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Low Temperature Methanol Synthesis in Slurry Phase With a Hybrid Copper-Formate System

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Abstract A novel catalyst system composed of sodium formate and copper magnesium catalyst was developed to synthesize methanol from syngas ($CO/H_2 = 1/2$) in ethanol solvent at 5.0 MPa and 160 °C. The pH value was found to exert an important effect on the reaction activity of the co-precipitated Cu/MgO–Na catalyst; the reaction performance of the catalyst system was also sensitively dependent on the reaction temperature in the range of 150–180 °C. The successive experiment results indicated that the combination of formate species and copper catalyst should be the active site. In addition, the carbonylation step was the limiting-rate step, which was restrained by the equilibrium.

Keywords Methanol synthesis · Low temperature · Active site · Limiting-rate step · Equilibrium

1 Introduction

Methanol synthesis has been well-developed by ICI, Lurgi, Topsoe and MGC etc. over the last century [1–3]. At present, industrial methanol production is based on the heterogeneous hydrogenation of carbon oxides over copper–zinc catalysts. However, it suffers several limitations, such as high temperature (250 °C) operation and insufficient heat transfer, which result in low syngas conversion per pass.

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From the viewpoints of industrial applications as an alternative route to the conventional methanol production, low temperature methanol synthesis (LTMS) rapidly proceeds in a liquid medium at temperatures of approximately 100 °C to improve syngas conversion and reaction heat removal. One typical previous process was proposed by Brookhaven National Laboratory (BNL) in tetrahydrofuran at 100 °C using a catalytic system of $Ni(OCOCH_3)_2$/tert-amyl alcohol/NaH. However, subsequent experiments demonstrated that the basic catalyst was too sensitive to trace amounts of CO_2 and H_2O, which made it impossible for actual industrial application [4, 5]. Another LTMS from pure CO and H_2 via the formation of methyl formate has been widely studied, where the carbonylation of methanol and the successive hydrogenation of produced methyl formate are considered to be two main steps, as shown below:

$$ROH + CO \rightleftharpoons HCOOR \quad (1)$$

$$HCOOR + 2H_2 \rightleftharpoons CH_3OH + ROH \quad (2)$$

$$\text{Net } 2H_2 + CO \rightleftharpoons CH_3OH \quad (3)$$

In this reaction, alkali alkoxide/nickel compound system [6, 7] and alkali alkoxide/copper compound system were developed [8–11]; however, the deactivation was still not solved due to use of alkali metal methoxide [9, 10]. Researchers have tried many kinds of compounds to replace alkali methoxide. Palekar found that potassium formate was as active as potassium methoxide on Cu/Cr catalyst in the concurrent synthesis [9]. However, Marchionna concluded sodium formate as the deactivation product of sodium methoxide [12]. These controversies have gone along with which little attention had been paid to alkali formate in LTMS. In another viewpoint, some studies were focused on LTMS from $CO/CO_2/H_2$ in alcohol solvent excluding the

alkali salts, where it was the presence of elementary alcohol such as methanol or ethanol that made it possible for CO hydrogenation to methanol at quite low temperatures. Cu/ZnO and Cu/MgO were claimed, however, their activities were not high enough [13–15].

In our early work, HCOONa was found to be the best active among the alkali fomates due to the ionization potential and blocking effect of alkali group over copper catalyst for LTMS in the presence of ethanol [16]. This paper would pay particular attention to the reaction performance of the formate-copper catalyst system, as well as the active site and limiting-rate step of reaction.

2 Experimental

2.1 Catalyst Preparation

The used Cu/MgO–Na catalyst was prepared by the conventional co-precipitation and impregnation methods. An aqueous solution of copper nitrate and magnesium nitrate with the Cu/Mg ratio of 1:1 and an aqueous solution of sodium carbonate were simultaneously added at 60 °C and a constant required pH value into a well-stirred thermostated container. The obtained precipitate was filtrated and washed with distilled water, followed by drying at 120 °C for 6 h and calcination in air at 350 °C for 1 h. Subsequently, the precursor was impregnated by sodium carbonate solution with a nominal composition of 9 wt% sodium material. The Cu/MgO–Na powder was finally reduced in a stream of H_2 at 250 °C for 2 h before its activity evaluation.

