



# A novel low-temperature methanol synthesis method from CO/H<sub>2</sub>/CO<sub>2</sub> based on the synergistic effect between solid catalyst and homogeneous catalyst

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## ABSTRACT

The activity of a binary catalyst in alcoholic solvents for methanol synthesis from CO/H<sub>2</sub>/CO<sub>2</sub> at low temperature was investigated in a concurrent synthesis course. Experiment results showed that the combination of homogeneous potassium formate catalyst and solid copper–magnesia catalyst enhanced the conversion of CO<sub>2</sub>-containing syngas to methanol at temperature of 423–443 K and pressure of 3–5 MPa. Under a contact time of 100 g h/mol, the maximum conversion of total carbon approached the reaction equilibrium and the selectivity of methanol was 99%. A reaction pathway involving esterification and hydrogenolysis of esters was postulated based on the integrative and separate activity tests, along with the structural characterization of the catalysts. Both potassium formate for the esterification as well as Cu/MgO for the hydrogenolysis were found to be crucial to this homogeneous and heterogeneous synergistically catalytic system. CO and H<sub>2</sub> were involved in the recycling of potassium formate.

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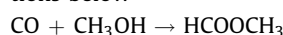
## 1. Introduction

Methanol is a bulk chemical, a kind of transportation fuel and energy material for fuel cell. Methanol economy receives increasing attention as a promising alternative for oil and natural gas [1]. Low-temperature conditions benefit one-pass conversion of syngas to methanol because methanol synthesis is a rather exothermic reaction. It is therefore desired to develop effective low-temperature catalysts to realize this process with thermodynamic advantage.

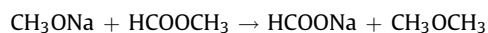
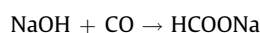
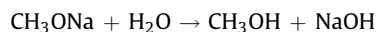
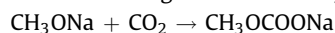
Several groups have developed the low-temperature methanol synthesis catalysts via a great deal of experiment study. Earlier Brookhaven National Laboratory patent revealed that methanol was highly produced from pure CO/H<sub>2</sub> at 373–393 K using a NaH/tertiary amyl alcohol/Ni(OAc)<sub>2</sub> catalyst or its combination with metal carbonyl component [2]. Researchers from University of Pittsburgh reported the multi-step, single stage slurry phase concurrent synthesis of methanol with a potassium methoxide/copper chromite catalyst system at 373–453 K [3,4]. Similar follow-up experiments indicated that the strong base-containing catalytic system is sensitive to the trace amount of CO<sub>2</sub> and water

in syngas produced from methane reformer or coal gasifier, and behaves the progressive deactivation [5], which implies low feasibility for industrial utilization where feedstock gas generally contains CO<sub>2</sub> in addition to CO and H<sub>2</sub>. One of the authors reported a new low-temperature process for methanol synthesis where the catalytically active alcoholic solvents were employed to promote the metallic catalysis [6,7]. Both CO<sub>2</sub> and H<sub>2</sub>O participated and were recycled in the synthesis at 423–443 K.

For the two-step low-temperature methanol synthesis reactions below



sodium/potassium methoxide and metallic copper are used as catalysts for the carbonylation of methanol and the successive hydrogenolysis of methyl formate, respectively [8,9]. When the former contacts CO<sub>2</sub> or H<sub>2</sub>O, the following undesired reactions occur and bring down the catalysts [10]:



But the catalytic system might be tolerant to a higher content of CO<sub>2</sub> and H<sub>2</sub>O if the rate of hydrogenation of HCOO<sup>-</sup> to CH<sub>3</sub>O<sup>-</sup> anion

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was quick enough under appropriate temperature and pressure conditions.

Our previous experiments demonstrated that potassium carbonate can be a promoter for the two-step methanol synthesis with potassium formate as an intermediate for the formation of methyl formate at 443 K [11]. In this paper a binary catalyst composed of homogeneous potassium formate and solid copper–magnesia, and its activity for the slurry phase methanol synthesis from CO/H<sub>2</sub>/CO<sub>2</sub> at low-temperature conditions are described. The possible reaction pathway for the salient catalytic performance is also investigated.

## 2. Experiments

Cu/MgO catalysts in different molar ratios were prepared by coprecipitation method from nitrates with sodium carbonate as precipitator. The precipitating pH and temperature were 10 and 338 K, respectively. The obtained precipitates were dried at 393 K for 6 h, followed by calcinations in air at 623 K for 1 h and then crushed into 20–40 meshes, reduced in a 5% H<sub>2</sub> flow at 623 K for 6 h and passivated by 1% O<sub>2</sub>. Activated carbon (AC) supported palladium catalyst for the separate experiments was prepared as follows: AC of 20–40 meshes was first vacuum pretreated at 393 K for 4 h, then impregnated with a Pd(NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub> aqueous solution and dried at 393 K for 12 h. Then it was heated at 673 K for 6 h in N<sub>2</sub> atmosphere, reduced in 5% H<sub>2</sub> for 6 h and passivated by 1% O<sub>2</sub>.

