

# An Introduction of CO<sub>2</sub> Conversion by Dry Reforming with Methane and New Route of Low-Temperature Methanol Synthesis

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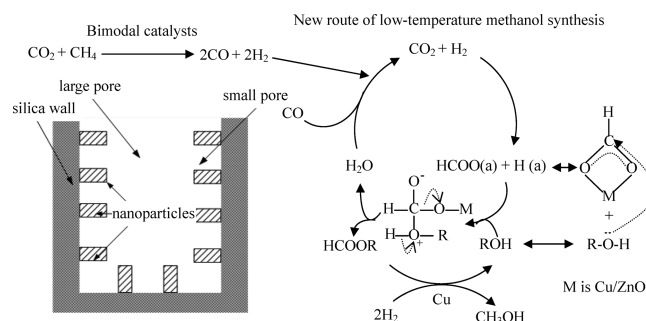
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## CONSPECTUS

Carbon dioxide is one of the highest contributors to the greenhouse effect, as well as a cheap and nontoxic building block for single carbon source chemistry. As such, CO<sub>2</sub> conversion is one of most important research areas in energy and environment sciences, as well as in catalysis technology. For chemical conversion of CO<sub>2</sub>, natural gas (mainly CH<sub>4</sub>) is a promising counterpart molecule to the CO<sub>2</sub>-related reaction, due to its high availability and low price. More importantly, being able to convert CH<sub>4</sub> to useful fuels and molecules is advantageous, because it is also a kind of “greenhouse effect” gas, and can be an energy alternative to petroleum oil. In this Account, we discuss our development of efficient catalysts with precisely designed nanostructure for CO<sub>2</sub> reforming of CH<sub>4</sub> to produce syngas (mixture of CO and H<sub>2</sub>), which can then be converted to many chemicals and energy products. This new production flow can establish a GTL (gas-to-liquid) industry, being currently pushed by the shale gas revolution.

From the viewpoint of GTL industry, developing a catalyst for CO<sub>2</sub> reforming of CH<sub>4</sub> is a challenge, because they need a very high production rate to make the huge GTL methane reformer as small as possible. In addition, since both CO<sub>2</sub> and CH<sub>4</sub> give off carbon deposits that deactivate non-precious metallic catalysts very quickly, the total design of catalyst support and supported metallic nanoparticles is necessary. We present a simple but useful method to prepare bimodal catalyst support, where small pores are formed inside large ones during the self-organization of nanoparticles from solution. Large pores enhance the mass transfer rate, while small pores provide large surface areas to disperse active metallic nanoparticles. More importantly, building materials for small pores can also be used as promoters or cocatalysts to further enhance the total activity and stability.

Produced syngas from methane reforming is generally catalytically converted in situ via one of two main routes. The first is to use Fischer–Tropsch synthesis (FTS), a process that catalytically converts syngas to hydrocarbons of varying molecular weights. The second is methanol synthesis. The latter has better atomic economy, since the oxygen atom in CO is included in the product and CO<sub>2</sub> can be blended into syngas as a reactant. However, production of methanol is very inefficient in this reaction: only 10–15% one-pass conversion typically at 5.0–10.0 MPa and 523–573 K, due to the severe thermodynamic limitations of this exothermal reaction (CO + 2H<sub>2</sub> = CH<sub>3</sub>OH). In this Account, we propose and develop a new route of low-temperature methanol synthesis from CO<sub>2</sub>-containing syngas only by adding alcohols, including methanol itself. These alcohols act as homogeneous cocatalysts and the solvent, realizing 70–100% one-pass conversion at only 5.0 MPa and 443 K. The key step is the reaction of the adsorbed formate species with alcohols to yield ester species at low temperatures, followed by the hydrogenation of ester by hydrogen atoms on metallic Cu. This changes the normal reaction path of conventional, high-temperature methanol synthesis from formate via methoxy to methanol.



## Introduction

For the past decades, increasing CO<sub>2</sub> emission has caused global warming problem through the “greenhouse effect”. On the other hand, CO<sub>2</sub> is also an attractive, nontoxic, and cheap building block for C<sub>1</sub> chemistry. Catalytic conversion of CO<sub>2</sub> to chemicals and fuels is of great importance and has attracted extensive research attention. Of which, CO<sub>2</sub> reforming with CH<sub>4</sub>, is promising both in energy and environmental aspects, which can convert two major greenhouse gases (CH<sub>4</sub> and CO<sub>2</sub>) to valuable synthesis gas (CO + H<sub>2</sub>) for C<sub>1</sub> chemistry processes such as Fischer–Tropsch synthesis (FTS)<sup>1</sup> or oxygenate synthesis.<sup>2</sup> Up to now, catalyst deactivation caused by coking and sintering of active metal is still a big challenge for CO<sub>2</sub> reforming of CH<sub>4</sub>. Great efforts have been devoted to design and prepare catalysts with higher activity and stability.