2.2 Catalyst Characterizations

The pore structure properties of catalyst were determined by the BET method using an Autosorb-1 Quantachrome apparatus with nitrogen as adsorbate at −195.7 °C.

The uptakes of H_2- and CO-chemisorptions were measured by chemisorption isotherms on the Autosorb-1 Quantachrome apparatus. For the fresh Cu/MgO and Cu/MgO–Na catalysts, in situ reduction process by H_2 identical to that in the activity evaluation was conducted before H_2- and CO-chemisorptions; the chemisorption temperature was also set at the same 160 °C as reaction temperature.

2.3 Reaction Procedures

A flow type semi-batch autoclave reactor with an inner volume of 85 mL was employed in the experiment. The configuration of reactor was reported elsewhere [16]. The sodium formate, the reduced Cu/MgO–Na and high purity ethanol were successively poured into the reactor inside a vacuum glove box (Miwa Seisakusho Co., Ltd). The ethanol above the catalyst layer also prevented the reduced Cu/MgO–Na from being oxidized by air during the short time of fixing the reactor onto the experimental apparatus. After N_2 was used to keep air out of the retention volume of the reactor, the system was purged with feed gas until the pressure of the reactor increased to the reaction level; then, the temperature was increased to 160 °C. The composition of standard feed gas was H_2/CO/Ar = 64.56/32.4/3.04. The stirring speed was 1,660 rpm. All products were analyzed by two gas chromatographs, in which GC-8A/TCD (Shimadzu) was used for gas products and GC353/FID (GL Science) was used for liquid products. Considering the retention volume, the conversion of syngas (CO/$2H_2$) was calculated by Eq. (4), as well as the flowrate of outgoing gas. The formation rates [(STY (mol/kg-cat./h))] and selectivities of methanol and other liquid components were calculated by using 1-propanol as external standard.

$$\text{Syngas} - \text{conv.}\% = \left(F_{\text{in, syngas}} - F_{\text{out, syngas}}\right)/F_{\text{in, syngas}} \times 100\%, \quad (4)$$

where, $F_{\text{in, syngas}}$ ($F_{\text{out, syngas}}$) is the molar flow rate of syngas in the inlet (outlet) gas phase.

3 Results and Discussions

3.1 Dependence of Cu/MgO-Na Performance on PH Value of Co-precipitation

Table 1 investigated the reaction performances of Cu/MgO–Na catalysts with different pH values in the co-precipitation process. We could see that the pH value should be controlled at about ten for high activity and methanol selectivity, when the color of precipitation was blue-dark.

SEM images of different calcinated catalysts were shown in Fig. 1. With increasing the pH value, particle size of the catalyst became smaller; the distribution of particle size was symmetrical. As well known, required pH value for precipitation of Mg^{2+} is higher than that for Cu^{2+}, amorphous particles or small crystalline particles during the precipitation could therefore enter into the initial formed particles to produce the bigger conglomeration [17]. It was concluded that the higher precipitation speed at higher pH value might tend to reduce the possibility of conglomeration.

The pore properties were also investigated in Table 1. It was clear that pore volume and pore size increased with the increase of pH value; however, BET specific area first increased and then decreased. When pH was 10, BET specific area was much bigger. Also, the uptakes of H_2 and CO chemisorptions of Cu/MgO–Na at the pH value of 10 were higher than the others. The results revealed that, the

Table 1 Reaction performances and textural properties of copper catalysts with different pH values

Cu/MgO–Na Catalysts	Methanol synthesis[a]		Pore volume (cc/g)[b]	Pore size (nm)[b]	BET (m^2/g)[b]	Chemisorption uptakes (μmol/g)[c]	
	Rate (mol/kg h)	Sel. (%)				H_2	CO
pH = 9.0	9.6	85.6	0.114	17.89	25.44	32.72	17.22
pH = 10.0	25.8	93.3	0.159	20.43	32.14	103.00	25.04
pH = 10.5	24.6	90.2	0.172	28.74	23.98	86.77	19.44

