Continuous Low-Temperature Methanol Synthesis from Syngas Using Alcohol Promoters

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Continuous low-temperature methanol synthesis from syngas containing CO_2 on various Cu/ZnO catalysts was investigated by using a semibatch autoclave reactor. Methanol was easily produced at a temperature as low as 443 K and with a pressure of 50 bar with the aid of 2-butanol, which showed a very high efficiency with a one-pass yield of 47.0% and a selectivity of 98.9%. Methanol itself used as alcohol promoter exhibited a higher activity than other 1-alcohols because it has the lowest spatial effect. 2-Alcohols, however, exhibited the highest conversion among the same carbon number because of its well-balanced effects produced by their of electronic and spatial factors. The one-pass conversion was improved by increasing the catalyst weight because no thermodynamic limitations existed at low temperatures. The continuous low-temperature methanol synthesis is a very promising process because completely purified syngas is not necessary.

Introduction

Methanol, which is a fundamental component for fuel cells and fuel for gas-fueled vehicles, is being produced by 30−40 million tons per year around the world from $CO/CO_2/H_2$. It is now commercially produced by an ICI process under high temperature and high pressure (523−573 K and 50−100 bar) using a copper−zinc-based oxide catalyst developed by ICI Co. However, the efficiency of methanol synthesis is severely limited by thermodynamics because methanol synthesis is an extremely exothermic reaction.[1,2] For example, at 573 K and 50 bar, the theoretical maximum of a one-pass CO conversion process is around 20%.[3] Therefore, developing a low-temperature process for methanol synthesis will greatly reduce the production cost by utilizing the intrinsic thermodynamic advantage at low temperature.[4]

Brookhaven National Laboratory (BNL), Upton, NY, realized this synthesis at 373−403 K and 10−50 bar using a very strong base catalyst (mixture of NaH, alcohol, and acetate) and pure syngas ($CO + H_2$). However, a remarkable drawback of this process is that trace amounts of carbon dioxide and water in the feed gas ($CO + H_2$) or reaction system will deactivate the strongly basic catalyst soon,[5,6] which implies a high cost for the complete purification of the syngas from the methane reformer or the gasification plant, as well as for the reactivation process of the deactivated catalyst.

Methanol synthesis from pure CO and H_2 via the formation of methyl formate has been widely studied, where carbonylation of methanol and successive hydrogenation of methyl formate were considered as two main steps of the reaction.[7,8]

$$CO + CH_3OH \overset{RONa}{=} HCOOCH_3 \qquad (1)$$

$$HCOOCH_3 + 2H_2 \overset{\text{solid catalyst}}{=} 2CH_3OH \qquad (2)$$

$$\overline{\hspace{20em}}$$

$$CO + 2H_2 = CH_3OH \qquad (3)$$

Similar to the BNL method, in this process, CO_2 and H_2O act as poisons to the alkoxide catalyst (RONa) and must be completely removed from syngas, making the commercialization of low-temperature methanol synthesis impossible.

The present authors proposed a new method of low-temperature synthesis of methanol from CO_2/H_2 on a Cu-based oxide catalyst using alcohol as a kind of catalytic solvent, by which methanol was produced at 443 K and 30 bar.[9] This new process consisted of three steps: (1) formic acid synthesis from CO_2 and H_2, (2) esterification of formic acid by ethanol to ethyl formate, and (3) hydrogenation of ethyl formate to methanol and ethanol. Considering the fact that the water−gas shift

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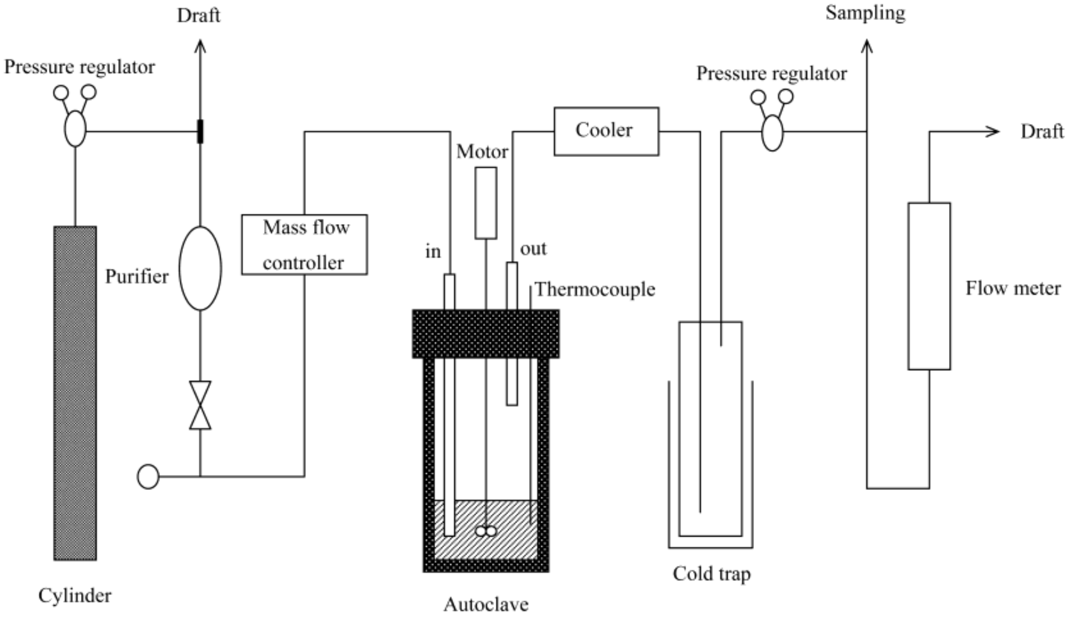