## Role of Bimodal Structure Supports

CO<sub>2</sub> reforming of CH<sub>4</sub> is a highly endothermic reaction, thus, some supports with high thermal stability, such as SiO<sub>2</sub>,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>,<sup>3</sup> and ZrO<sub>2</sub>,<sup>4</sup> are preferred. The role of support is not limited to dispersing the active metal; it may also affect the catalytic performance due to the pore morphology, confinement and chemical effect. It is generally accepted that highly dispersed metals on support could avoid the sintering of metal and retard coking.<sup>5,6</sup> A large active surface area could be obtained by employing some supports with large BET surface area. However, a support with large surface area usually consists of fine micropores or mesopores, which will influence the diffusion of reactants and products, consequently resulting in poor efficiency of the as-prepared catalyst. This issue is especially critical for methane reforming, because the syngas production plant accounts for more than half of the capital investment of the gas-to-liquid (GTL) total process.<sup>7</sup> To downsize the scale of methane reformer and reduce the cost, it is desirable to enhance the diffusion efficiency of reactants and products inside the catalyst pellet as highly as possible. By using a support with large macropores, the diffusion limitation could be reduced. The methane reforming kinetics and diffusion limitation of a large pore Ni/Al<sub>2</sub>O<sub>3</sub> nickel catalyst were studied by Rodrigues et al.<sup>8</sup> The results suggest that the presence of large pores has an important contribution in decreasing the resistance to mass transfer in catalyst pellets with  $1.1 \times 10^{-2}$  m diameter. However, this kind of support is not beneficial to obtain the finely dispersed active phase, restricted by its lower surface area.

A new catalyst support<sup>9</sup> preparation method containing both mesopores and macropores simultaneously, called

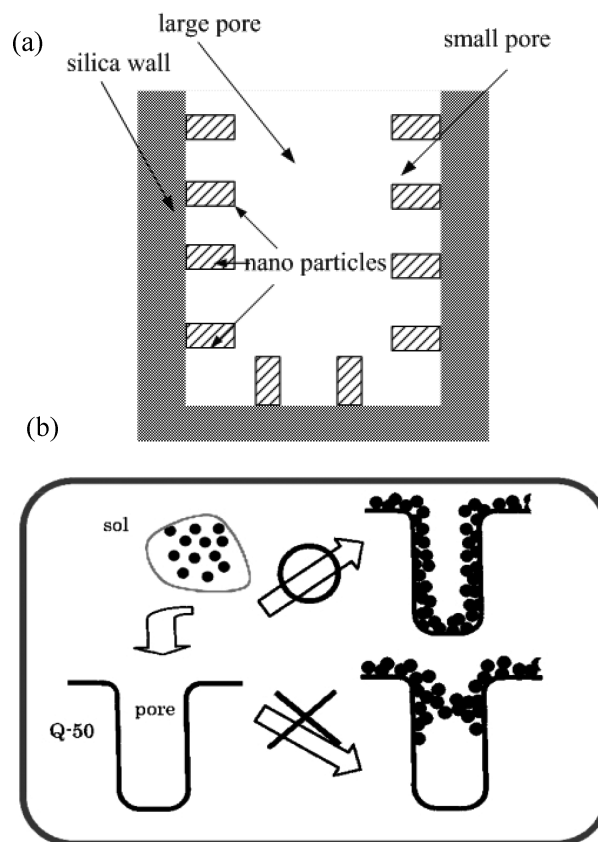


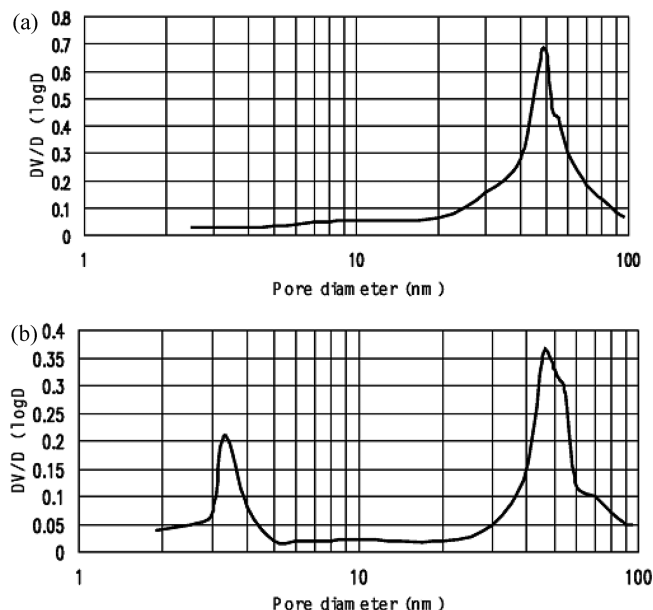
FIGURE 1. Bimodal pore structure.

bimodal pore support, is first proposed for FTS, which is also of great significance in CO<sub>2</sub> reforming of CH<sub>4</sub>. The presence of macropores greatly enhances the mass transfer of reactants and products, while the mesopores improve the dispersion of the active metal. The SiO<sub>2</sub>–SiO<sub>2</sub> bimodal pore supports are simply prepared by introducing silica nanoparticles into the macropores through incipient wetness impregnation method (Figure 1a). The precursor sol containing nanoparticles first enters into the 50 nm large pores of Q-50 silica gel. Mesopores, which are derived from the polycondensation of nanoparticles during the calcination process, are formed inside the large pores. The BET surface area of the bimodal support significantly increases from 94 m<sup>2</sup> g<sup>−1</sup> (for silica gel Q-50) to 156 m<sup>2</sup> g<sup>−1</sup>, due to the contribution from the newly formed small pores, as summarized in Table 1. As the porous silica structure is formed inside the large pores of silica gel Q-50, the pore volume of bimodal support decreases from 1.35 mL g<sup>−1</sup> of Q-50 to 0.81 mL g<sup>−1</sup>. The increased BET surface area and the decreased pore volume prove that the particles of silica indeed enters the large pores of Q-50, and deposits on the inner walls of Q-50 to form the small pores, as illustrated in Figure 1b. If the silica particles are deposited at the entrance of large pores of