Activity evaluation of the catalysts was carried out in a flow-type semi-batch autoclave reactor with an inner volume of 100 mL. Typical reaction conditions were as follows unless specially indicated: catalyst: Cu/MgO 2 g/HCOOK 2 g, ethanol solvent: 40 mL, charge gas: CO/H<sub>2</sub>/CO<sub>2</sub>/Ar = 31.34/63.69/1.99/2.98, W/F = 75 g h/mol, temperature 423 K, pressure 3 MPa, stirring speed, 1000 rpm and time-on-stream, 12 h. Evaluation procedure was as follows: catalysts were first ground in ethanol to slurry and transferred into reactor. The reactor was then sealed, purged 3 times using charge gas and poured to the desired reaction pressure. Once the desired reaction temperature was reached, the reaction started. Effluent gas was analyzed on a GC-920 (TCD) connecting a 2 m AC separation column using argon as internal standard. After the reaction, the reactor was cooled rapidly to ambient temperature. Liquid products were analyzed on a GC-16A (TCD) connecting a 2 m GDX-203 separation column using 1-propanol as internal standard. Result calculations were as follows:

$$\text{CO conv. (\%)} = \frac{(A_{\text{CO(in)}}/A_{\text{Ar(in)}} - A_{\text{CO(out)}}/A_{\text{Ar(out)}})}{A_{\text{CO(in)}}/A_{\text{Ar(in)}}} \times 100$$

$$\text{CO}_2 \text{ conv. (\%)} = \frac{(A_{\text{CO}_2(\text{in})}/A_{\text{Ar(in)}} - A_{\text{CO}_2(\text{out})}/A_{\text{Ar(out)}})}{A_{\text{CO}_2(\text{in})}/A_{\text{Ar(in)}}} \times 100$$

$$\text{Total carbon conv. (\%)} = \text{CO conv.} \times \frac{A_{\text{CO(in)}}}{(A_{\text{CO(in)}} + A_{\text{CO}_2(\text{in})})} + \text{CO}_2 \text{ conv.} \times \frac{A_{\text{CO}_2(\text{in})}}{(A_{\text{CO(in)}} + A_{\text{CO}_2(\text{in})})}$$

$$\text{Sel. (\%)} = p_i (\text{mol}) / \sum p_j (\text{mol}) \times 100$$

The phase of the catalysts was analyzed on a Rigaku D/MAX-2200PC X-ray diffractometer with Cu K $\alpha$  radiation, 40 kV, 40 mA at scanning speed of 8°/min. The morphology was observed on a KYKY-2008B scanning electron microscopy (SEM) instrument. BET surface areas were determined on a Micromeritics ASAP-2010 M N<sub>2</sub> physisorption instrument. NMR analysis was carried out at 213 K on a JEOL JNM-A400 ALPHA FT NMR System equipped with a JEOL Superconducting Magnet 400 MHz.

H<sub>2</sub>-TPR (temperature programmed reduction) was conducted on a TP-5000 adsorption instrument: 50 mg unreduced catalyst sample was enclosed in a quartz tube and pretreated at 623 K in He (30 mL/min) atmosphere for 1 h and then reduced by 5% H<sub>2</sub>

(30 mL/min) from room temperature to the desired temperature in a ramp rate of 5 K/min.

Cu dispersion was analyzed as follows: 200 mg catalyst sample was first reduced at 533 K by 5% H<sub>2</sub> (30 mL/min) for 1 h and purged by He (30 mL/min) at 363 K for 1 h. Then N<sub>2</sub>O was pulse injected and the effluents N<sub>2</sub>O and N<sub>2</sub> were synchronously analyzed on a GC-950(TCD) until the reaction of N<sub>2</sub>O on the Cu surface finished. Cu dispersion and surface areas were calculated based on the consumed N<sub>2</sub>O.

Cu dispersion (%) = surface Cu atom number/total Cu atom number

Cu surface area (m<sup>2</sup>/g) = 4 $\pi$ r<sup>2</sup> × surface Cu atom number/catalyst weight, where r presented Cu atom radius, 0.1278 nm.

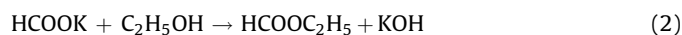
## 3. Results and discussion

### 3.1. Catalytic activity

Cu/MgO catalyst alone showed lower activity for methanol formation from CO/H<sub>2</sub>/CO<sub>2</sub> at 423 K in ethanol solvent as shown in Table 1. Using Cu/MgO (1:1) only as the catalyst, the conversion of CO and the total carbon conversion were 10.4% and 8.6%, respectively. As the molar ratio of Cu/MgO increased to 3:1, the conversion of CO and the total carbon conversion were 18.9% and 16.1%, respectively, and the selectivity of methanol was 99.4%. In addition, the conversion of CO<sub>2</sub> was negative, suggesting that CO<sub>2</sub> was produced accompanying the synthesis reaction. Because of the existence of trace amount of water in ethanol or by-product water, the CO<sub>2</sub> formation could be attributable to water gas shift reaction (1) even at lower temperature condition.



In the presence of HCOOK only as the catalyst, CO showed very low reaction while CO<sub>2</sub> exhibited high conversion as shown in Fig. 1. The product was merely ethyl formate and the reaction terminated at ethyl formate. The possible reactions involved are:



Reaction (3) happened at a low extent while CO<sub>2</sub> quickly reacted with KOH and was consumed.

