysts were also prepared, and the highest DMC yield (41.2%) was obtained over the catalyst with Zn/Ca molar ratio of 4, caused by the synergistic effect between ZnO and CaO [151,152].

To overcome the problems of unfavorable equilibrium and complicated side reactions, a catalytic distillation technique was then introduced into the DMC synthesis in our laboratory. Catalytic distillation, that combines chemical synthesis with separation by distillation, is a well suited technology [153]. It was found that catalytic distillation reactor effectively increased the DMC yield by stripping off DMC from the reaction zone, which also minimized the side reactions simultaneously. The highest DMC yield reached 60%–70% over a Zn based catalyst using catalytic distillation [154]. The modeling of the catalytic distillation process for the synthesis of dimethyl carbonate by urea methanolysis is also studied for more understanding of the whole process [155,156]. Wang *et al.* [155] developed a nonequilibrium Wilson model of the catalytic distillation to account for the non-ideality of the liquid phase. The results indicated that as

Figure 9   Catalytic performance of CaO-ZrO$_2$ catalysts with different Ca/(Ca+Zr) ratios (*x*=0.1, 0.2, 0.3, 0.4, 0.5) in reactive distillation [137].

the process includes the formation of a binary azeotrope and the removal of the noncondenser component of ammonia, the catalytic distillation is appropriate for the process of DMC synthesis and product separation. Zhang *et al.* [156] carried out akinetic experiment on the synthesis of DMC by urea and methanol over ZnO catalyst in an isothermal fixed-bed reactor. The experimental and simulated results indicated that the reaction from MC to DMC is the rate-controlling step in the DMC synthesis process from urea and methanol. It seems necessary to remove the DMC and by-product ammonia to achieve a high selectivity of DMC. This implied that reactive distillation might be used in the synthesis of DMC on an industrial scale to achieve a higher selectivity of DMC.

4.3.2 Possible mechanism

An interesting phenomenon was observed [157–159], where ZnO, that is usually insoluble in alcohol even at extremely high temperature, dissolved in the reaction solution, and some precipitate quickly appeared once the temperature decreased. Sample analyses suggested that the soluble zinc existed in the form of $Zn(NCO)_2(NH_3)_2$, which originated from the reaction of ZnO with urea. Furthermore, it was found that ZnO was hardly active toward the reaction of MC and methanol, though it was highly active in the synthesis of DMC from urea and methanol. The yield of DMC from urea reached 34.0%, while that from MC was only 4.2% [158]. Similar phenomenon was observed for the synthesis of diethyl carbonate (DEC) over ZnO. The precipitated $Zn(NCO)_2(NH_3)_2$ showed high activity for the reaction of EC and ethanol, yielding 40.6% of DEC [158]. Based on the experimental results and analyses, a mechanism for the catalytic activation of ZnO with urea is proposed [159]. As illustrated in Scheme 4, urea is decomposed into isocyanic acid and ammonia first when the reaction temperature goes above the melting point of urea (411 K). The urea decomposition is promoted in the presence of zinc oxide. Generally, isocyanic acid is an active intermediate compound that is highly unstable in nature. Because the concentration of methanol is much higher than that of urea or ZnO in the reaction system, most of isocyanic acid react with methanol to formmethyl carbamate, and a very small part of HNCO reacts with zinc oxide to form zinc isocyanate. ZnO is the
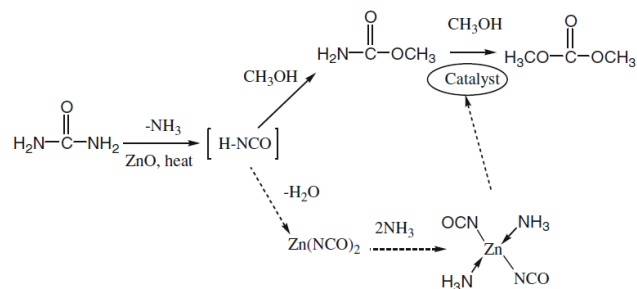
Scheme 4   Activation of ZnO in the urea methanolysis [159].

precursor of the homogeneous catalyst for urea methanolysis and complex $Zn(NCO)_2(NH_3)_2$ which is formed during the reaction behaves as the catalyst in urea ethanolysis.

5   Conclusions and outlook

Conversion of CO_2 to chemicals plays a key role in the global effort for CO_2 reduction. In our research works, CO_2 hydrogenation to methanol, CO_2 dry reforming to syngas and CO_2 conversion to linear and cycle carbonate were investigated for their industrial applications. Novel catalysts were designed, prepared and applied in these processes through understanding of the CO_2 activation mechanism and correction between catalytic performance and structure. However, processes of CO_2 conversion to chemicals that can be completed with a net CO_2 reduction at commercial scale are yet to be demonstrated. Therefore, more studies are to be carried out aiming at developing technologies for better energy-effective CO_2 conversion as below.

(1) Catalysts play a crucial role in reducing the energy consumption. High performance catalysts are usually characterized by high conversion of substrates and high selectivity, and they should be easily recovered. The reactions should be taken place at low temperature and pressure. Better insight into the reaction mechanisms as well as the nature and functionality of active site would enable better design of novel catalysts.

(2) Reactor engineering is another key factor. Most of CO_2 chemical conversion reactions are equilibrium-limited processes, this limitation could be surpassed through designing a new reaction system to make this reaction simpler and increase the yield of aimed products. Membrane reactor is a suitable alternative to the separation/removal of reaction components. It can avoid equilibrium conversions and high energy consumption by preferential removal of products from the reaction system.

(3) Strategies of CO_2 conversion to chemicals must be carefully evaluated to guarantee that more CO_2 is converted than emission from the conversion process before its practical applications.

(4) CO_2 is a chemically inert molecule, and conversion of CO_2 into chemicals requires energy in the form of heat, electrons or hydrogen. Renewable energy, such as solar, wind, nuclear and geothermal energy can be used instead of fossil energy in conversion.

(5) In order to further convert renewable energy into more useable form as a chemical, photochemical and electrochemical catalytic conversion of CO_2 would be a future research direction.

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