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RESEARCH NOTE

A New Method of Low-Temperature Methanol Synthesis

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A novel reaction system has been developed to synthesize methanol from carbon monoxide and hydrogen containing carbon dioxide as well as water by copper-based catalysts at low temperature and low pressure, compared to the present industrial process. This may be a new method for commercial methanol production. Carbon dioxide and water, which usually act as poisons to alkali metal methoxide catalyst in the low-temperature methanol synthesis reaction, play a promotional role in this new route. Accompanying alcohol, as a "catalytic liquid medium," with the aid of copper-based solid catalyst, altered the reaction path to a low-temperature direction. © 2001 Academic Press

INTRODUCTION

Methanol is a basic chemical, a kind of transportation fuel and energetic material for fuel cells, being produced at 30–40 million tons per year around the world, from carbon monoxide and hydrogen (syngas) where several percent of carbon dioxide is included. The conventional method in methanol production plants uses copper–zinc-based oxide catalyst developed by ICI Co. Ltd. under extreme reaction conditions, 523–573 K and 50–100 bar, even if the methanol synthesis reaction from CO_2-containing syngas is extremely exothermic. In the commercial process, one-pass conversion of the reactant gas is limited to 15–25% due to the limitation of thermodynamics and, in some cases, to avoid the accumulation of a large amount of reaction heat (1, 2). Low one-pass conversion results in a large cost in recycling of the unreacted gas. The efficiency of the industrial methanol process is severely limited by thermodynamics. For example, at 573 K and 50 bar, the theoretic maximum CO conversion is around 20%. As a means to reduce the production costs and to utilize the thermodynamic merit of this reaction, low-temperature synthesis of methanol is challenging and important (3). At 373 K and 10 bar, conversion from thermodynamic calculation is higher than 90%. The BNL method first reported by Brookhaven National Laboratory (USA), using a very strongly basic catalyst (mixture of NaH, alcohol, and acetate), realized this synthesis to some extent at 373–403 K and 10–50 bar. However, trace amounts of carbon dioxide and water in the feed gas deactivate the basic catalyst quickly (4, 5). Here we describe a novel route for low-temperature synthesis of methanol where carbon dioxide and water are utilized as intermediates. This new route can use syngas containing CO_2 and/or H_2O directly from an industrial reformer and can be operated at significantly low temperature and low pressure, such as 423–443 K and 30–50 bar.

Methanol synthesis from pure CO and H_2 via the formation of methyl formate has been widely studied, where carbonylation of methanol and hydrogenation of methyl formate were considered as two main intermediate steps of the reaction (6–8).

$$CO + CH_3OH = HCOOCH_3 \qquad [1]$$

$$HCOOCH_3 + 2H_2 = 2CH_3OH \qquad [2]$$

$$\overline{\qquad\qquad\qquad\qquad\qquad\qquad}$$

$$CO + 2H_2 = CH_3OH. \qquad [3]$$

But in this reaction, where the catalyst for step [1] is homogeneous alkali metal methoxide, CO_2 and H_2O act as poisons to this catalyst and must be completely removed from the syngas. The catalyst for step [2] is often modified copper solid catalyst. The BNL method is an effective route for low-temperature methanol synthesis from syngas and its reaction path is also similar to the steps mentioned above (5). The BNL catalyst is derived from coexisting nickel acetate, *tert*-amyl alcohol, and sodium hydrid. Thus, to maintain the activity of the highly basic BNL catalyst in methanol process, the syngas must be free of CO_2 and H_2O, which leads to high cost, making its commercialization impossible.

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We propose a new reaction route, which is composed of several steps as listed below.

$$CO + H_2O = CO_2 + H_2 \quad [4]$$

$$CO_2 + 1/2H_2 + Cu = HCOOCu \quad [5]$$

$$HCOOCu + ROH = HCOOR + CuOH \quad [6]$$

$$HCOOR + 2H_2 = ROH + CH_3OH \quad [7]$$

$$CuOH + 1/2H_2 = H_2O + Cu \quad [8]$$

$$CO + 2H_2 = CH_3OH. \quad [3]$$

Cu represents the catalytic site of Cu-based catalysts. ROH is the accompanying alcohol which is cycled during the reaction. CO_2 and H_2O are reactants as well as byproducts during the reaction and are also cycled in the reaction.

