Low temperature methanol synthesis from CO hydrogenation over Cu-based catalyst

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Abstract: A novel liquid phase methanol synthesis process from syngas ($CO/H_2 = 1/2$) was realized by combined catalyst system of Cu-based catalyst with alkali formate, high CO conversion (>80%) as well as methanol selectivity (~90%) were achieved with a mass space velocity of 2700 L/h.kg-cat. at 433 K and 5.0 MPa via ethyl formate in slurry phase. This study investigated the influences of co-precipitation PH value of copper magnesium catalyst, types of alkali compounds as carbonylation promoters and impregnation agents, alcohol solvent on the reaction performances. It was also found that formate exhibited synergic function with alkali impregnated solid copper catalyst rather than other anion precursors, such as carbonate, bicarbonate and hydroxide, which contributed to the high catalytic performance in the presence of alcohol solvent. The proposed catalyst system was more highly active than industrial G99 and MK-121 catalysts under the mild conditions.

Keywords: methanol synthesis, CO hydrogenation, formate, slurry phase, low temperature

1.Introduction

The production of methanol has been commercialized for many decades. At present, over 75% of the world's production has been made through the gas phase process. The process using typical $Cu/Zn/Al_2O_3$ or, less preferably, $Cu/Zn/Cr_2O_3$ with natural gas-, coal- derived syngas has been operating under severe conditions (220 - 300 ℃, 5 - 8 MPa) [1, 2]. However, the one-pass conversion of syngas to methanol in current commercial plants is limited at a lower level of about 25% by exothermic equilibrium.

An alternative method of methanol synthesis from pure CO and H_2 has been widely studied, where carbonylation of methanol and hydrogenation of the formed methyl formate are considered as the two main steps of the reactions, as described by following equations (1)-(3). The reaction is carried out in a slurry reactor with consequent good heat transfer rates and with a rate of reaction at low catalyst loadings comparable with that in the commercial synthesis. Ohyama, Aika and Wender realized this synthesis in liquid phase using a mixed catalyst comprised of alkali metal alkoxide and copper-based or nickel-based compounds under the mild conditions of 373-453 K and 5.0-6.5 MPa [3-6]. However, the used alkoxide catalysts facilely reacted with water or CO_2 to form alkali formates (e.g. HCOONa) and alkali methyl carbonates (e.g. $NaOCOOCH_3$), respectively [7]. One of the present authors has claimed that utilization of alcohol solvent remarkably lowered the reaction temperature of methanol synthesis and realized the low temperature methanol synthesis (LTMS) from syngas containing carbon dioxide over Cu/ZnO catalysts [8-10].

$$\mathrm{ROH + CO \rightleftharpoons HCOOR} \tag{1}$$

$$\mathrm{HCOOR + 2H_2 \rightleftharpoons CH_3OH + ROH} \tag{2}$$

$$\text{Net}\quad \mathrm{2H_2{+}CO \rightleftharpoons CH_3OH} \tag{3}$$

In the present work, we propose new hybrid catalytic systems comprised of alkali metal formates and Cu/MgO-Na to realize the LTMS from syngas (CO/H_2) with ethanol as a promoter solvent. The catalysts showed quite high reaction activity and had some potential for being commercialized.

2. Experimental

2.1. Catalyst preparation

Coprecipitation was applied to prepare copper magnesium oxide catalyst. Metal nitrates were used as precursors, and an aqueous solution of Na_2CO_3 was added as precipitation agent. Good reproducibility was attained by controlling the preparation conditions (purity of the chemicals, concentrations, temperature, stirring velocity, pH value, aging time, and washing treatment) carefully [11]. 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 523 K for 2 h before its activity evaluation.

The surface structure of catalyst was indicated by a Hitachi S-5200 Scanning Electron Microscope (SEM). The phases of reduced catalyst with different ratios of Cu to Mg were characterized by X-ray diffraction (XRD) with an RINT 2000 System (Rigaku) diffraction meter using Cu Kα radiation. Patterns were recorded from 15° to 80° (2θ) at 40KV and 20mA.