[a] Reaction conditions: 433 K, 5.0 MPa, 90 mL/min, 2 g Cu/MgO–Na, 10 mmol HCOONa, 30 mL ethanol, 5 h

[b] Determined by BET method with N_2 as the adsorbate described in the text

[c] Determined by H_2-, CO- chemisorption isothermals described in the text

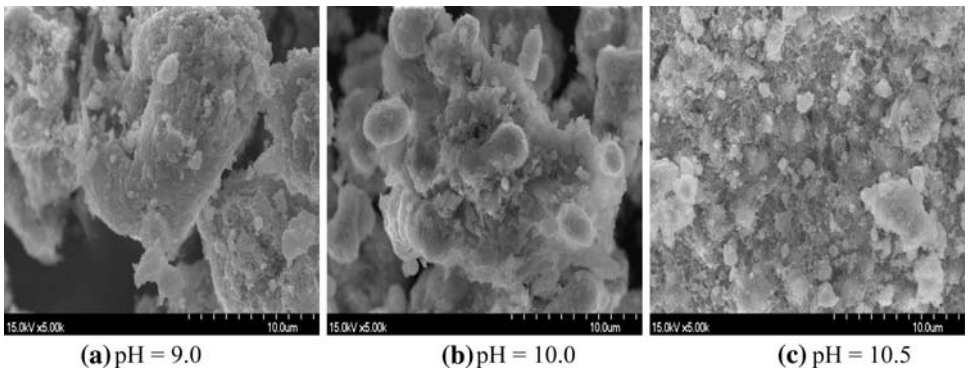

Fig. 1 SEM images for the calcinated Cu/MgO–Na catalysts with different pH values

amount of active site of the reduced catalyst at the pH value of 10 after reduction was large; the specific area of active copper phase did play a vital role in the activity of catalyst compared to other textural properties.

3.2 Optimization of Reaction Temperature

It was reported that low temperature shifted the equilibrium composition towards the formation of ROOCH for the carbonylation reaction of ROH from the viewpoint of the thermodynamics; but the hydrogenolysis rate was too low at lower temperature according to kinetic theory [18]. The effect of reaction temperature in the range 150–180 °C on LTMS in ethanol solvent was investigated in Fig. 2. The activity and the stability were sensitive to reaction temperatures in which 160 °C was relatively appropriate and the higher temperature decreased the activity more quickly.

In our previous study, the transformation of HCOONa to inactive $NaHCO_3$ was one of the reasons for the deactivation of the catalyst system due to the formation of CO_2 [16]. We thus conclude that high reaction temperature could promote the transformation process of HCOONa, leading to the rapid deactivation at 170 and 180 °C. In addition, the phase structures of the Cu/MgO–Na catalysts before reaction and after reactions of at 160 and 180 °C were compared by XRD patterns, as shown in Fig. 3. It is found that a mixing carbonate $Na_2Mg(CO_3)_2$ obviously appeared on the surface of the used catalysts in Fig. 3b, c, which was probably attributed to the deposition and the

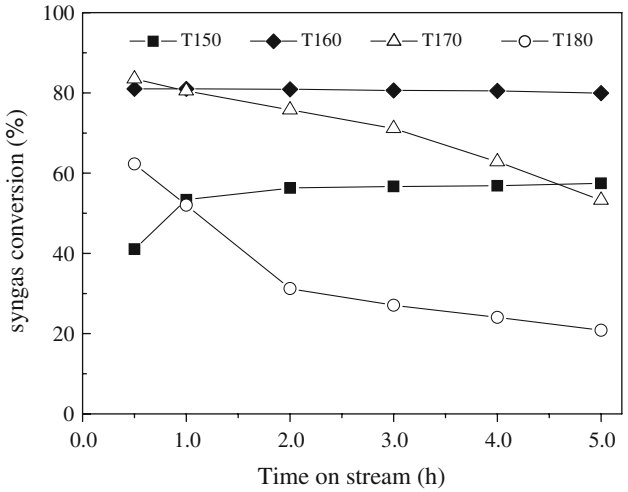

Fig. 2 The syngas conversion as a function of reaction temperature. Reaction conditions: 5.0 MPa, 90 mL/min, 2 g Cu/MgO–Na catalyst, 10 mmol HCOONa, 30 mL ethanol