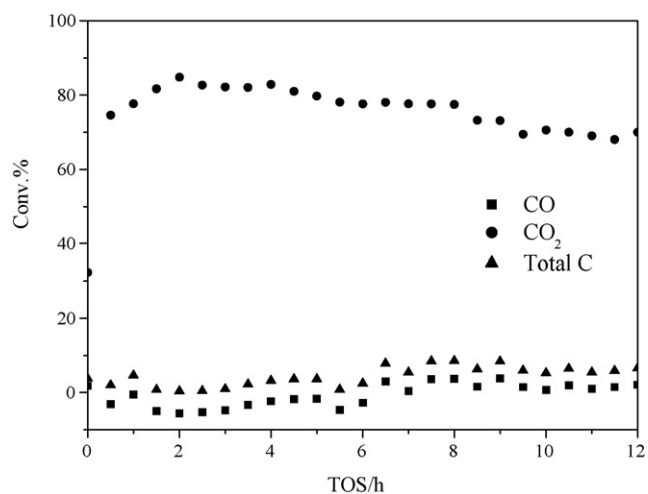
Table 2 shows the activity of Cu/MgO catalysts in different compositions combining with HCOOK for the conversion of CO/H<sub>2</sub>/CO<sub>2</sub> at 423 K. It is clear that the conversion of CO and the total carbon conversion changed as the molar ratio of Cu/MgO changed. The CO conversion increased from 31.7% to 58.9% as the molar ratio of Cu/MgO increased from 1:1 to 3:1, with the selectivity of methanol above 96%. Side-products were found to be low amounts of ethyl formate and ethyl acetate, similar to that using Cu/MnO as catalyst [11]. CO<sub>2</sub> was similarly formed in this case. As discussed later in the reaction mechanism, HCOOK regeneration from CO<sub>2</sub>-related KHCO<sub>3</sub> hydrogenation resulted in water formation and water might accelerate CO<sub>2</sub> formation by reaction (1) on Cu/MgO catalyst.

**Table 1**  
CO/H<sub>2</sub>/CO<sub>2</sub> conversion over Cu/MgO.

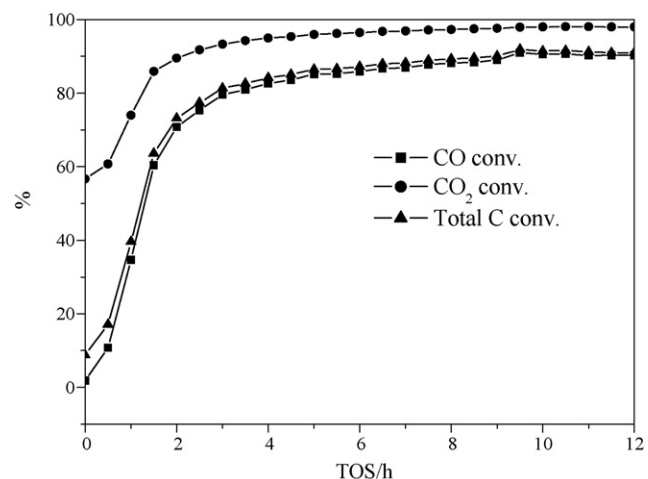
| Catalysts        | Conv. % |                 |         | Methanol sel. % |
|------------------|---------|-----------------|---------|-----------------|
|                  | CO      | CO <sub>2</sub> | Total C |                 |
| Cu/MgO (1:1) 2 g | 10.4    | -32.0           | 8.5     | 100             |
| Cu/MgO (3:1) 2 g | 18.9    | -47.0           | 16.1    | 99.4            |

These findings indicated the promotion of HCOOK to the activity of Cu/MgO for methanol synthesis from CO/H<sub>2</sub>/CO<sub>2</sub> at low temperature.

As the reaction temperature rose from 413 K to 443 K the conversion of CO reached a maximum at 423 K as shown in Table 3. Even at low temperatures, methanol synthesis is an exothermic reaction and very high temperature such as 443 K was unfavorable to the reaction. When the reaction pressure increased from 2 MPa to 5 MPa, the conversion of CO and the selectivity of methanol showed increasing trends, as shown in Table 4. At 2 MPa, the selectivity of methanol was slightly low. Because methanol synthesis is a molecule-number-decreasing reaction, higher pressure benefits the synthesis reaction. Furthermore, the conversion of CO<sub>2</sub> tended to ascend compared with that in Tables 1 and 2. This was mainly because reaction (4) was enhanced and might



**Fig. 1.** CO/H<sub>2</sub>/CO<sub>2</sub> conversion with HCOOK (2 g) catalyst.



**Fig. 2.** CO/CO<sub>2</sub>/H<sub>2</sub> conversion over Cu/MgO and HCOOK.

**Table 2**  
CO/H<sub>2</sub>/CO<sub>2</sub> conversion over Cu/MgO and HCOOK.

| Catalysts                    | Conv. % |                 |         | Methanol sel. % |
|------------------------------|---------|-----------------|---------|-----------------|
|                              | CO      | CO <sub>2</sub> | Total C |                 |
| Cu/MgO (1:1) 2 g + HCOOK 2 g | 31.7    | -35.8           | 27.2    | 96.1            |
| Cu/MgO (2:1) 2 g + HCOOK 2 g | 35.7    | -53.1           | 29.9    | 98.5            |
| Cu/MgO (3:1) 2 g + HCOOK 2 g | 58.9    | -87.9           | 48.4    | 98.6            |