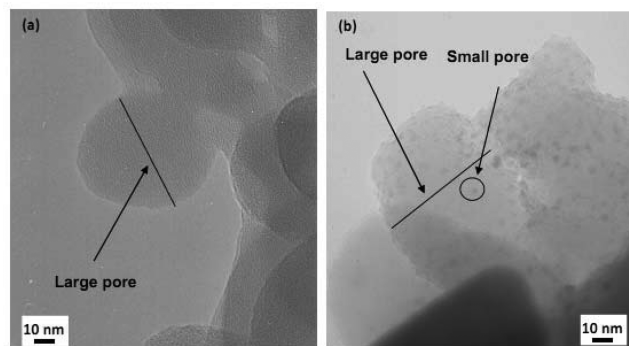
**TABLE 1.** Properties of Various Catalysts

catalyst <sup>a</sup>	pore sizes (nm)	pore volume (mL/g)	BET (m <sup>2</sup> /g)	Pt <sup>b</sup> (nm)	Pt surface area <sup>c</sup> (m <sup>2</sup> /g)	uptake (μmol/g) <sup>c</sup>
Q-50	59	1.35	94	16	0.92	19.1
Q-3	3	0.30	546	7	2.56	53.1
SiO <sub>2</sub> bimodal	5.2, 55	0.81	156	13	1.53	27.0
ZrO <sub>2</sub> bimodal	3.7, 52	0.70	308	10	2.25	46.7
Al <sub>2</sub> O <sub>3</sub> bimodal	8.0, 57	1.30	144	9	2.30	47.7

<sup>a</sup>Pt loading was 3 wt % for all calcined catalysts. <sup>b</sup>Pt particle size calculated from XRD. <sup>c</sup>Estimated from CO chemisorption; catalyst is in situ reduced at 773 K.

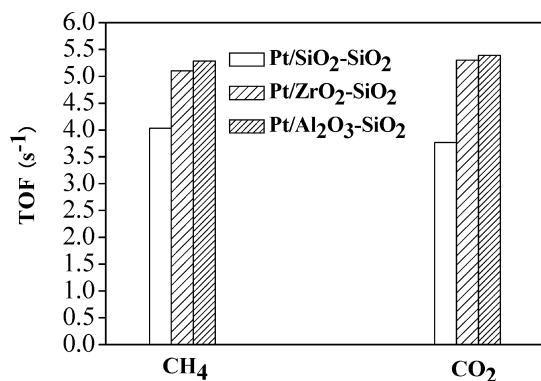
**FIGURE 2.** Pore size distributions of (a) Q-50 and (b) SiO<sub>2</sub>–ZrO<sub>2</sub> bimodal support.

Q-50, the large pores would be blocked, and the BET surface area of the bimodal support will decrease significantly. However, the above results clearly indicate that the bimodal support is formed according to the route in Figure 1b. With similar methodology, a series of ZrO<sub>2</sub>–SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> supports with distinct bimodal pore structure were synthesized. As shown in Figure 2, it is clear that the as-prepared ZrO<sub>2</sub>–SiO<sub>2</sub> support has two distinctly small and large kinds of pores, unlike the case of silica gel Q-50 with one kind of pore only. As the pores are not easy to be directly observed by TEM because of the poor contrast of amorphous silica, all pores in the bimodal support are first occupied by CuO, then, reversely observed (Figure 3). As compared in Figure 3a, CuO particle with a diameter of about 55–60 nm is clearly observed, corresponding to the original pore of silica Q-50. In Figure 3b, a lot of small dots and clusters with diameters of about 3–4 nm are formed on the surface of bulky copper oxide. The small dots and clusters are CuO confined in the small pores of bimodal pore support, and the bulky CuO is derived from the large pores. The bimodal pore structure is clearly observed by the reverse TEM image.

**FIGURE 3.** TEM images of (a) large-pore-only Q-50 and (b) ZrO<sub>2</sub>–SiO<sub>2</sub> bimodal pore support with pores fully filled by CuO.

The effect of various supports on the catalytic performance of Pt based catalyst for CO<sub>2</sub> reforming of CH<sub>4</sub> is systematically investigated.<sup>10,11</sup> Pt supported bimodal pore catalyst exhibits increased Pt dispersion and decreased Pt particle size due to the enhanced BET surface area of bimodal porous supports compared with that of host Q-50 silica (Table 1). The apparent activation energy of Pt/SiO<sub>2</sub> bimodal is just slightly lower than that of Pt/Q-50, which suggests that the bimodal catalyst is almost free of the control of diffusion due to its special porous structure. Besides, different bimodal catalysts display different TOF (turnover frequency): Pt/SiO<sub>2</sub>–SiO<sub>2</sub> < Pt/ZrO<sub>2</sub>–SiO<sub>2</sub> < Pt/Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>, as compared in Figure 4. Pt/Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> bimodal catalyst shows the best catalytic performance for CO<sub>2</sub> reforming of CH<sub>4</sub> in the aspects of activity as well as stability. The role of bimodal pore support is multifunctional that with the increased surface area, the enhanced intrapellet diffusion efficiency, and the chemical promotional effect of introduced metal oxide (ZrO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>) all together contributing to their superior catalytic performances.

The kinetics and pore diffusion simulation model of bimodal structure supports for Fischer–Tropsch synthesis is studied.<sup>12</sup> A mathematical model is developed to elucidate the kinetics coupled with mass transfer effect inside the pores of both unimodal and bimodal catalyst. In small pores, the smaller metal particles give higher metal surface area and higher surface catalytic activity, but stronger reactant



**FIGURE 4.** TOF values for Pt based bimodal pore catalyst. Pt loading: 3 wt % ( $T = 973$  K,  $P = 0.1$  MPa,  $W/F = 1$  g-cat · h/mol).

diffusion resistance. On the contrary, the large pore catalyst has lower surface activity, even without diffusion resistance. The as-prepared bimodal catalyst develops their good qualities, but avoids the defects as designed. The differential equations of simulation are solved with a computational software (EQUATRAN-G all-purpose equation solver for Windows, version 3.0.1, Omega Simulation Co., Ltd.).