combination of $NaHCO_3$ with magnesium carbonate on the surface of the Cu/MgO–Na catalyst. The crystalline sizes of metallic copper phase exhibiting the sharper peaks on the used catalysts evidently became larger than the reduced catalyst. The used catalyst at high temperature of 180 °C in Fig. 3c has also stronger peak intensities of metallic copper and Na_2 $Mg(CO_3)_2$ than that at low temperature of 160 °C in Fig. 3b, indicating that high reaction temperature could increase the crystalline percentage of the two phases. These

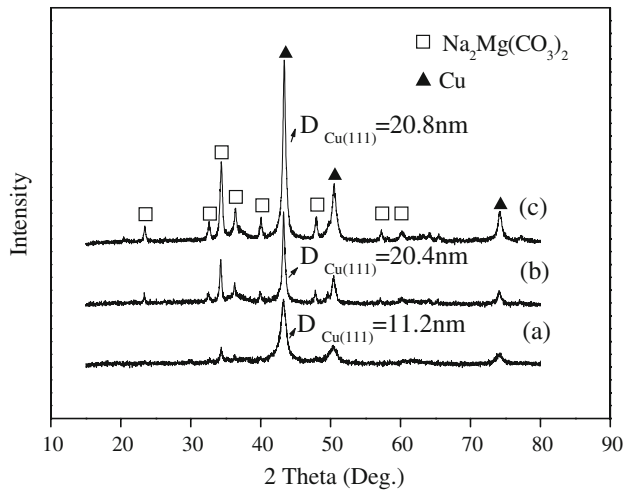

Fig. 3 XRD patterns for the Cu/MgO-Na catalysts: (*a*) after reduction and before reaction; (*b*) after reaction at 160 °C and (*c*) after reaction at 180 °C. $D_{Cu(111)}$ is the crystalline size ($2\theta = 43.5^{\circ}$) calculated by Scherrer equation

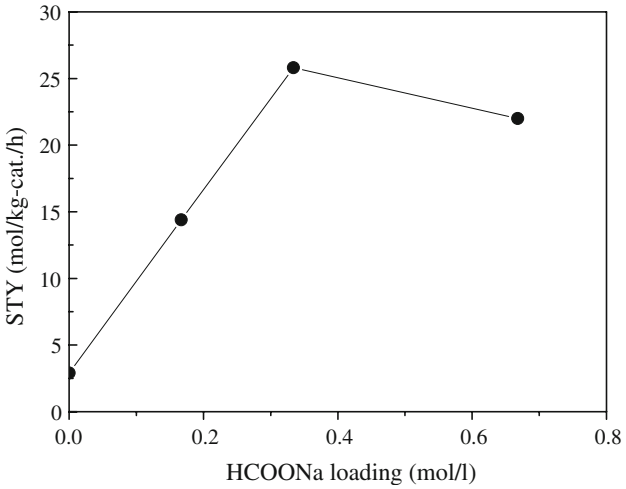

Fig. 4 Dependence of methanol synthesis rate on the loading concentration of HCOONa. Reaction conditions: 160 °C 5.0 MPa, 90 mL/min, 2 g Cu/MgO–Na catalyst, 30 mL ethanol, 5 h

data indicated that the sintering of metallic copper and the formation of Na_2 $Mg(CO_3)_2$ at higher reaction temperature probably decreased the activity.

3.3 Effects of HCOONa and Cu-based Catalyst Loadings

Firstly, we examined the possibility that gas–liquid mass transfer limitations may affect the methanol synthesis as the increase of copper magnesium catalyst loading. It was found that the rate of methanol formation was not changed above 800 rpm for 30% catalyst loading. Since our normal experiments were performed at 1,660 rpm and <15% catalyst loadings, the possibility of gas–liquid mass transfer seemed remote.