METHOD

A closed typical batch reactor with an inner volume of 70 ml was employed in the experiment. Solid Cu–Zn–O catalyst was prepared by coprecipitation from copper nitrate and zinc nitrate, using sodium carbonate as precipitant. The molar ratio of copper to zinc was 1. The obtained precipitate was dried at 393 K for 12 h, followed by calcination in air at 623 K for 1 h. The precursor was reduced by flowing 100% H_2 at 523 K for 2 h and then passivated by diluted oxygen (1% O_2 + 99% Ar) at a separate catalyst reduction line. It was then transferred to the reactor. The catalyst here is denoted as Cu/ZnO (B). A commercially available ICI catalyst (ICI 51-2) was also used through the same reduction pretreatment, denoted here as Cu/ZnO (A). To confirm the influence of the catalyst passivation, a tailor-made reactor where *in situ* reduction of the catalyst before ethanol introduction was used to perform the catalyst reduction and reaction, but no difference in reaction behavior was observed. So, using passivated catalyst reduced separately had no influence. The BET surface areas for Cu/ZnO (B) and (A) were 44 and 20 m^2/g, respectively. In some experiments, Cu/Al_2O_3 (Cu, 10 wt%) catalyst was also used with Cu/ZnO (A) in the form of a physical mixture. The weight ratio of these two catalysts in the physical mixture was 1. Cu/Al_2O_3 catalyst was prepared by impregnation of copper nitrate aqueous solution on $\gamma-Al_2O_3$ (Nikki Chem., 140 m^2/g), followed by the same preparation method as that used for Cu/ZnO (B). The BET surface area of the obtained Cu/Al_2O_3 catalyst was 113 m^2/g.

In the experiment, after the catalyst and a magnetic stirrer were placed in the reactor, a desired amount of ethanol was added into the reactor as solvent. All of the catalysts were ground in the ethanol solvent to avoid possible oxidation. The reactor was then closed and the air inside the reactor was purged by the reactant gas. Pressurized mixture gas ($CO/CO_2/H_2 = 30/5/65$) was introduced and then the reaction took place at the desired temperature. The reactor was heated by a band-type heater at the body as well as a hot-stirrer at the bottom. It should be noted that CO_2 was also added into the syngas, similar to the case in ICI process (9, 10). In some cases, water was added to ethanol to investigate the influence of water. The standard reaction conditions were as follows: catalyst weight = 0.20 g; no additive; ethanol = 172 mmol (10 ml at room temperature); initial total pressure = 30 bar. At the standard reaction temperature such as 443 K, the pressure was calculated to be 55 bar, including the vapor pressure of about 10 bar from ethanol (11). The reaction conditions, including catalyst weight and stirring speed, were carefully checked to prevent the occurrence of the diffusion-controlled regime. Conversion was calculated on the basis of all carbon in CO and CO_2.

RESULTS AND DISCUSSION

Methanol synthesis from CO and H_2 is favored thermodynamically at low temperature, indicating the feasibility of this new route. In fact, step [5] should not be difficult, as formate is a well-recognized intermediate of the water–gas shift reaction of step [4], especially in Cu-catalyzed water–gas shift reaction (12–14). Step [6], esterification, can proceed under mild conditions if acidic catalyst exists (15). Step [7] is industrially operated at 453 K and 30 bar on modified Cu–Cr-based catalyst (6). Theoretically, this new route seems not to be very kinetically difficult, if a suitable catalyst is developed. It seems that copper or Cu–Zn–O structure was the main catalytic site for step [4] while a copper-based cluster-like site catalyzed step [7].

We aim to accomplish these reaction steps in one reactor, in the form of a one-pot reaction. In contrast to the previous research, solid catalyst was employed to solve the possible separation problem from products.

The results in Fig. 1 exhibit the necessity of the coexisting alcohol, which showed catalytic function here. In the absence of ethanol, the reaction did not proceed at 423 K in cyclohexane medium. In this experiment, a hybrid catalyst composed of Cu/ZnO (A) and Cu/Al_2O_3 was utilized. In the alcohol-free medium, the reaction route was the same as that of ICI commercial process. The direct hydrogenation could not proceed at a temperature lower than 483 K. But in the presence of ethanol, the activity of catalyst appeared. The conversion of reactant, and the yields of methanol and methyl formate, increased with increasing the amount of ethanol added in the reaction mixture. Interestingly enough, the reaction is quite selective to the final product methanol. It is clear that the existence of ethanol changed the reaction route from (A) to (B), making the low-temperature path possible, as compared in Scheme 1. Accompanying alcohol acted as a catalytic liquid medium

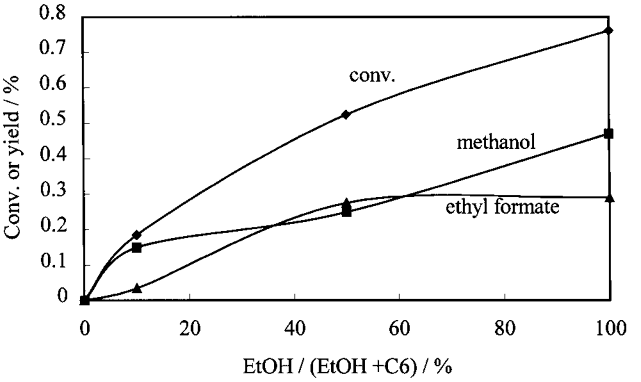


FIG. 1. Effect of coexisting alcohol. Catalyst weight, 0.20 g; total solvent amount, 5 ml; reaction time, 2 h; 423 K; 30 bar; Cu/ZnO (A) + Cu/Al_2O_3 catalyst.

here because it was not consumed if the overall reaction was accomplished.