## New Route of Low-Temperature Methanol Synthesis

Produced syngas from methane reformer is generally catalytically converted in situ via either of two main routes. One is FTS to get varied hydrocarbons and another is methanol synthesis, while the latter has better atomic economy because the oxygen in CO is included in the product and CO<sub>2</sub> can be blended into syngas as reactant. Methanol is widely used as feedstock in chemical and energy industries,<sup>13</sup> and also as one of the most important liquid fuels that can be supplied to the modified internal combustion engines or fuel cells via either reforming to hydrogen<sup>14</sup> or the methodology of direct methanol fuel cell (DMFC).<sup>15</sup> Recently, the conversion of methanol to hydrocarbons such as paraffins or olefins has also received much attention. Methanol with a worldwide demand of ~50 Mtons per year is industrially produced from synthesis gases (H<sub>2</sub>/CO/CO<sub>2</sub>) under high temperatures and elevated pressures (523–573 K, 5–10 MPa), mainly using Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts developed by ICI Co.<sup>16</sup>

Recently, the crucial atomic structure motif<sup>16</sup> for this industrial catalyst is identified by using experimental evidence in combination with density functional theory calculations. The active site consists of Cu steps decorated with Zn atoms, all stabilized by a series of well-defined bulk defects and surface species that need to be present jointly for the system to work. The thermodynamics, the development of methanol synthesis catalysts, reaction mechanism, active

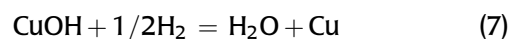
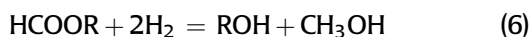
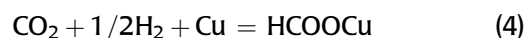
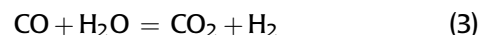
sites, and kinetics of conventional methanol synthesis are critically reviewed.<sup>17</sup> However, the efficiency of methanol synthesis is severely limited by thermodynamics because it is an extremely exothermic reaction. One-pass conversion of and ICI plant is limited to only 14%, and it will become zero if synthesis temperature is lower than 473 K. Therefore, developing a low-temperature process for methanol synthesis will make higher one-pass CO conversion become a reality and greatly reduce the production cost.

As known, production of methanol in inert solvent can contribute to efficient removal of the heat from the reaction and greatly reduce the operation temperature. Until now, methanol synthesis from pure CO and H<sub>2</sub> via the formation of methyl formate has been widely studied,<sup>18,19</sup> where carbonylation of methanol and hydrogenation of methyl formate are considered as two main intermediate steps of the reaction:<sup>18,19</sup>



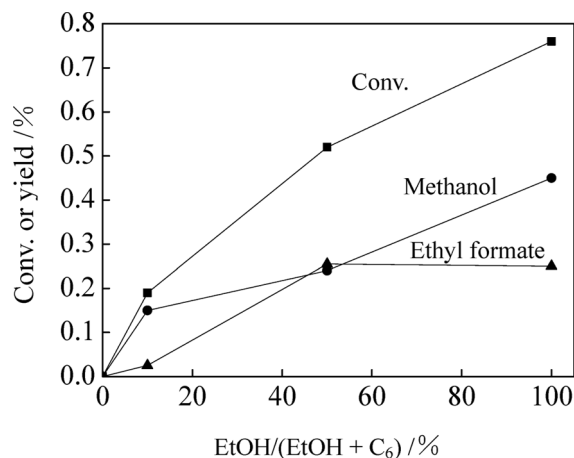
Alkali alkoxides are efficient catalysts for the former reaction and metallic Cu shows excellent hydrogenation activities for the latter one. However, a remarkable drawback of this process is that a trace amount of carbon dioxide and water in feed gas (CO + H<sub>2</sub>) or reaction system will deactivate the strongly basic catalyst rapidly. The high cost derived from complete purification of the syngas from the methane reformer, biomass gasifier, or the coal gasification plant as well as the reactivation process of the deactivated catalysts make commercialization impossible now.

In our previous study,<sup>2,20</sup> a new process of low-temperature methanol synthesis with alcohol as solvent and catalyst is proposed. This new route is composed of several steps as listed below:



Cu represents the active site Cu<sup>0</sup> or Cu<sup>1+</sup> from Cu-based catalysts. ROH is the accompanying alcohol which is cycled



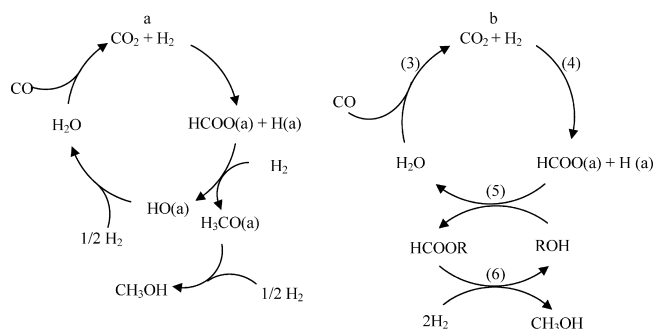


**FIGURE 5.** Effect of coexisting alcohols. Hybrid Cu/ZnO (ICI 51–2) and Cu/Al<sub>2</sub>O<sub>3</sub> catalysts; catalyst weight, 0.2 g; total solvent amount, 5 mL; reaction time, 2 h; 423 K; 3.0 MPa.