2.2. Reaction procedures

A flow type semi-batch autoclave reactor with an inner volume of 85 ml was employed in the experiment. The alkali compound (10 mmol) was added to the reactor, and then the reduced catalyst (2.0 g) and high purity alcohol (30 ml) were poured into the reactor without exposure to air. 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 433 K within 20 minutes. The composition of standard feed gas was $H_2/CO/Ar = 64.56/32.4/3.04$. The stirring speed was 1660 rpm. Considering the retention volume, the conversion of syngas ($CO/2H_2$) was calculated by equation (4), as well as the flowrate of outgoing gas. The formation rates (STY (mmol/(g-catalyst. h)) and selectivities of methanol and other liquid components were calculated by using 1-propanol as external standard.

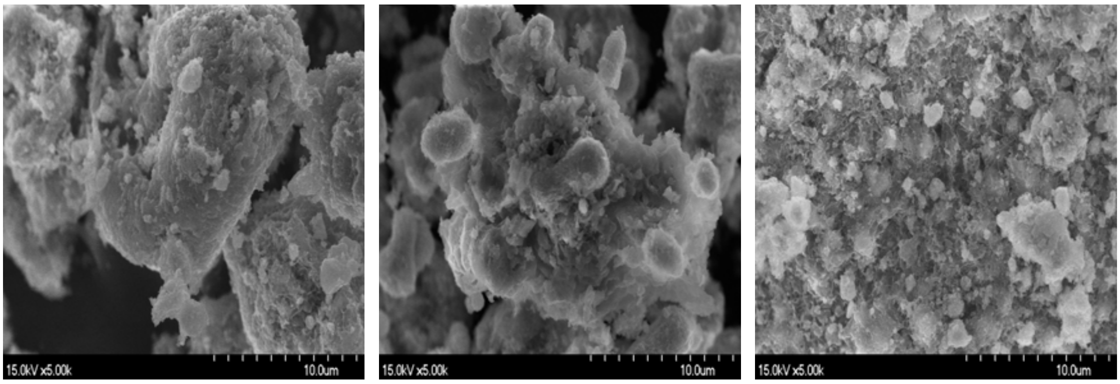
$$\text{Syngas-conv.\%} = (F_{\text{in, syngas}} - F_{\text{out, syngas}}) / F_{\text{in, syngas}} \times 100\% \tag{4}$$

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

3. Results

3.1. Dependence of Cu/MgO-Na performance on PH value of co-precipitation

During the co-precipitation process, PH value has important effects on composition and phase of catalyst, which successively affects the activity and product selectivity of catalyst. Fig.1 was SEM micrographs of different catalysts. With increasing the PH value, particle size of catalyst became smaller; the distribution of particle size was symmetrical. It was concluded that the changes of textural morphology might be attributed to the different precipitation speed of salt components at different PH value. As well known, required PH value for precipitation of Mg^{2+} is higher than that for Cu^{2+}; therefore, amorphous particles or small crystal particles during the precipitation could enter into the initial formed particles to produce the bigger conglomeration [12], so higher precipitation speed at higher PH value might tend to reduce the possibilities of conglomeration. We also saw that a lot of white particles appeared in the visual field (c), which might be the conglomeration of magnesium oxide or magnesium carbonate.



(a) PH=9 (b) PH=10 (c) PH=10.5

Fig.1. SEM micrographs for Cu/MgO-Na catalysts prepared at different PH values

Reaction performances of Cu/MgO-Na catalysts with different PH values for precipitation were investigated in Table 1. The big differences were presented that appropriate PH value should be controlled at about 10 for high activity, while the color of precipitation was blue-dark. At the same reaction conditions, amounts of alkyl formates such as methyl formate and ethyl formate were small in the case of PH = 10, suggesting that the Cu/MgO-Na catalyst had much stronger hydrogenolysis ability. Therefore, the catalyst at PH=10 was used for the following study.

Table 1. The reaction performances of copper catalysts with different PH value[a]

Cu Cat.	Methanol		Amount of byproducts, mmol			
	STY	Sel.%	CO_2	CH_4	Methyl formate	Ethyl formate
PH=9	9.5	81.2	3.6	0.5	12.1	24.2
PH=10	17.4	93.3	2.2	0.7	8.4	2.5
PH=10.5	17.1	84.5	1.8	0.6	25.5	22.5

[a] Reaction conditions: Cu/MgO-Na catalyst (red.) weight, 2.0 g; HCOONa, 10 mmol; flowrate of syngas, 90 ml/min; solvent, ethanol, 30 ml; 433 K, 5 Mpa; reaction time, 24 h.