**Table 3**  
Effects of temperature on the activity.

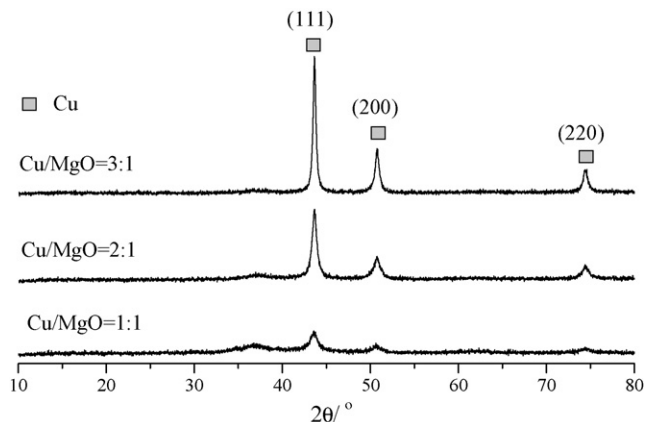
| T (K) | Conv. % |                 |         | Methanol sel. % |
|-------|---------|-----------------|---------|-----------------|
|       | CO      | CO <sub>2</sub> | Total C |                 |
| 393   | 9.2     | -17.8           | 7.4     | 100             |
| 423   | 58.9    | -87.9           | 48.4    | 98.6            |
| 443   | 47.5    | -78.3           | 39.3    | 95.9            |

Cu/MgO (3:1) 2 g + HCOOK 2 g.

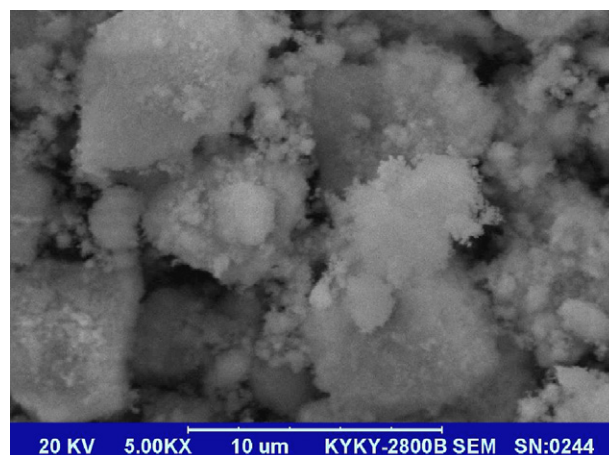
**Table 4**  
Effects of pressure on the activity.

| P (MPa) | Conv. % |                 |         | Methanol sel. % |
|---------|---------|-----------------|---------|-----------------|
|         | CO      | CO <sub>2</sub> | Total C |                 |
| 2       | 58.1    | -78.4           | 49.1    | 91.3            |
| 3       | 58.9    | -87.9           | 48.4    | 98.6            |
| 5       | 69.3    | -43.6           | 61.9    | 98.9            |

Cu/MgO (3:1) 2 g + HCOOK 2 g.



**Fig. 3.** XRD patterns of Cu/MgO.



**Fig. 4.** SEM image of Cu/MgO (3:1).

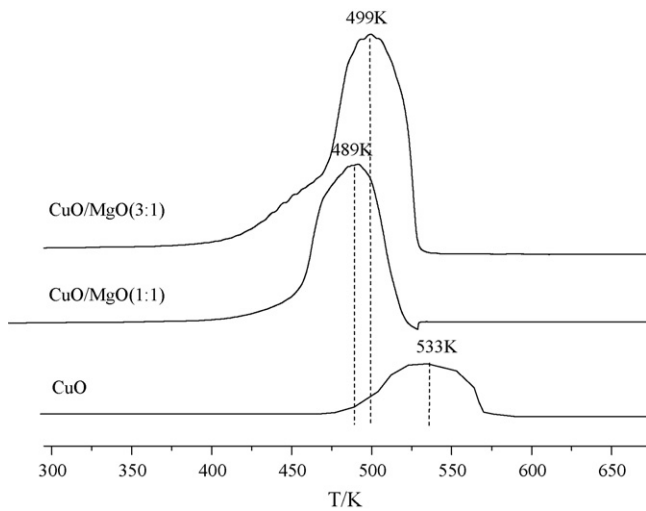


Fig. 5. H<sub>2</sub>-TPR profiles of Cu/MgO.

exceed reaction (1) by the accelerated reactions (5) and (2):