during the reaction. CO<sub>2</sub> and H<sub>2</sub>O are reactants as well as byproducts during the reaction and are also cycled in the reaction. In this reaction procedure, step 4 is not difficult, as formate is well-recognized intermediate from the water-gas shift (WGS) reaction of step 3, especially in Cu-catalyzed reaction. Esterification, step 5, can proceed under mild conditions if weak acidic or basic catalysts exist. Step 6, hydrogenation of accompanying ester is industrially operated at low temperature (453 K) on Cu-based catalysts. Theoretically, this new route seems to be very kinetically easy if appropriate catalysts are developed. It should be noted that ROH has triple roles: acting as solvent, catalyst, and product if ROH is methanol.

### Effects of the Amount of Ethanol Solvent, Reaction Time, Different Feed Gases, and Alcohols Solvent

We accomplish the above-mentioned reaction steps in a one-pot reactor with a hybrid catalyst composed of commercially available Cu/ZnO (ICI 51-2) and Cu/Al<sub>2</sub>O<sub>3</sub> catalysts. As compared in Figure 5, the reaction does not proceed at 423 K in pure cyclohexane medium without solvent (ethanol). The reaction route is the same as that of ICI commercial process and direct hydrogenation of formate cannot conduct at a temperature as low as 423 K. However, in the presence of ethanol, the conversion of syngas, the yields of methanol and ethyl formate increase with the increased amount of ethanol added in the initial reactant mixture. Interestingly, the reaction is quite selective to the final product of methanol than ethyl formate when pure ethanol is used as initial solvent. The reaction results reveal the necessity of coexisting alcohol that obviously changes the reaction route from ICI process (Figure 6a) to this proposed new route



**FIGURE 6.** Changing the reaction course from a high-temperature ICI process (a) to a new low-temperature route (b) by addition of alcohol.

(Figure 6b), making low-temperature path possible. Here, the accompanying ethanol acts as both solvent and catalyst because no ethanol is consumed when the overall reaction is accomplished.

The effect of reaction time on the conversion or yield at 443 K is investigated.<sup>20</sup> By continually increasing the reaction time, the conversion (from 2.1% at 2 h to 19.0% at 20 h) and yield of methanol are linearly enhanced. However, the yield of ethyl formate is nearly constant (about 1.1%) during the total reaction process. This indicates that this low-temperature methanol synthesis proceeds via the designed steps, in which ethyl formate is the intermediate first formed from step 5 and then eliminated by step 6. Further support is provided by the reaction results for the relationship between selectivity and conversion at 423 K.<sup>2,20</sup> At low conversion, ethyl formate is the main product, while at high conversion ethyl formate is converted into methanol, showing a typical consecutive reaction pattern.

The influence of various reactant gas compositions is studied<sup>2</sup> using ethanol solvent. The results indicate that the total reaction rate gradually increases with the increased content of CO<sub>2</sub> (from 0.0 to 7.5%) in the syngas. Hydrogenation of pure CO<sub>2</sub> exhibits the highest reaction rate. Interestingly, while using CO and H<sub>2</sub> as reactant gases, only ethyl formate is obtained and methanol is not formed. If a small amount of water, the same as that coming from CO<sub>2</sub> via water-shift gas reaction, is added into ethanol, the similar results with methanol generation are attained. If only pure CO is used as reactant gas, the reaction does not proceed at 423 K, suggesting that direct carbonylation of ethanol to ester at this condition is impossible. These phenomena prove that methanol synthesis rate from CO<sub>2</sub> and H<sub>2</sub> is faster than that from CO and H<sub>2</sub>, which also supports that step 3 in this low-temperature methanol synthesis route is reasonable.

Besides ethanol, multiple alcohols<sup>21,22</sup> are used as solvent in low-temperature methanol synthesis. As compared

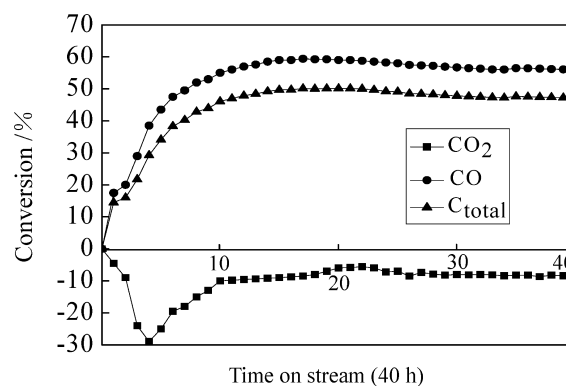
**TABLE 2.** Effects of Multiple Alcohols on the Synthesis of Methanol<sup>a</sup>

solvent	total conv (%)	methanol yield (%)	HCOOR yield (%)
none	0	0	0
cyclohexane	0	0	0
ethanol	11.35	10.22	1.13
1-propanol	9.43	9.27	0.16
2-propanol	23.46	13.19	10.27
1-butanol	8.97	8.97	0
2-butanol	21.48	11.26	10.22
isobutanol	8.19	8.19	0
<i>t</i> -butanol	5.83	5.83	0
1-pentanol	7.74	7.74	0
2-pentanol	11.81	3.72	8.09
cyclopentanol	6.71	6.71	0
1-hexanol	7.17	7.17	0
ethylene glycol	0	0	0
benzyl alcohol	0	0	0