It is known that Cu–Zn–O catalyst, developed by du Pont and Girdler, is the industrial catalyst for the water–gas shift reaction. For Cu/ZnO (A), its activity was not high; it was lower than that of Cu/ZnO (B). In order to enhance conversion, Cu/Al_2O_3 was also used separately or physically mixed with Cu/ZnO (A). It is interesting that if only Cu/Al_2O_3 was used, only ethyl formate was formed and no alcohol was observed. In the hybrid catalyst system containing both Cu/Al_2O_3 and Cu/ZnO (A), conversion was the highest, but selectivities of ethyl formate and methanol were the same as those of Cu/ZnO (A) only. It seems that Cu/Al_2O_3 catalyzed steps [4]–[6]. But the active site of the catalyst for step [7] was of Cu–Zn–O structure. It is concluded that the main role of the added Cu/Al_2O_3 was to increase the rate of step [4].

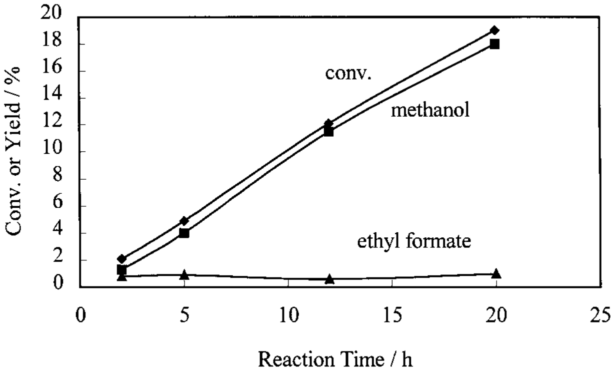
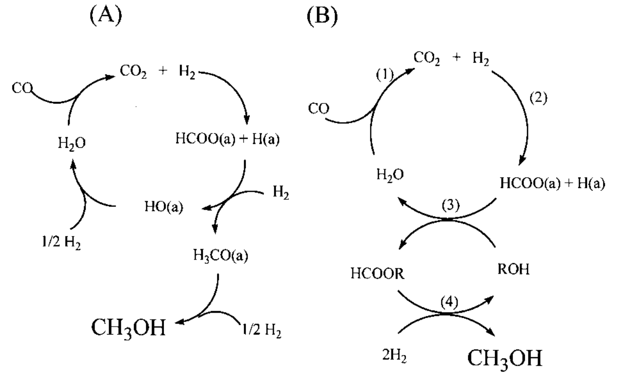


FIG. 2. Effect of reaction time on the conversion and yields. Catalyst weight, 0.20 g; solvent, ethanol, 10 ml; 443 K; 30 bar; Cu/ZnO (B) catalyst.



SCHEME 1. Changing the reaction course from a high-temperature ICI process (A) to a new low-temperature route (B) by addition of alcohol.

In Fig. 2, the effect of reaction time on the conversion or yield at 443 K is shown. With increasing the reaction time, the conversion and yield were linearly enhanced. Conversion increased from 2.1% at 2 h to 19.0% at 20 h. But the yield of ethyl formate was nearly constant until 20 h of reaction time. This indicated that the reaction proceeded via the designed steps where ethyl formate was only the intermediate.

The existence or disappearance of ethyl formate depends on the relative rate of steps [6] and [7]. Due to the existence of a large amount of EtOH, step [7] was not fast enough, resulting in a low level of ethyl formate concentration. This is believed to influence equilibrium limitation.

From Fig. 3, where the relationship between selectivity and conversion is shown for the reaction at 423 K, it is clear that at low conversion, ethyl formate was the main product, while at high conversion, ethyl formate shifted to methanol, proving that ethyl formate was the intermediate for this methanol synthesis route.

Further support for this mechanism was the fact that methanol formed very fast if ethyl formate was used as a reactant with CO, CO_2, and H_2 at the same reaction conditions. This means that the transformation of ethyl formate with H_2 to methanol and ethanol is very fast and the concentration of ethyl formate always exists at the minimum level. Increasing the reactant concentration of step [7] also enhanced the total reaction rate.