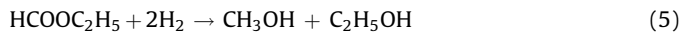


Fig. 2 shows the activity of the coexisting Cu/MgO and HCOOK catalyst at higher reaction pressure and W/F conditions. The used Cu/MgO was 4 g and W/F = 100 g h/mol. Both CO and CO<sub>2</sub> exhibited very high and stable conversion throughout 12 h of time-on-stream. The total carbon conversion approached 91% and the selectivity of methanol was 99%. Compared with Tables 2–4, increased Cu/MgO dosage improved remarkably the conversions of CO and CO<sub>2</sub>, implying the synthesis reaction proceeded in a favorable pathway. This enhancement was related likely to the accelerated hydrogenolysis reaction (5) catalyzed by Cu/MgO

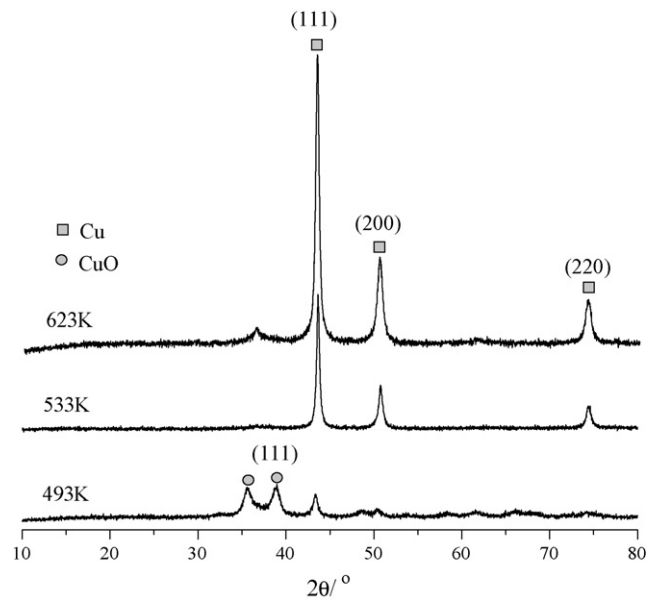


Fig. 6. XRD patterns of Cu/MgO (3:1) reduced at different temperatures.

catalyst. Meanwhile, reactions (2)–(4) were forced and the conversions of CO and CO<sub>2</sub> increased.

### 3.2. Catalyst characterization

The XRD patterns of Cu/MgO are shown in Fig. 3. The characteristic diffractive peaks at  $2\theta = 43.4^\circ$ ,  $50.6^\circ$  and  $74.4^\circ$ , versus indices (1 1 1), (2 0 0) and (2 2 0) were assigned to Cu. The diffractive intensity became strong as the molar ratio of Cu/MgO increased. The average particle size of Cu with increasing Cu/MgO

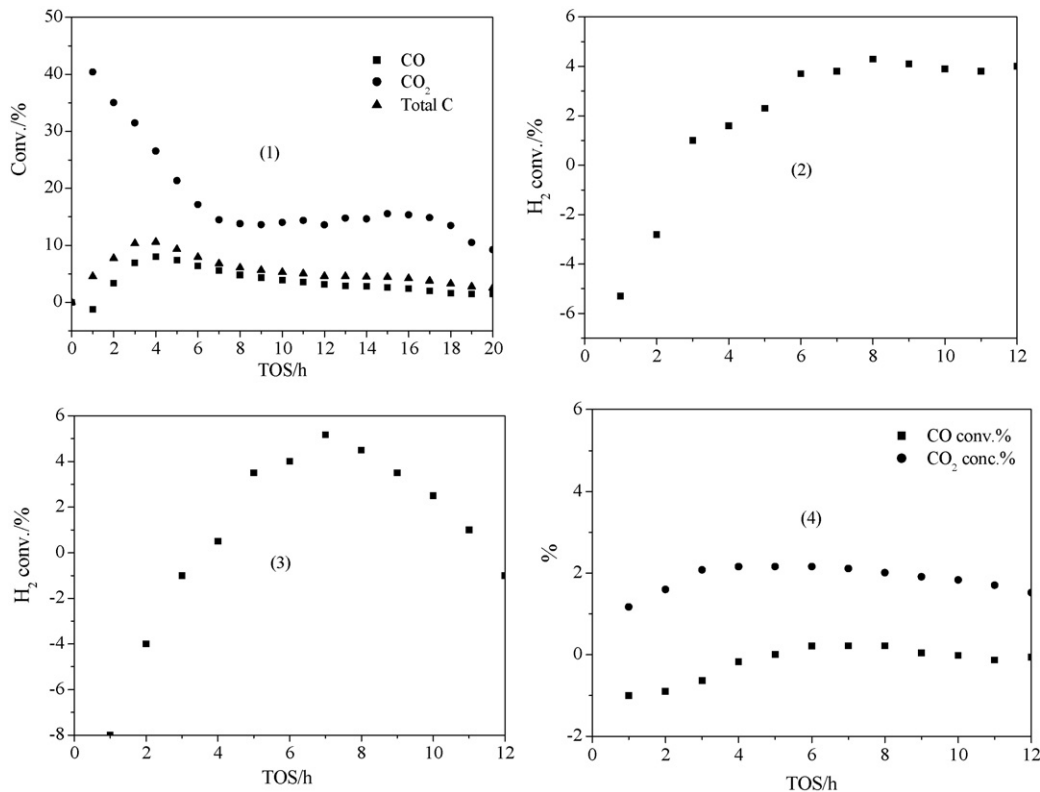


Fig. 7. Test results of separate reactions.