<sup>a</sup>Temperature, 443 K; pressure, 3.0 MPa; reaction time, 2 h; Cu/ZnO, 1.0 g; alcohols, 20 mL; CO/CO<sub>2</sub>/H<sub>2</sub>/Ar = 31.90/5.08/60.08/2.94.

in Table 2, for six 1-alcohols or three 2-alcohols, the total carbon conversions gradually decrease with the increased carbon number. All 2-alcohols exhibit much higher activity than 1-alcohols with the same carbon number. When alcohols with larger spatial obstacle are used as solvent, in cases of isobutanol, *tert*-butyl alcohol, and cyclopentanol, the methanol synthesis reaction performs a lower activity. For ethylene and benzyl alcohol, no activity is observed. 2-Propanol exhibits the highest activity among all alcohols. The liquid phase productions for all alcohols as solvent are methanol and accompanying esters. 1-Alcohols show higher selectivity to methanol, and no esters are observed when their carbon number is more than three, while 2-alcohols display much higher selectivity to corresponding esters.

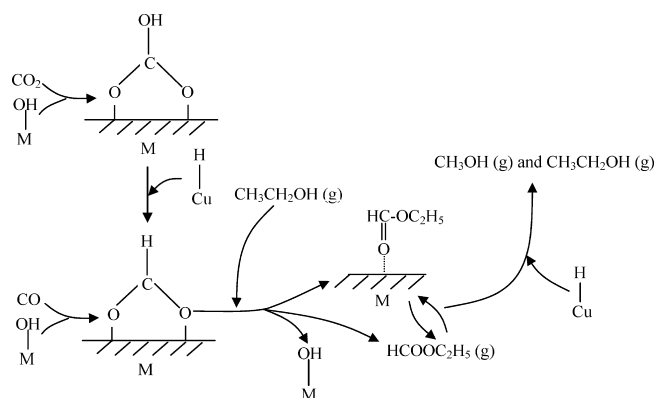
Continuous low-temperature methanol synthesis with multiple alcohols as solvent and catalyst is also studied<sup>23,24</sup> on various Cu/ZnO catalysts with different Cu/Zn ratios<sup>25</sup> at 443 K and elevated pressures from 3.0 to 5.0 MPa. For all types of alcohols, the selectivity of methanol is very high, up to 98–100%. The reaction with 2-butanol solvent exhibits higher activity (conversion: 47.0%) and methanol selectivity (98.9%). The time-on-stream activity change by using 2-butanol as solvent is shown in Figure 7. At the initial stage of the reaction, as the dead volume of the reactor and cold trap are filled by pressurized feed gas, the apparent conversions are low but increase gradually. After 12 h, the conversions are stable. The reaction shows a very high CO conversion about 60%; nevertheless, CO<sub>2</sub> production is found about 8%. The total carbon conversion, combining CO and CO<sub>2</sub>, is about 47%. The negative CO<sub>2</sub> rate suggests that very little part of CO in the feed gas converts to CO<sub>2</sub> via water-gas shift reaction. Furthermore, at the initial 5 h, the CO<sub>2</sub> formation comes to a maximum of 29% and then decreases to

**FIGURE 7.** Variations of CO, CO<sub>2</sub>, and total carbon conversions with time on stream for continuous low-temperature methanol synthesis. 443 K; 5.0 MPa; catalysts weight, 3.0 g; 2-butanol, 20 mL; flow rate, 20 mL/min.

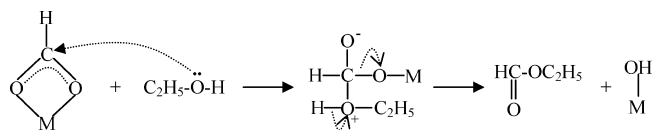
about 8%. Considering the dilution effect of the initial gas in the dead volume, the real CO<sub>2</sub> rate at the initial stage should be faster than the apparent one, even if the absolute CO<sub>2</sub> concentration in the feed gas is limited.

### The Reaction Mechanism and Kinetics Analysis for Low-Temperature Methanol Synthesis

The reaction mechanism of low-temperature methanol synthesis from syngas (CO/CO<sub>2</sub>/H<sub>2</sub>) using ethanol as solvent and catalyst is investigated by in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFT).<sup>26,27</sup> First, the catalyst is exposed to syngas at 443 K and 0.1 MPa for 3 h and then swept in helium for 20 min. The DRIFT spectra are recorded for different adsorption times. In order to identify the gas phase species from DRIFT, inert quartz sands are used as blank reference. The assignments of the adsorbed species on the surface of Cu/ZnO catalyst are identified by comparison with the spectra of well-known compounds or with published literature. Thereafter, the adsorbed catalyst is exposed to hydrogen between 443 and 573 K at atmospheric pressure. The experimental results indicate that the band intensities of HCOO–Zn and HCOO–Cu species do not change clearly when the temperature is lower than 493 K, but those band intensities decrease rapidly with the increased temperature from 523 to 573 K, and the formate adsorption species almost cannot be detected when the temperature rises to 573 K. These phenomena prove that formate adsorption species cannot be hydrogenated at lower temperature than 493 K without the help of ethanol. If the saturated ethanol vapor (298 K) is carried by syngas into an IR cell at 443 K and 0.1 MPa after formate species formation on Cu/ZnO, the formate adsorption species



**FIGURE 8.** Proposed mechanism for low-temperature methanol synthesis (M is Cu/ZnO).



**FIGURE 9.** Nucleophilic reaction process.

(HCOO–Zn and HCOO–Cu) absolutely disappear, suggesting that formate adsorption species can be transformed with ethanol vapor as low as at 443 K. Meanwhile, the bands of ethoxy, acetate, and carbonate species are newly observed. In order to confirm the assignment of gas-phase and physisorbed ethyl formate species above, the experiment of pure ethyl formate adsorption on Cu/ZnO is performed as reference at the same reaction condition. With increasing the reaction pressure from ambient pressure through 0.3 to 1.0 MPa, the bands of acetate and carbonate species disappear. At last, a great deal of ethoxy adsorption species after reaction is left. It implies that the formate species does not react with adsorbed ethoxy and instead that it should directly react with ethanol in gas phase.