3.2. Effect of alkali catalysts on reaction performance of Cu/MgO-Na

The results in Table 2 showed the promotion performances of alkali catalysts for methanol synthesis on copper magnesium catalyst using ethanol solvent at 433 K and 5.0 MPa. Differently from other carbonylation catalysts such as RONa, function of HCOONa on carbonylation of ethanol without copper catalyst was much lower, CO conversion was only 6.11%. Under the reaction conditions, methanol synthesis reaction could proceed on Cu/MgO-Na catalyst, syngas conversion reached to 15.5% with a lower selectivity to methanol. After combining HCOONa with Cu/MgO-Na catalyst, CO conversion was remarkably increased to 81%, thus addition of HCOONa enhanced the reaction activity to a larger extent and decreased the possibilities of bypass reactions. The evidence simultaneously convinced that there existed synergic function between HCOONa and

Cu/MgO-Na catalyst, which contributed to higher overall reaction rate than that of either separate reaction. The synergic function was also reported between alkali methoxide and copper chromite by Liu et al [13], Onsager [14].

Table 2. Reaction performance of alkali promoted copper magnesium catalyst system for LTMS[a]

Alkali	Copper catalyst	Conversion (%)[b]	STY (mol/Kg.h)	Selectivity (%) Methanol	$CO2$	CH_4	Alkyl formate	Other C2+
HCOONa	---	6.1	0.0	0.0	15.1	0.0	84.8	0.0
---	Cu/MgO-Na	15.5	5.1	54.7	0.6	0.0	22.2	22.5
HCOONa	Cu/MgO-Na	81.1	17.4	93.3	0.2	0.1	2.1	4.3
$Ba(HCOO)_2$	Cu/MgO-Na	44.1	12.6	90.5	0.2	0.1	2.3	6.9
Na_2CO_3	Cu/MgO-Na	36.9	10.3	93.0	0.2	0.1	3.0	4.7
NaOH	Cu/MgO-Na	51.2	16.2	92.9	0.3	0.1	1.9	4.8
$NaHCO_3$	Cu/MgO-Na	19.6	4.5	72.3	2.9	0.1	10.6	14.1

[a] Reaction conditions: Cu/MgO-Na catalyst (red.) weight, 2.0 g; HCOONa, 10 mmol; flowrate of syngas, 90 ml/min; solvent, ethanol, 30 ml; 433 K, 5 Mpa; reaction time, 24 h.

[b] The data are the syngas conversions at 5th reaction hour.

To clarify the role of HCOONa, it was necessary to investigate its consumption and conversion after the reaction. Solid sample in the final liquid phase after reaction was qualitatively analyzed with FTIR, as shown in Fig.2. Assignments of the bands were made by analogy with the spectra of known compounds and by comparison with published reports. The bands at 1600, 1450 and 1360 cm^{-1} before the reaction were detected. The bands at 1600 cm^{-1} and 1360 cm^{-1} were the antisymmetric and symmetric stretching vibrations of carbon-oxygen bonds, respectively; while the band at 1450 cm^{-1} was the label bands of CO_3^{2-} species. So we concluded that, besides the added HCOONa, some part of Na_2CO_3 in the solid Cu-based catalyst was dissolved into ethanol solvent under high pressure synthesis gas. After reaction, the three bands remained; several new bands at 1420, 1380 and 1300 cm^{-1} were also observed. These could be attributed to HCO_3^-[15, 16]. Obviously, the relative peak intensity of CO_3^{2-} weakened compared to that of $HCOO^-$. These results demonstrated that CO_3^{2-} would not be the intermediate species; $HCOO^-$ was possibly the intermediate species, since the employed HCOONa may first offer $HCOO^-$ species to form the intermediate ethyl formate [11] and then have been regenerated during the catalytic circulation. The loss of CO_3^{2-} and the appearance of HCO_3^- were probably related to catalytic process, which will be certified by further study.

In addition, $Ba(HCOO)_2$ and other alkali precursors were chosen as the carbonylation promoters, the corresponding reaction performances were shown in Table 2. Compared with HCOONa, the $Ba(HCOO)_2$ as Group II A alkali formate gave lower reaction activity. It was concluded that the balanced effect between dissociation activity and ion radius of alkali group in alkali formates affected the synergic function between formate and copper magnesium catalyst.