**Table 5**  
Cu surface areas and Cu dispersion of Cu/MgO.

| Cat.        | Cu dispersion (%) | $S_{Cu}$ (m <sup>2</sup> /g) | BET surface areas (m <sup>2</sup> /g) |
|-------------|-------------------|------------------------------|---------------------------------------|
| Cu/MgO(1:1) | 1.0               | 11.2                         | 34.5                                  |
| Cu/MgO(3:1) | 2.2               | 17.8                         | 33.8                                  |

ratio was 6.7 nm, 19.6 nm and 21.5 nm, respectively. The peaks of MgO were not found. This phase trend is in accordance with the Cu/MgO molar ratio enhancement. Cu/MgO exhibited uneven aggregate of particles as morphology observation in Fig. 4.

Cu/MgO was easily reduced at lower temperatures compared with pure CuO as shown in H<sub>2</sub>-TPR profiles of Fig. 5. Furthermore, as the ratio of Cu to MgO increased the reduction temperature slightly ascended from 489 K to 499 K, suggesting that as the Cu concentration in Cu/MgO increases, the reduction of Cu/MgO needs

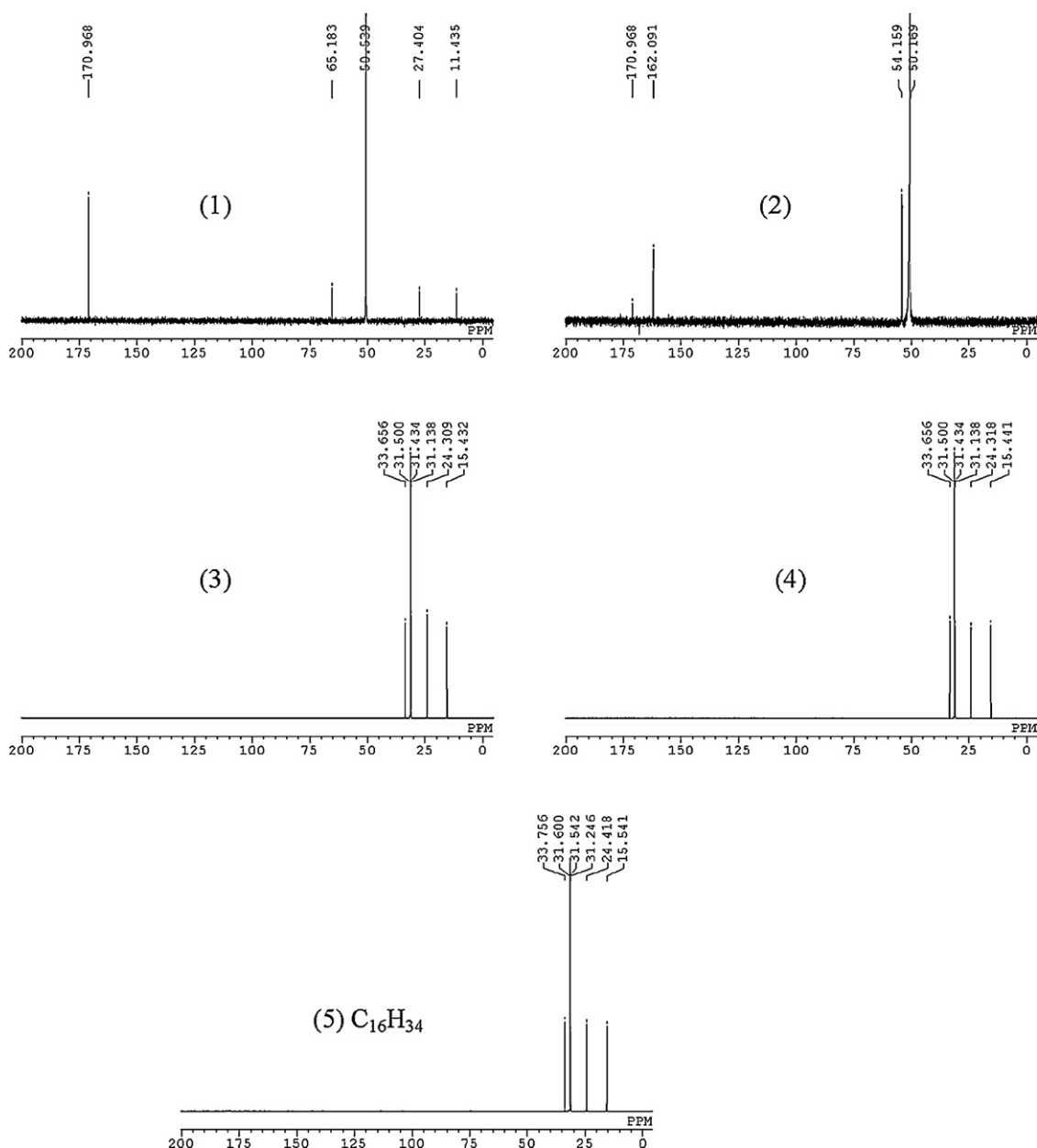
**Table 6**  
Experiment conditions for reaction pathway investigation.