The similar experiment of in situ DRIFT research is performed by using 2-propanol<sup>28</sup> as solvent or using Cu/MgO as catalysts.<sup>29</sup> Based on the experimental results above, a possible mechanism is proposed in Figure 8. At first, formate species are formed from syngas adsorbed on Cu/ZnO catalysts. Then, gas-phase and physisorbed ethyl formate, the reactive intermediate, is obtained by the reaction of adsorbed formate with gas-phase ethanol. This reaction is a nucleophilic addition–elimination reaction. Ethanol with lone pair electrons in oxygen atom is the nucleophilic reagent. The nucleophilic reaction process is illustrated in Figure 9. Finally, gas-phase and physisorbed ethyl formate are hydrogenated by hydrogen atoms on Cu to form gas-phase methanol. According to the mechanism mentioned above, it is clear that different alcohols affect the esterification reaction, by both electronic and spatial

effects. High electron density of oxygen atom in branched ROH makes ROH more efficient to attack the carbon atom of HCOOCu or HCOOZn (the intermediate). Low steric hindrance in linear ROH is favorable to nucleophilic attack in the esterification reaction. As a compromise effect, secondary alcohol exhibits the fastest reaction rate.

The reaction kinetics of low-temperature methanol synthesis is investigated by in situ DRIFTS with different alcohols as solvent and catalysts.<sup>30–32</sup> This reaction is conducted via two main processes: one is the formation of alkyl formate, and another is hydrogenation of alkyl formate. For the formation of alkyl formate, the kinetic analysis of the formate species is represented by the reaction of HCOOCu or HCOOZn with alcohols. The reactions of the formate species should obey the first-order reaction kinetics because the dosage of alcohol, which is much more than the limited amount of formate at the surface of the catalyst, is constant in the flowing reaction system. Therefore, the reaction rate of formate species with alcohols should be expressed as:

$$\gamma_{(\text{HCOOCu})} = k_1 C_{(\text{HCOOCu})} \quad (9)$$

$$\gamma_{(\text{HCOOZn})} = k_2 C_{(\text{HCOOZn})} \quad (10)$$

where  $k_1$  and  $k_2$  are rate constants;  $C_{(\text{HCOOCu})}$  and  $C_{(\text{HCOOZn})}$  are the concentrations of HCOOCu and HCOOZn species on catalyst surface, which are in direct proportion to the in situ FTIR peak areas of formate species, respectively. First, the variation of  $\ln(C_0/C)$  as a function of reaction time is drawn, where  $C_0/C$  corresponds to  $A_0/A$  with  $A_0$  being the initial peak area of HCOOCu or HCOOZn species, and  $A$  being the peak area at time  $t$ . Then, the rate constant  $k$  can be calculated. The rate constant for the reaction of HCOOCu species with ethanol is  $0.44 \text{ min}^{-1}$  and with 2-propanol is  $0.95 \text{ min}^{-1}$ , while the reaction rate constant of HCOOZn species with ethanol is  $0.38 \text{ min}^{-1}$  and with 2-propanol is  $0.94 \text{ min}^{-1}$ . The reaction rate constants with 2-propanol are larger than those with ethanol. Therefore, it can be concluded that the reaction activity of the adsorbed formate species with 2-propanol is higher than that of them with ethanol.

For the process of hydrogenation of ethyl formates, this reaction also obeys the first-order model, as the high pressure hydrogen is present in excess in the reaction process. Therefore, the hydrogenation reaction rate of alkyl formate can be expressed as

$$\gamma_{(\text{HCOOCu})} = k_3 P_{(\text{HCOOR})} \quad (11)$$

where  $k_3$  is the rate constant and  $P_{(\text{HCOOR})}$  is the partial pressure of gas-phase alkyl formate, which is proportional to the peak area of the gas-phase alkyl formate. According to the in situ DRIFT peak areas of gas-phase alkyl formate, the rate constant  $k_3$  can be calculated by the similar method as that of  $k_1$  and  $k_2$ . The hydrogenation reaction rate constant of ethyl formate is  $0.18 \text{ min}^{-1}$ , and that of 2-propyl formate is  $0.21 \text{ min}^{-1}$ . Obviously, both the formation and the hydrogenation rates of 2-propyl formate are faster than those of ethyl formate. Therefore, low-temperature methanol synthesis reaction is easier to proceed by using 2-propanol as a catalyst than ethanol on Cu/ZnO catalyst at 443 K, which is in good accordance with the catalytic reaction results.

### Low-Temperature Methanol Synthesis via Different Catalysts

A kind of mesoporous Cu/ZnO catalyst<sup>33</sup> prepared by a sol–gel method with copper and zinc acetate as precursors and Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by coimpregnation method<sup>34</sup> are tested in low-temperature methanol synthesis. The calcination and reduction conditions<sup>34</sup> and deactivation phenomena<sup>35</sup> of Cu-based catalysts are systematically studied.