Effect of HCOONa concentration on reaction performance with 2 g Cu/MgO–Na was shown in Fig. 4. The methanol formation rate was linearly increased when the concentration of HCOONa was added from 0 to 0.33 mol/L. However, at higher concentration of 0.66 mol/L, the rate of methanol synthesis decreased markedly. The negative effect might result from the blocking of some active hydrogenolysis sites by excessive alkali groups [10].

Figure 5 showed the effect of loading of copper magnesium catalyst on the rate of methanol formation with the HCOONa loading of 0.33 mol/g. It was seen that the space time yield (STY) of methanol synthesis was almost proportional to the Cu-based catalyst amount in the range of 0–2 g, where the deviation from the line at 1 g copper catalyst might derive from the blocking effect of excessive HCOONa. The data supported the idea that the apparent reaction rate expressed the turnover rate on the catalyst

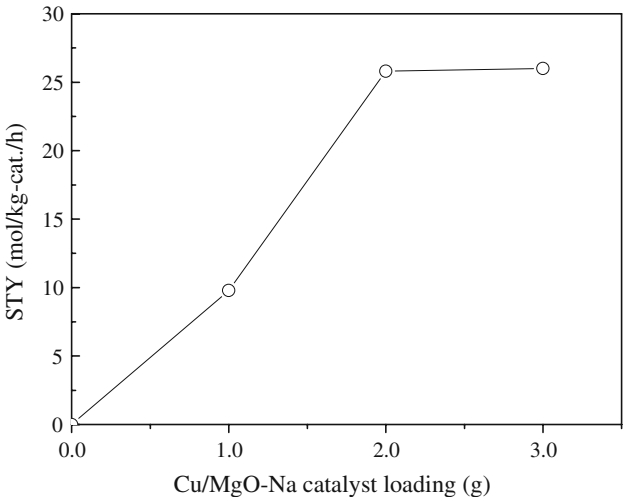

Fig. 5 Dependence of methanol synthesis rate on the Cu/MgO–Na catalyst loading. Reaction conditions: 160 °C, 5.0 MPa, 90 mL/min, 10 mmol HCOONa, 30 mL ethanol, 5 h

surface-that was, the concentration of active site did depend on the amount of copper catalyst at the lower loadings. When excessive Cu-based catalyst was used, the rate of methanol synthesis kept almost constant.

From foregoing results, the rate of methanol synthesis was linearly dependent on either HCOONa or Cu/MgO–Na loadings in a small range, each step reaction did not carry out in a separate way. We proposed that the special complex of formate and copper catalyst should behave as real active site in catalytic process, as well as according to another experiment fact demonstrated early that there existed a synergic function between the two components [16].

3.4 Dependence of Reaction Rate on H_2 and CO Partial Pressures

The initial partial pressures of CO and H_2 were attained by subtracting the ethanol vapor pressure from the total pressure, because initial methanol amount was zero. The data in Fig. 6 showed that the formation rate of methanol, concentrations of methyl formate (MeF) and ethyl formate (EtF) linearly increased in the range 0.5–1.5 MPa of CO partial pressure with the constant H_2 partial pressure of 3.5 MPa. Therefore, a first order dependence of methanol formation rate on CO partial pressure was obtained when the ratio of CO to H_2 was always lower than the stoichiometric ratio of 1/2.

Figure 7 showed that the rate of methanol synthesis first increased when H_2 partial pressure was lower than 2 MPa and then leveled through the stoichiometric $CO/2H_2$ point (CO = 1.5 MPa, H_2 = 3.0 MPa). The results suggested that, the concentration of alkyl formate had already reached to the equilibrium level due to the lower hydrogenolysis rate at the insufficient H_2 partial pressure; the superfluous CO concentration promoted the more rapid arrival of the equilibrium than the hydrogenolysis rate of alkyl formate during the reaction process. The rate of total reaction was thus experimentally determined by H_2 partial pressure. We could conclude that when the standard syngas (CO/H_2 = 1/2) was used, the rate of total reaction was not relevant to the H_2 concentration. The observed change tendencies of concentrations of MeF and EtF were in logical accordance with the formation of methanol and the increase of H_2 partial pressure.

