Promotional Effect of Potassium Salt in Low-temperature Formate and Methanol Synthesis from $CO/CO_2/H_2$ on Copper Catalyst

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Alkyl formates can be formed from CO_2-containing syngas with C_1–C_4 alkyl alcohol solvents in the presence of potassium carbonate, which changed to potassium formate as catalyst. The formates can be in situ hydrogenolysized further to produce methanol effectively over manganese oxide or magnesia-supported copper catalysts. These homogeneous and heterogeneous catalysts constitute a novel system for methanol synthesis from $CO/CO_2/H_2$ even at 443 K.

Methanol economy receives increasing attention as a reasonable and practical alternative after oil and natural gas.[1] The commercial methanol synthesis from synthesis gas uses $Cu/ZnO/Al_2O_3$ catalysts under conditions of 523–573 K and 50–100 bar. The one-pass conversion of this exothermal reaction at such high temperatures is 15–25% due to the limitation of thermodynamics. This inevitably causes higher energy consumption by recycling the unreacted gas.

Without thermodynamic limitation, methanol synthesis at low temperature has been extensively studied. One typical previous process was operated in tetrahydrofuran at 373 K using the Ni catalyst derived from NaH/tertiary-amyl alcohol/$Ni(OAc)_2$.[2] However, subsequent experiments demonstrated that the basic catalyst was too sensitive to even low concentration of CO_2,[3] which means impossible for industrial application where feedstock gas from methane reformer or coal gasifier generally contains trace acidic CO_2 in addition to CO and H_2. Another low-temperature process was via a two-step pathway: methanol carbonylation to methyl formate and successive hydrogenolysis of methyl formate to methanol.[4] Alkali methoxide/nickel compound[5] or alkali methoxide/copper compound[6] catalysts were developed for this process. However, the catalysts still encountered deactivation by the reaction between alkoxides with trace amounts of CO_2 and H_2O in feedstock gas.[7]

The present authors reported a new low-temperature process for methanol synthesis where catalytically active alcoholic solvents were employed in addition to solid Cu catalysts.[8] Both CO_2 and H_2O participated the reaction, and the reaction exhibited stable conversion of $CO/CO_2/H_2$ at 423–473 K. The rate-determining step for this methanol synthesis reaction was the formation of alkyl formate. To increase the rate of the total reaction at low temperature, we report in this letter the addition effect of potassium salt to the catalytic system mentioned above, acting as new catalyst for the first half part and synthesizing formate in homogeneous phase, faster than in the solid Cu catalyst surface.[8] Alkyl formates were firstly formed from $CO/CO_2/H_2$ in C_1–C_4 alkyl alcohol solvents in the presence of potassium carbonate. And then the obtained formates were further hydrogenolysized in situ to produce methanol effectively over tailor-made copper metal catalyst.

Table 1. Ethyl formate formation from $CO/CO_2/H_2$ in the presence of alkali metal salts (0.25 mmol salt)

Alkali metal salt	Li_2CO_3	Na_2CO_3	Cs_2CO_3	K_2CO_3	$KHCO_3$	HCOOK
Yield of Ethyl formate/%	0.26	1.48	10.6	4.10	3.1	2.94

Table 1 shows the results of the formation of ethyl formate from $CO/CO_2/H_2$ in the presence of various alkali salts with ethanol as solvent.[9] It is clear that ethyl formate was formed in the presence of IA group alkali carbonates, and Cs_2CO_3 showed the best activity; for different potassium salts, potassium carbonate (K_2CO_3) exhibited the highest activity.

In the presence of K_2CO_3, the corresponding alkyl formates were produced from $CO/CO_2/H_2$ in C_1–C_4 alkyl alcohol solvents as shown in Figure 1. Among them, methanol showed the highest yield to the formation of methyl formate. As K_2CO_3 amount increased, the yield of ethyl formate increased and reached almost equilibrium state as in Figure 2. It should be noted that products other than the alkyl formates were not observed. The total carbon amount ($CO + CO_2$) in the reactor was 32.20 mmol, and the converted carbon at 4% yield was 1.29 mmol, rather larger than the amount of K_2CO_3 (0.25 mmol, Table 1). So K_2CO_3 including other species should be catalytic.

Figure 3 shows the ^{13}C NMR spectra of $CO/CO_2/H_2$ conversion in methanol solvent in the presence of K_2CO_3.[10] By comparison with standard spectra, $KH\underline{C}O_3$ (δ 161 ppm) and $H\underline{C}OOK$ (δ 170 ppm) were found besides solvent $\underline{C}H_3OH$ (δ

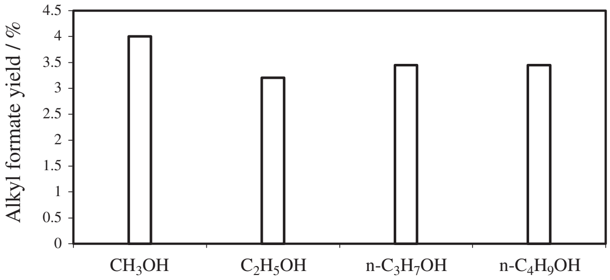

Figure 1. Alkyl formate formation from $CO/CO_2/H_2$ and alkyl alcohol solvents in the presence of K_2CO_3 (0.025 g).

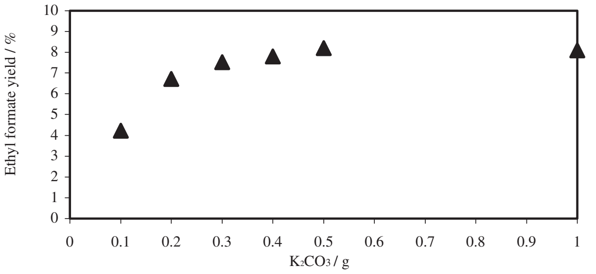

Figure 2. Effect of K_2CO_3 amount on ethyl formate formation from $CO/CO_2/H_2$.