| Expt. | Charge gas  | Catalysts                           | Solvent                         |
|-------|---|-------------------------------------|---------------------------------|
| (1)   | CO/H <sub>2</sub> /CO <sub>2</sub> /Ar<br>(31.9/60.1/5.08/2.94) | HCOOK 2 g                           | CH <sub>3</sub> OH              |
| (2)   | H <sub>2</sub> /N <sub>2</sub> (5.14/94.86)                     | KHCO <sub>3</sub> 2 g + 5%Pd/AC 2 g | CH <sub>3</sub> OH              |
| (3)   | H <sub>2</sub> /N <sub>2</sub> (87.6/12.4)                      | KHCO <sub>3</sub> 2 g + 5%Pd/AC 2 g | C <sub>16</sub> H <sub>34</sub> |
| (4)   | CO/Ar(97.01/2.99)   | KHCO <sub>3</sub> 2 g + 5%Pd/AC 2 g | C <sub>16</sub> H <sub>34</sub> |

Cu/MgO (3:1) 4 g + HCOOK 2 g, W/F=100 g h/mol and 5 MPa.

higher temperature. The XRD patterns of Cu/MgO reduced at different temperatures in Fig. 6 indicated that CuO/MgO was in fact reduced well at above 623 K. The reduction was incomplete at low temperature. The Cu surface areas and Cu dispersion of Cu/MgO are listed in Table 5. Cu/MgO (3:1) catalyst with higher Cu content had larger Cu metallic surface area and dispersion.

Taking into account the aforementioned activity test results, it was inferred that HCOOK addition played an important role in low-



**Fig. 8.** <sup>13</sup>C NMR spectra of separate reaction products.

temperature methanol synthesis besides metal Cu acting as main active centers. As the molar ratio of Cu/MgO increased from 1:1 to 3:1, the BET surface areas and Cu metallic surface areas were not remarkably changed. The conversion of CO, however, was highly enhanced in the presence of HCOOK, from 31.7% to 58.9% as listed in Table 2. Furthermore, at higher pressure and W/F conditions, the total carbon conversion even reached 91% and CO<sub>2</sub> was simultaneously converted.

### 3.3. Reaction pathway investigation

Four separate experiments were carried out to understand the reaction pathway and the experimental conditions are listed in Table 6. The experiment results are shown in Figs. 7 and 8.

In Expt. (1), mixed CO/H<sub>2</sub>/CO<sub>2</sub> gas was introduced into CH<sub>3</sub>OH with HCOOK dissolved in, where CH<sub>3</sub>OH had similar function to ethanol as solvent. Both CO and CO<sub>2</sub> showed conversion as shown in Fig. 7(1). The <sup>13</sup>C NMR analysis of the reaction liquid is shown in Fig. 8(1), where HCOOK ( $\delta$  170 ppm) was found besides CH<sub>3</sub>OH ( $\delta$  50 ppm). The conversions of CO and CO<sub>2</sub> were associated with the foregoing reactions (3) and (4).

Reaction (6) between H<sub>2</sub> and KHCO<sub>3</sub> should be beneficial by mean of Pd catalyst [12]:



In Expt. (2), H<sub>2</sub>/N<sub>2</sub> gas was imported into CH<sub>3</sub>OH containing KHCO<sub>3</sub> and Pd/AC catalyst. H<sub>2</sub> was consumed in a conversion of about 4% as shown in Fig. 7(2). The <sup>13</sup>C NMR spectra of the products indicated that KHCO<sub>3</sub> ( $\delta$  162 ppm), HCOOK ( $\delta$  170 ppm), HCOOCH<sub>3</sub> ( $\delta$  54 ppm) and CH<sub>3</sub>OH ( $\delta$  50 ppm) appeared as shown in Fig. 8(2), suggesting the conversion of H<sub>2</sub> was likely via reaction (6). Expt. (3) was conducted in the way similar to Expt. (2), but the solvent was C<sub>16</sub>H<sub>34</sub> (hexadecane) and the H<sub>2</sub> concentration in H<sub>2</sub>/N<sub>2</sub> gas was high. H<sub>2</sub> showed conversion at some extent as indicated in Fig. 7(3). In Expt. (4), the reaction of CO/Ar gas was checked in C<sub>16</sub>H<sub>34</sub> containing KHCO<sub>3</sub> and Pd/AC catalyst. As shown in Fig. 7(4), CO exhibited low conversion and CO<sub>2</sub> was produced, which was probably by the reaction between CO and KHCO<sub>3</sub> catalyzed by Pd/AC such as CO + KHCO<sub>3</sub> → HCOOK + CO<sub>2</sub>.

Compared with the spectrum of C<sub>16</sub>H<sub>34</sub> in Fig. 8(5), no products were found in Fig. 8(3) and (4) although the charged gases in Expts. (3) and (4) were observed to convert. In these cases, due to the absence of alcohol solvent and copper catalyst, only limited reaction happened and the amount of the products was low.