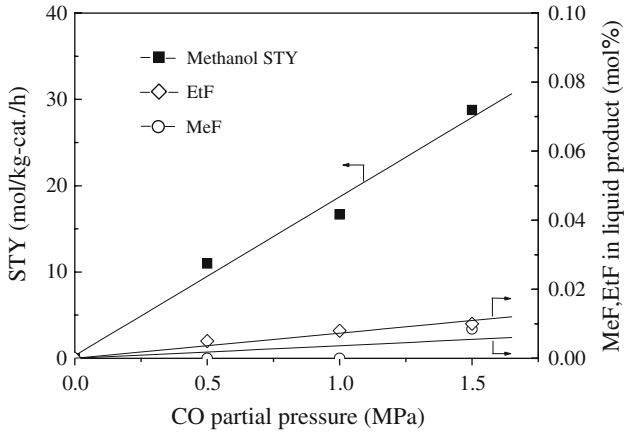

Fig. 6 Methanol synthesis rate, concentrations of MeF and EtF in liquid at different CO partial pressure (H_2 partial pressure = 3.5 MPa). Reaction conditions: 160 °C, 90 mL/min, 10 mmol HCOONa, 2 g Cu/MgO–Na catalyst, 30 ml ethanol, 5 h

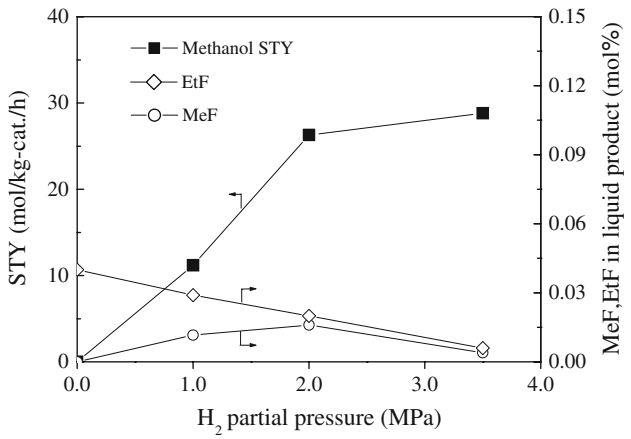

Fig. 7 Methanol synthesis rate, concentrations of MeF and EtF in liquid at different H_2 partial pressure (CO partial pressure = 1.5 MPa). Reaction conditions: 160 °C, 90 mL/min, 10 mmol HCOONa, 2 g Cu/MgO–Na catalyst, 30 mL ethanol, 5 h

Based on these results, we suggested that the carbonylation step (Eq. 1) be controlled by equilibrium and be the limiting-rate step. The conclusion was different from Liu's study where the limiting-rate step was considered as the hydrogenolysis reaction on CH_3OK–Cu/Cr catalysts [19]. Whereas, the hydrogenolysis step (Eq. 2) over the used Cu/MgO–Na was rapid even under the present milder conditions.

4 Conclusions

The co-precipitated copper magnesium catalyst at pH value of 10 was found to highly catalytically active for methanol synthesis in ethanol solvent at around 160 °C and 5.0 MPa. The syngas conversion reached up to 80% and the selectivity to methanol was higher than 90%; only significant products were methanol and alkyl formates.

The combination of formate species and copper catalyst was found to be the novel active site differently from the well known copper-alkali methoxide system. Additionally, the carbonylation reaction of alcohol restrained by the reaction equilibrium was experimentally the limiting-rate step. Although the proposed hybrid copper-formate system has shown no enough tolerance abilities to CO_2 and H_2O yet which can cause the consumption of HCOONa, these obtained results will make the further work on improving the stability of the present catalyst system in promising progress.

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