A binary catalyst<sup>36,37</sup> combined with homogeneous HCOOK and solid Cu/MgO is investigated in concurrent synthesis route at temperature 423–443 K and pressure 3–5 MPa. The total carbon conversion of 91% with methanol selectivity of 99% is achieved under 5.0 MPa, 423 K, and with contact time of 100 g h/mol. During the reaction, HCOOK can greatly accelerate the esterification process, meanwhile, HCOOK is easily regenerated by the hydrogenation of KHCO<sub>3</sub> which comes from the reaction CO<sub>2</sub> and KOH.

Recently, a series of Cu/ZnO catalysts are prepared directly by a novel route of sol–gel<sup>38</sup> or solid-state<sup>39</sup> combustion method without further reduction using metal nitrates and citric acid. These new methods are easily operated, wastewater-free, and reduction-free. TG-DTA analysis of the catalyst precursor burnt in the argon atmosphere is compared in Figure 10. The DTA plot presents one sharp exothermic peak at about 493 K in a very narrow temperature range, and at the same time the TG plot shows an abrupt weight loss, which indicates that the combustion process of precursor happens as a severe redox reaction wherein citric acid acts as reductant, and nitrate ions as well as Cu<sup>2+</sup> in the chelated compound act as oxidant. During this combustion process, a large amount of gases such as H<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>, NO,

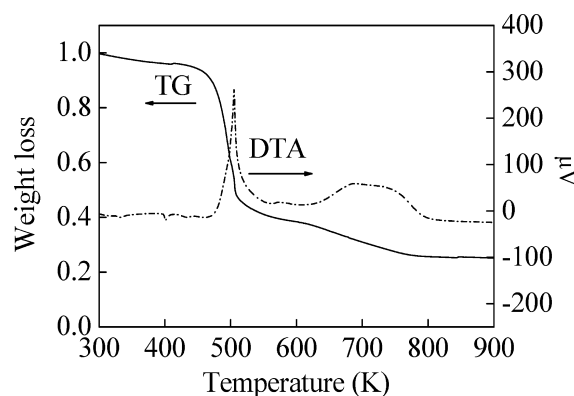


FIGURE 10. TG-DTA analysis of the catalyst precursor burnt in argon.

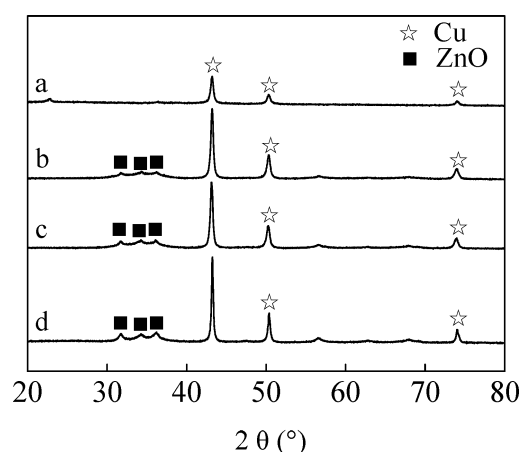


FIGURE 11. XRD patterns of (a) the solid-state precursor burnt in argon at 523 K for 1 h and (b) at 673 K for 3 h; (c) the sample of (b) after 10 h reduction by 5% H<sub>2</sub>; and (d) the sol–gel combustion precursor burnt in argon at 673 K for 3 h (☆, Cu; ■, ZnO).

CO<sub>2</sub>, NH<sub>3</sub>, and NO<sub>2</sub> are liberated. H<sub>2</sub> and CH<sub>4</sub> are the reducing agents in the redox process for obtaining metallic Cu from Cu<sup>2+</sup> in the chelated compound. The whole reduction process can be separated in three steps: (1) generation of CH<sub>4</sub> and H<sub>2</sub> by the decomposition of citric acid at the beginning of 483 K; (2) severe redox process between CH<sub>4</sub>–H<sub>2</sub> and NO<sub>3</sub><sup>−</sup> at about 493 K; (3) reduction of metallic Cu from Cu<sup>2+</sup> in the chelated compound by CH<sub>4</sub> and H<sub>2</sub>. The second exothermic broad peak from 650 to 800 K arises from the pyrolysis of the residue organics. The TPR analysis<sup>38,39</sup> of the as-burnt catalysts without further reduction illustrates that almost no hydrogen is consumed.

The XRD patterns of the as-burnt catalysts in argon are compared in Figure 11. Only Cu and ZnO characteristic diffraction peaks are observed. Comparing with the XRD patterns of the catalyst in Figure 11a burnt at 523 K for 1 h, the intensity of metallic Cu and ZnO characteristic peaks in Figure 11b which is burnt at 673 K for 3 h are obviously



enhanced. No obvious difference is found between Figure 11b and c which shows further reduction by 5% H<sub>2</sub> for 10 h, indicating that Cu<sup>2+</sup> in the metal-citric complexes is almost reduced to the metallic Cu during the decomposition of metal-citric complexes process in the argon atmosphere. Figure 11d (sol–gel combustion) exhibits much sharper Cu peaks than Figure 11c (solid-state combustion), suggesting that solid-state combustion method is more suitable to prepare Cu-based catalysts with smaller crystalline sizes.

## Conclusion

In summary, we report that efficient catalysts based on precisely designed nanostructure are developed for CO<sub>2</sub> reforming of CH<sub>4</sub>, to produce syngas (mixture of CO and H<sub>2</sub>), where syngas can be converted to methanol at mild conditions with maximum 100% one-pass conversion by Cu-based catalyst with the coexisting catalytic alcoholic solvent. This new production flow can establish a new GTL (gas-to-liquid) industry.

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## FOOTNOTES

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