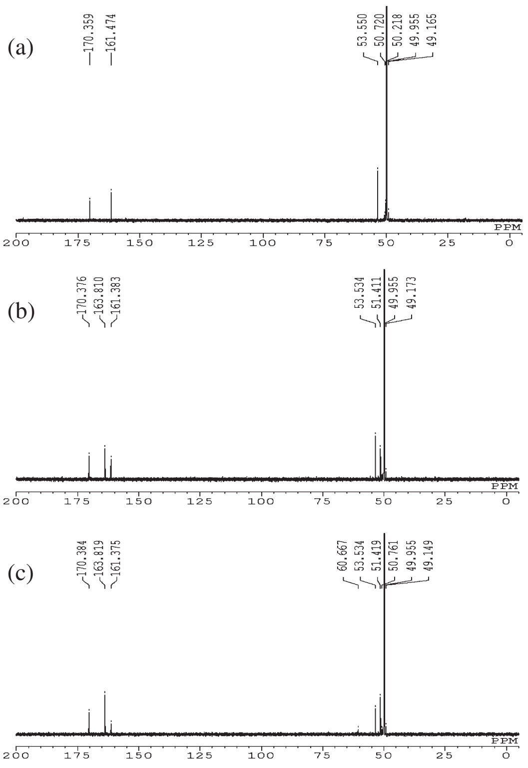

Figure 3. ^{13}C NMR spectra for $CO/CO_2/H_2$ conversion in methanol solvent in the presence of K_2CO_3. (a) before reaction (b) during reaction (c) after reaction.

50 ppm) before the reaction (Figure 3a). During the reaction, the spectra of $KH\underline{C}O_3$, $H\underline{C}OOK$, $H\underline{C}OO\underline{C}H_3$ (δ 51 ppm, δ 163 ppm), and $\underline{C}H_3OH$ appeared (Figure 3b). Similarly, these four species were observed after the reaction (Figure 3c). These findings suggested that HCOOK was an intermediate for the formation of methyl formate.

Table 2 shows the results of methanol synthesis from $CO/CO_2/H_2$ in the ethanol-slurry batch reactor using K_2CO_3 and metallic copper catalyst. In the presence of K_2CO_3 and Cu/MnO, the conversion of total carbon reached 79.3%, and the selectivity of methanol was 98.4%. By increasing the amount of Cu/MnO, the total carbon conversion[11] rose up to 90.2%. Cu/MnO alone showed very lower activity to the conversion of total carbon while the selectivity of methanol was 100%, proving that the catalytic role of K_2CO_3 is important here even considering the methanol contribution from the route of solid catalyst system only.[8] In addition, the combination of HCOOK and Cu/MgO also showed excellent activity from $CO/CO_2/H_2$ at 443 K. Ethyl acetate was almost sole by-product. It was originated from dehydrogenation of ethanol solvent on the surface of copper metal. Ethanol firstly dehydrogenated to form aldehyde followed by reacting with another molecule of ethanol to form hemiacetal. The hemiacetal further dehydrogenated to produce ethyl acetate.[12]

Table 2. Methanol synthesis from $CO/CO_2/H_2$ in the presence of potassium salts and copper metal[13]

Catalyst	Total C conv./%	$HCOOC_2H_5$ sel./%	CH_3OH sel./%	$CH_3COOC_2H_5$ /mmol
K_2CO_3 0.2 g + Cu/MnO 2 g	79.3	1.6	98.4	2.6
K_2CO_3 0.2 g + Cu/MnO 4 g	90.2	0.9	99.1	5.9
K_2CO_3 0 g + Cu/MnO 2 g	37.5	0	100	1.0
HCOOK 0.2 g + Cu/MgO 2 g	86.7	0.6	99.4	0.2

The present studies demonstrated that K_2CO_3 in alcohol solvent combining with copper metal catalytically promoted the conversion of $CO/CO_2/H_2$ to methanol in a single reactor, providing a new route for methanol synthesis at low temperature.

References and Notes

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9 Activity evaluation was performed in a batch reactor (internal volume: 85 mL). $CO/CO_2/H_2/Ar = 31.9/5.08/60.1/2.94$. Alcohol solvent 10 mL, initial gas pressure 3.0 MPa, temperature 443 K, stirring speed 1200 rpm, time 2 h. Reactant gas was analyzed on a GL Science GC320 (TCD) with a 2 m A.C. column. Liquid products were analyzed on a Shimadzu GC-8A (FID) with a column of 2 m Propark N plus 1 m Gasukupak 54 linked with a methanator, using 1-propanol as internal standard.
10 NMR analysis was carried at 213 K on a JEOL JNM-A400 ALPHA FT NMR system equipped with a JEOL superconducting magnet 400 MHz.
11 Assuming a is the CO percentage and b is the CO_2 percentage in the feed gas, total carbon conversion = CO conversion $\times a/(a+b)$ + CO_2 conversion $\times b/(a+b)$.
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13 Cu/MnO (1:1) and Cu/MgO (1:1) catalysts were prepared by coprecipitation method from nitrates with sodium carbonate as precipitant. The obtained precipitates were dried at 393 K for 6 h, followed by calcination in air at 623 K for 1 h and then crushed into 20–40 mesh, reduced in a 5% H_2 flow at 623 K for 6 h and passivated by 1% O_2. BET surface areas were 119 and 139 m^2/g, respectively. The passivated catalyst pellets were crushed in alcohol solvent just before loaded into the reactor with alcohol solvent.