We also found that Na_2CO_3, NaOH and $NaHCO_3$ exerted the promotion effects on the activation of Cu/MgO-Na catalyst, which increased the possibility of use of other alkali promoter. Among them, NaOH and Na_2CO_3 promoted Cu/MgO-Na catalyst systems exhibited the activities to some extent and high methanol selectivities. $NaHCO_3$ had a little promotion effect accompanied with more selectable to alkyl formates and other by-products. According to the applications of these alkali compounds, formate coordinated with the employed Cu/MgO-Na at the largest benefit, showing that the complex of formate with Cu/MgO-Na played an important role in the catalytic procedures.

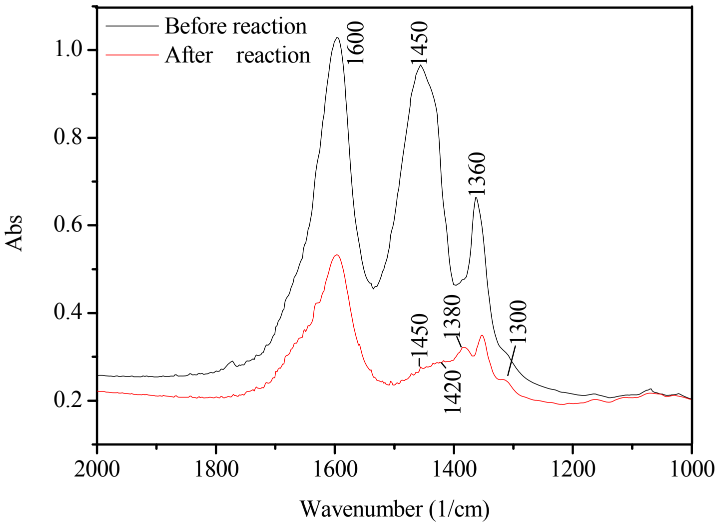


Fig.2. FT-IR spectra for solid components in liquid phase before reaction and after reaction

3.3. Effect of different alkali precursors as impregnation agents on reaction performance

To investigate whether different anion precursors will affect the ester hydrogenolysis of sodium impregnated copper magnesium catalyst, Table 3 compared the reaction performance of the standard Na_2CO_3 case with those of HCOONa and NaOH as impregnation agents in the same Cu/MgO precursor. In all cases, sodium contents were same. The latter two were calcinated in the N_2 ambience and at the same temperature of 623 K to prevent their possible reactions in air. The data showed that, HCOONa impregnation exhibited the activity to a little lower extent which gave no higher selectivity to methyl formate; NaOH impregnation had quite low activity, and the selectivities to methyl formate and ethyl formate were zero. This could be ascribed to highly selectable by-pass reactions to produce methyl formate and dimethyl carbonate. The series of results indicated interestingly that alkali dopant promoted the process more efficiently in the form of carbonate. An adducible finding by Campbell proposed that Cs combined with carbonate played a role of O mediator in the water - gas shift reaction over Cu (110) [17].

X-ray powder diffraction traces of these catalysts showed well defined crystalline patterns of Cu metal in the reduced state, as were compared in Fig.3 (a)-(d). In all cases, the peaks of metallic Cu appeared ($2\theta = 43.4°$, $50.5°$ and $74.2°$). Differently, the trace of Cu/MgO-Na_2CO_3 appeared a mixing carbonate of $Na_2Mg(CO_3)_2$ at a smaller diffraction angle than those of Cu/MgO-HCOONa and Cu/MgO-NaOH, donating the increase of crystal face distance (d). This indicated that anion precursors determined the chemical interaction between the alkali and the copper magnesium surface, which was assumed to affect the activity of alkali impregnated copper magnesium catalyst.

