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A novel low-temperature methanol synthesis method from $CO/H_2/CO_2$ 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 $CO/H_2/CO_2$ 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_2-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_2 were involved in the recycling of potassium formate.

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 exothermal 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_2 at 373–393 K using a NaH/tertiary amyl alcohol/$Ni(OAc)_2$ 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_2 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_2 in addition to CO and H_2. 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_2 and H_2O participated and were recycled in the synthesis at 423–443 K.

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

$$CO + CH_3OH \rightarrow HCOOCH_3$$

$$HCOOCH_3 + 2H_2 \rightarrow 2CH_3OH$$

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_2 or H_2O, the following undesired reactions occur and bring down the catalysts [10]:

$$CH_3ONa + CO_2 \rightarrow CH_3OCOONa$$

$$CH_3ONa + H_2O \rightarrow CH_3OH + NaOH$$

$$NaOH + CO \rightarrow HCOONa$$

$$CH_3ONa + HCOOCH_3 \rightarrow HCOONa + CH_3OCH_3$$

But the catalytic system might be tolerant to a higher content of CO_2 and H_2O if the rate of hydrogenation of $HCOO^-$ to CH_3O^- 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 $CO/H_2/CO_2$ 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_2 flow at 623 K for 6 h and passivated by 1% O_2. 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 $Pd(NH_3)_2(NO_2)_2$ aqueous solution and dried at 393 K for 12 h. Then it was heated at 673 K for 6 h in N_2 atmosphere, reduced in 5% H_2 for 6 h and passivated by 1% O_2.

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: $CO/H_2/CO_2/Ar = 31.34/63.69/1.99/2.98$, 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:

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

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

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

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

The phase of the catalysts was analyzed on a Rigaku D/MAX-2200PC X-ray diffractometer with Cu Kα 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_2 physioadsorption 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_2-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_2 (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_2 (30 mL/min) for 1 h and purged by He (30 mL/min) at 363 K for 1 h. Then N_2O was pulse injected and the effluents N_2O and N_2 were synchronously analyzed on a GC-950(TCD) until the reaction of N_2O on the Cu surface finished. Cu dispersion and surface areas were calculated based on the consumed N_2O.

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

Cu surface area (m^2/g) = $4\pi r^2 \times$ 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 $CO/H_2/CO_2$ 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_2 was negative, suggesting that CO_2 was produced accompanying the synthesis reaction. Because of the existence of trace amount of water in ethanol or by-product water, the CO_2 formation could be attributable to water gas shift reaction (1) even at lower temperature condition.

$$H_2O + CO \rightarrow CO_2 + H_2 \tag{1}$$

In the presence of HCOOK only as the catalyst, CO showed very low reaction while CO_2 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:

$$HCOOK + C_2H_5OH \rightarrow HCOOC_2H_5 + KOH \tag{2}$$

$$CO + KOH \rightarrow HCOOK \tag{3}$$

$$CO_2 + KOH \rightarrow KHCO_3 \tag{4}$$

Reaction (3) happened at a low extent while CO_2 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 $CO/H_2/CO_2$ 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_2 was similarly formed in this case. As discussed later in the reaction mechanism, HCOOK regeneration from CO_2-related $KHCO_3$ hydrogenation resulted in water formation and water might accelerate CO_2 formation by reaction (1) on Cu/MgO catalyst.