Figure 1. The semibatch continuous apparatus for methanol synthesis reaction.

reaction is easily conducted on a Cu/ZnO catalyst,[10−20] a new route of methanol synthesis from CO/H_2 containing CO_2 is proposed as a more practical way of methanol synthesis. It consists of the following fundamental steps:

$$CO + H_2O = CO_2 + H_2 \tag{4}$$

$$CO_2 + {}^1/_2H_2 + Cu = HCOOCu \tag{5}$$

$$HCOOCu + ROH = HCOOR + CuOH \tag{6}$$

$$HCOOR + 2H_2 = CH_3OH + ROH \tag{7}$$

$$CuOH + {}^1/_2H_2 = H_2O + Cu \tag{8}$$

$$CO + 2H_2 = CH_3OH \tag{3}$$

Because formic acid was not detected in the products, we suggested the reaction path be composed of steps 5 and 6 above. The present authors reported that ethanol solvent lowered the reaction temperature of methanol synthesis from syngas containing carbon dioxide in a closed autoclave.[21] In this study, the influence of chemical composition of the Cu/ZnO catalyst was studied in a batch reactor. The catalytic effects of different alcohols on the synthesis of methanol from $CO/CO_2/H_2$ on the Cu/ZnO catalyst were investigated. Furthermore, the effect of catalyst amount and alcohol volume was investigated for optimizing the reaction condition. A flow-type semibatch reactor was employed, in which a catalyst lifetime change could be observed.

Experimental Section

Catalyst Preparation. The catalyst was prepared by the conventional coprecipitation method. An aqueous solution containing copper, zinc nitrates, and an aqueous solution of sodium carbonate were added simultaneously to water of 300 mL with constant stirring. The molar ratio of Cu/Zn was varied. The precipitation temperature and pH value were maintained at 338 K and 8.3−8.5, respectively. The obtained precipitates were filtrated and washed with distilled water, followed by drying at 383 K for 24 h and calcination in air at 623 K for 1 h. This precursor was then reduced by a flow of 5% hydrogen in nitrogen at 473 K for 13 h and successively passivated by 2% oxygen diluted by argon. The homemade catalyst (Cu/Zn in molar ratio = 1) is denoted as Cu/ZnO (A). The BET surface area for the catalyst used was $60m^2/g$. The Cu specific surface area, determined by N_2O adsorption method, was $30.1m^2/g$.[22]

A commercial ICI catalyst (ICI 51−2) was also used, denoted as Cu/ZnO (B), to study the effect of catalyst weight and amount of alcohol solvent. The Cu/ZnO (B) was prepared using the same reduction pretreatment. The BET surface area for the catalyst used was $20.1m^2/g$.

Low-Temperature Methanol Synthesis. The reaction apparatus was a flow-type semibatch autoclave reactor with an inner volume of 85 mL. It was connected with a high-pressure gas flow controller system upstream and an autoanalysis system for effluent gas at exit. The configuration of the reactor is showed in Figure 1. The 3.0 g (100−200 mesh) of passivated catalyst and 20 mL of alcohol (purity >99.5%) were poured in the reactor. Then the reactor and a downstream cold trap were closed. The tube between the exit of the reactor and the cold trap was cooled at 273 K by flowing cool water to prevent the possible escaping of solvent alcohol from the reactor. After the system was purged with feed gas at room

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temperature, increasing the pressure of reactor to 50 bar, the temperature was enhanced to 443 K in 20 min. The composition of feed gas was $CO/CO_2/H_2/Ar = 32.6:5.2:59.2:3.0$, in which argon was employed as an internal standard. The stirring speed of the reactor was set at 1260 rpm and carefully checked to prevent the occurrence of the diffusion-controlled regime. During the reaction, the effluent gas from the reactor went first through the ice−water-cooled cold trap where liquid products were accumulated and then was introduced to the autoanalysis system with two gas chromatographs. One contained a TCD for CO, Ar, and CO_2 analyses and the other was equipped with an FID with methanator for other possible oxygenates in the effluent gas. The effluent gas was not cycled. The liquid products in the cold trap and those remaining in the reactor were collected together and then analyzed by FID with methanator after the reaction. The presence of all liquid products was confirmed on GC-MS (Shimadzu GCMS 1600).