Considering the above experiments, a reaction pathway for methanol synthesis using the current catalyst system was postulated. As the main reaction route, the important reactions happened as shown in Fig. 9(I). Two molecules of C<sub>2</sub>H<sub>5</sub>OH firstly reacted with two molecules of HCOOK and ethyl formate was produced via reaction (2). The ethyl formate was hydrogenolyzed with four molecules of H<sub>2</sub> to produce two molecules of methanol on Cu/MgO catalyst via reaction (5). The regeneration of HCOOK included two ways as shown in Fig. 9(II). One was via reaction (3). Another was via reactions (4), (6) and (1) as discussed in Figs. 7 and 8 although without alcoholic solvent and copper catalyst, the rate of reaction (6) was slow. The total neat reaction was methanol synthesis from syngas. Both CO<sub>2</sub> and water were recycled even if they were contained in the low-purity syngas feed and C<sub>2</sub>H<sub>5</sub>OH acted as a catalytically active solvent here. CO and H<sub>2</sub> may be the source of HCOOK at appropriate reaction conditions.

It is worthy to note that whether CO<sub>2</sub> was produced or converted depended on reaction conditions. With Cu/MgO or HCOOK alone as catalyst, as discussed in Table 1 and Fig. 1, CO<sub>2</sub> produced and converted, respectively. Under the combination of Cu/MgO and HCOOK, the CO<sub>2</sub> behavior was associated with a series

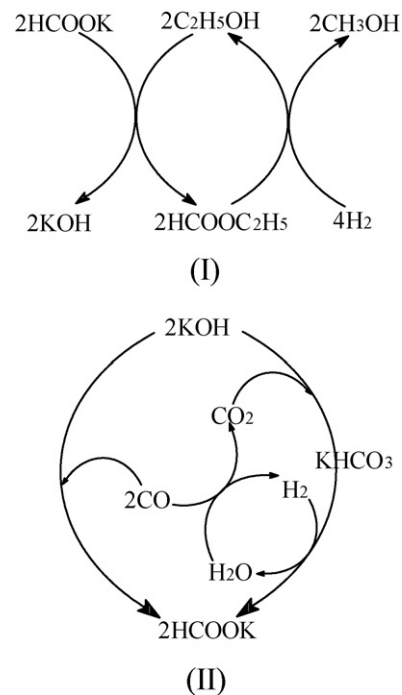


Fig. 9. Scheme for reaction pathway.

of reactions. At the conditions of less Cu/MgO and lower pressure as in Tables 2–4, the rate of hydrogenolysis or the consumption rate of HCOOK in reaction (2) was not fast enough; the water gas shift reaction (1) would competitively occur and resulted in the formation of CO<sub>2</sub>. As the dosage of Cu/MgO increased from 2 g to 4 g as shown in Fig. 2, the hydrogenolysis of ethyl formate was accelerated and resulted in the consecutive forward shift of reactions (2)–(4). Furthermore, the properties of Cu/MgO itself showed significant effect on the catalytic performance.

## 4. Conclusions

The binary combination catalyst composed of potassium salt and copper–magnesia was found to be highly catalytically active for methanol synthesis from CO/CO<sub>2</sub>/H<sub>2</sub> at as low reaction temperature as 423 K in a gas–liquid–solid slurry reactor. The total carbon conversion of around 91% was achieved under reaction pressure of 5 MPa and contact time of 100 g h/mol, with the selectivity of methanol of 99%. Integrative and separate activity evaluations and catalyst characterization suggested that methanol was produced via esterification and hydrogenolysis of ester steps, catalyzed by potassium formate and copper–magnesia, separately, and both two parts should be indispensable to this homogeneous and heterogeneous coexisting catalytic system. Hydrogen and carbon monoxide were found to aid the catalytic recycling of potassium salt.

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## References

- [1] G.A. Olah, Catal. Lett. 93 (2004) 1.

- [2] R.S. Sapienza, W.A. Slegeir, T.E. O'Hare, D. Mahajan, U.S. Patent 4,623,634 (1986).
- [3] Z. Liu, J.W. Tierney, Y.T. Shah, I. Wender, *Fuel Process. Technol.* 23 (1989) 149.
- [4] V.M. Palekar, H. Jung, J.W. Tierney, I. Wender, *Appl. Catal. A: Gen.* 102 (1993) 13.
- [5] S. Ohyama, *Appl. Catal. A: Gen.* 180 (1999) 217.
- [6] N. Tsubaki, M. Ito, K. Fujimoto, *J. Catal.* 197 (2001) 224.
- [7] R. Yang, Y. Fu, Y. Zhang, N. Tsubaki, *J. Catal.* 228 (2004) 23.
- [8] V.M. Palekar, H. Jung, J.W. Tierney, I. Wender, *Appl. Catal. A: Gen.* 103 (1993) 105.
- [9] W. Chu, T. Zhang, C. He, Y. Tang, *Catal. Lett.* 79 (2002) 129.
- [10] M. Marchionna, M. Lami, A.M.R. Galletti, *CHEMTECH* 27 (1997) 27.
- [11] T.-S. Zhao, Y. Yoneyama, K. Fujimoto, N. Yamane, K. Fujimoto, N. Tsubaki, *Chem. Lett.* 36 (2007) 734.
- [12] O.-T. Onsager, M.S.A. Brownrigg, R. Lødeng, *Int. J. Hydrogen Energy* 21 (1996) 883.