In fact, methanol itself could be used here instead of ethanol initially and the pure reaction was independent of

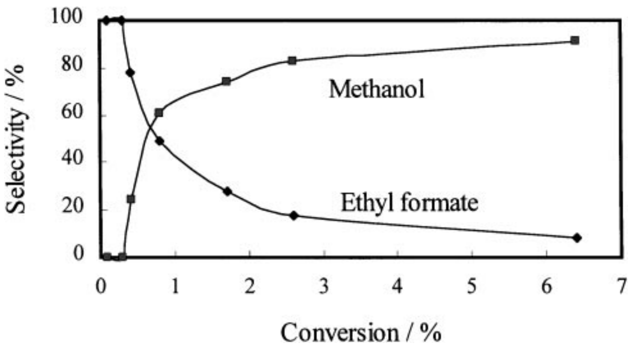


FIG. 3. Relationship between selectivities and conversion. Catalyst weight, 0.20 g; solvent, ethanol, 5 ml; 423 K; 30 bar; Cu/ZnO (A) + Cu/Al_2O_3 catalyst.

the alcohol originally used. We tested the influence of various alcohols where *n*-butanol exhibited the highest activity, about twice that of ethanol. Normal 1-alcohol (straight chain) exhibited higher activity than its branched analogue. On the basis of these results, it is concluded that step [6] is the rate-determining step, slower than step [7]. Varying alcohol type affected step [6] more remarkably because the electron density of oxygen atoms is higher in higher alcohols. As a result, ROH attacked the carbon atom of HCOOCu more efficiently. This is the characteristic feature of the esterification reaction (15). Branched alcohol is not favorable in this reaction due to its steric obstacle in the nucleophilic attack.

If 3.5 mmol of water, the same amount as that of CO_2 in the gas under the standard conditions, was added into ethanol and the same experiment was implemented, similar results were attained, indicating that water did not affect the reaction behavior at these reaction conditions.

Furthermore, the methanol yield also increased linearly with increasing the amount of catalyst, proving high efficiency of the mass transfer of syngas in the reactor.

It is reported that the space yield of methanol of in the ICI commercial plant was 0.4–1.0 kg of MeOH/l · h at 523–573 K and 50–100 bar (16, 17). In our case, where *n*-butanol of 10 ml was used, the space yield was 0.17 kg of MeOH/l · h at 443 K and 30–50 bar. Although the space yield is lower than that in the ICI process now, the temperature and pressure are significantly lower than those of the ICI process.

In conclusion, a novel synthetic route to methanol from syngas has been developed using a Cu-based catalyst. Since the reaction employs a conventional solid catalyst, very mild reaction conditions, and syngas containing CO_2 and H_2O, it has the potential to be industrialized in the future.

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REFERENCES

1. Herman, R. G., Simmons, G. W., and Klier, K., *Stud. Surf. Sci. Catal.* **7**, 475 (1981).
2. Graaf, G. H., Sijtsema, P., Stamhuis, E. J., and Joosten, G., *Chem. Eng. Sci.* **41**, 2883 (1986).
3. Marchionna, M., Lami, M., and Galletti, A., *CHEMTECH* April, 27, (1977).
4. Haggin, J., *Chem. Eng. News* Aug 4, 21 (1986).
5. U.S. Patents 4614749, 4619946, 4623634, 4613623 (1986), 4935395 (1990), assigned to Brookhaven National Laboratory.
6. Palekar, V. M., Jung, H., Tierney, J. W., and Wender, I., *Appl. Catal.*, **102**, 13 (1993).
7. "Kirk-Othmer, Encyclopedia of Chemical Technology," 2nd Ed., Vol. 13, p. 390. Wiley, New York, 1964.
8. Gormley, R. J., Rao, V. H. S., Soong, Y., and Micheli, E., *Appl. Catal.* **87**, 81 (1992).
9. Chinchen, G. C., Denny, P. J., Parker, D. G., Spencer, M. S., and Whan, D. A., *Appl. Catal.* **30**, 333 (1987).
10. Fan, L., Sakaiya, Y., and Fujimoto, K., *Appl. Catal.* **180**, L11 (1999).
11. Perry, F., and Chilton, T., "Chemical Engineers' Handbook," 5th Ed., pp. 3–62. McGraw-Hill, New York, 1975.
12. Vannice, M. A., *in* "Catalysis, Science and Technology" (J. R. Anderson and M. Boudart, Eds.), Vol. 3, Chap. 3. Springer-Verlag, New York, 1982.
13. Fischer, I. A., and Bell, A. T., *J. Catal.* **172**, 222 (1997).
14. Chen, C. S., Cheng, W. H., and Lin, S. S., *Catal. Lett.* **68**, 45 (2000) and references therein.
15. Morrison, R. T., and Boyd, R. N., "Organic Chemistry," Chap. 20. Allyn and Bacon, Boston, MA, 1973.
16. Hermann, R. G., *J. Catal.* **56**, 407 (1979).
17. Chinchen, G. C., Denny, P. J., Jennings, J. R., Spencer, M. S., and Waugh, K. C., *Appl. Catal.* **36**, 1 (1988).