Table 3. Reaction performances of alkali impregnated copper magnesium catalysts for the LTMS in slurry phase in the presence of sodium formate[a]

Catalyst	Conversion	STY	Selectivity, C (mol%)					
	(%)[b]	(mmol/g.h)	Methanol	MeF	EtF	CO_2	CH_4	Other C2+
Cu/MgO	7.2	1.6	57.5	0.0	1.2	2.7	0.0	38.6
Cu/MgO-HCOONa	52.5	12.9	91.7	1.3	0.3	0.3	0.1	6.3
Cu/MgO-Na_2CO3	80.9	17.4	93.3	1.9	0.3	0.2	0.1	4.2
Cu/MgO-NaOH	31.7	8.5	89.9	0.0	0.0	0.8	0.0	9.3

[a] Reaction conditions: Cu/MgO-Na catalyst (red.) weight, 2.0 g; HCOONa, 10 mmol; flowrate of syngas, 90 ml/min; solvent, ethanol, 30 ml; 433 K, 5 Mpa; reaction time, 24 h.

[b] The data are the syngas conversions at 5th reaction hour.

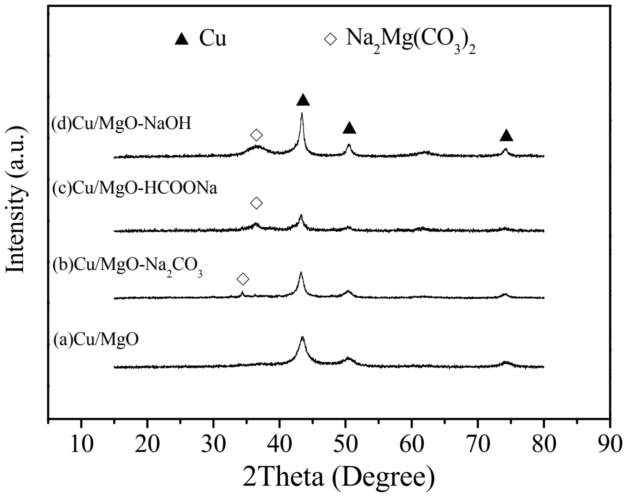


Fig. 3. XRD patterns for various alkali impregnated copper magnesium catalysts after reduction

3.4. Effect of solvent type on the reaction performances

It has been reported that methanol can not be synthesized at the temperature lower than 473K without alcohol solvent by N. Tsubaki [8]. In this study, several different types of alcohols were utilized as solvent to investigate the effect of molecule structure of alcohols on reaction performance of HCOONa/Cu-based catalyst; reaction performances were shown in Fig.4. It was seen that ethanol exhibited the highest rate of methanol synthesis; 2-propanol exhibited the lowest one. The activity sequence of the 1-alcohols (methanol, ethanol, 1-propanol and heptyl alcohol) as solvents were not in accordance with the rate sequence of different 1-alcohols in the esterification [18]. These results revealed that the esterification of alcohol was not the sole influencing factor in the catalytic system; spatial obstacle influence might play a role in the reaction. It was previously reported by N. Tsubaki that different alcohol types affected the formation of HCOOR by both the electronic effect and spatial effect [8, 19]. The spatial effect of alcohol solvent was proven in two cases of 2-propanol and benzyl alcohol, in which 2-propyl and benzyl have bigger spatial obstacle than the other 1-alcohols. Additionally, the conjugated electrons in the benzyl group assisted the formation of benzyl formate, leading to a higher activity than 2- propanol. Therefore, it was evident that ethanol owing higher electron density of oxygen and smaller spatial obstacle of ethyl group was easy to be esterified into alkyl ester.

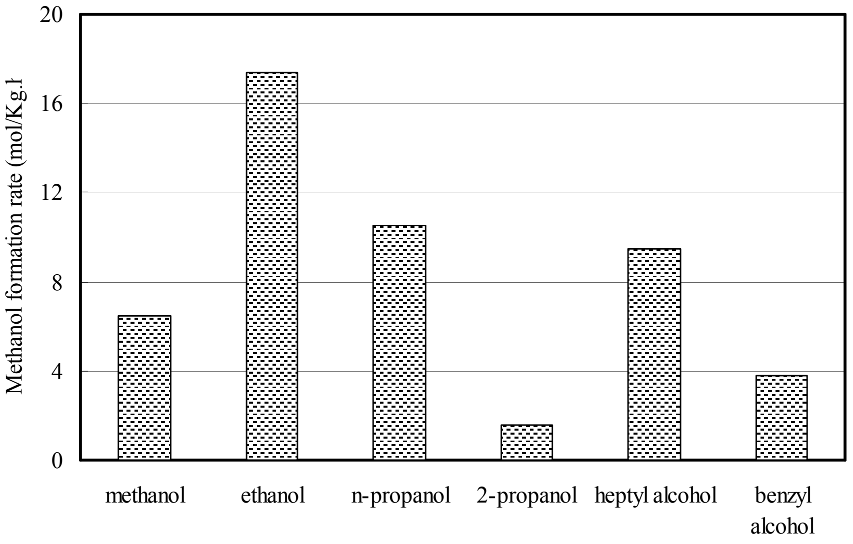


Fig. 4. Methanol formation rate of alkali formate promoted Cu/MgO-Na catalyst system in different alcohol solvents

3.5. Activity comparison for present Cu/MgO-Na catalyst and industrial catalysts

Fig. 5 compared the methanol formation rate of the proposed Cu/MgO-Na with those of several typical industrial catalysts G99 (Cu/Cr/Mn/Ba) and MK-121 (Cu/Zn/Al) for methanol synthesis at the present reaction conditions in the presence of HCOONa. The sodium impregnated G99-Na and MK-121-Na catalysts were prepared following the same procedures as that for Cu/MgO-Na.

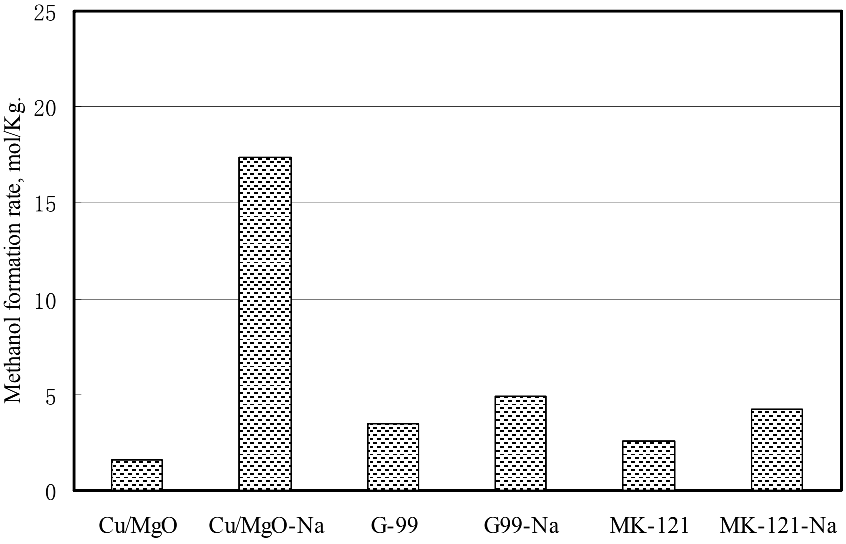


Fig. 5. Comparison of methanol formation rate of present Cu/MgO-Na with industrial copper-based catalysts for methanol synthesis

Cu/MgO-Na catalyst obviously was more active than other catalysts at low operation temperature. It was reported that the space time yield of methanol in the ICI commercial plant was 0.1-1.0 kg/l.h at 523-573 K and 5.0-10.0 MPa [1]. Comparatively, the present catalyst system produced methanol with a space yield of 0.32 kg/l.h in the early period. Under the conditions of 140-180 ℃ and 50 atm, the reaction was carried out in a slurry reactor with consequent good heat transfer rates and with a rate of reaction at low catalyst loadings which was comparable with that in the commercial synthesis. High per pass conversions was obtained, and the only significant products were methanol and alkyl formates together with the alcohol solvent, which could be separated easily.

4. Conclusions

The methanol synthesis process took place at 160℃, yielding > 80% syngas conversion per pass with over 95% selectivity to methanol (including alkyl formates). At the mild conditions, the present catalyst system comprised of HCOONa and Cu/MgO-Na exhibited much higher methanol space time yield than typical commercial catalysts, such as G-99 and MK-121. Among the chosen alkali promoters, formate exerted the coordination with copper catalyst rather than carbonate, bicarbonate and hydroxide. Moreover, a synergic interaction between alkali formate and alkali impregnated copper-magnesium catalyst was found to give the overall rate being higher than that for either reaction. The actual rate of methanol synthesis depended also on the type of alcohol solvent, which was the magnitude of electronic effect and spatial effect.

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