The reactions to test the activities of the homemade Cu/ZnO catalyst with different Cu/Zn ratios were conducted in a closed batch reactor with an inner volume of 85 mL.

CO, CO_2, and total carbon conversions were calculated as follows:

$$\text{CO conversion} = 100[(\text{CO/Ar in feed} - \text{CO/Ar in effluent})]/(\text{CO/Ar in feed})$$

$$\text{CO}_2\text{ conversion} = 100[(\text{CO}_2\text{/Ar in feed} - \text{CO}_2\text{/Ar in effluent})]/(\text{CO}_2\text{/Ar in feed})$$

$$\text{total carbon conversion} = [(\text{CO conversion})a/(a+b)] + (\text{CO}_2\text{ conversion})[b/(a+b)]$$

(a and b were the contents of CO and CO_2 in the feed gas)

The average yields of liquid products (methanol and formates), P_i yields, were calculated from liquid analysis. They were obtained as follows:

$$P_i\text{ yield} = 100[P_i(\text{C-mol number/total moles of carbon in the feed gas in total time})]$$

It should be noticed that the carbon obtained from the solvent, ROH, was not counted in the calculation above to ensure proper selectivities of the reacted CO and CO_2.

The selectivities of the above liquid products, P_i selectivities, were calculated as follows:

$$P_i\text{ selectivity} = 100(P_i\text{ yield}/\Sigma P_i\text{ yield})$$

Results and Discussion

Catalyst Development with a Batch Reactor. In Figure 2, the reaction activity and its relationship with the chemical composition of Cu/ZnO in a closed reactor were displayed. It is clear that too much Cu or Zn percentage was not favorable to the catalyst activity. Cu/ZnO with the molar ratio of 1 (Cu/ZnO(A)) exhibited the best reaction activity. More interestingly, while the total conversion was lower, the selectivity of ethyl formate was high. With the enhanced conversion, the selectivity of methanol increased, indicating that methanol was the final product and formate was intermediate in this consecutive reaction series.

As compared in Table 1, when the Cu/Zn ratio was high or low, the BET surface area as well as the metallic Cu surface area determined by N_2O was low. As the active site, metallic Cu, was believed to be well dispersed in ZnO lattice: a moderate Cu/Zn ratio is critical to ensure high catalytic activity. We prepared many Cu/ZnO catalysts with various Cu/Zn ratio by different methods, such as using oxalic acid solution in ethanol for coprecipitation besides the Na_2CO_3-contained coprecipitation reported here. It is found that the activity was almost proportional to the metallic copper surface area of the obtained catalyst. All these findings suggested that metallic copper was the active site for this reaction, and it acted via a redox cycle as shown in steps 5−8. To realize a high metallic Cu surface area in ZnO, it is important to enhance the activity. A very strong interaction between Cu and ZnO might make the reduction of Cu difficult, although the dispersion of Cu would be increased. But a weak interaction between Cu and ZnO could not ensure a high dispersion of Cu, leading to a low metallic Cu surface area as well.

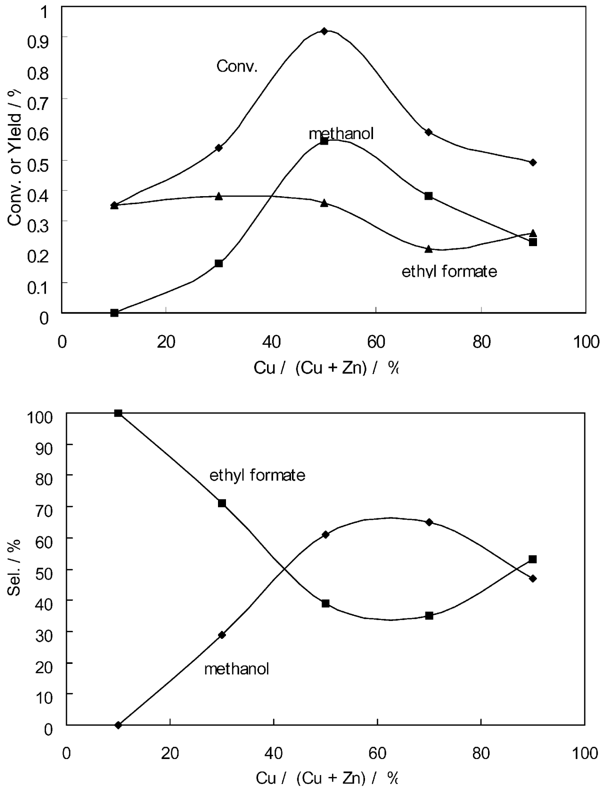

Figure 2. The reaction performances of Cu/ZnO catalysts with different Cu/(Cu + Zn) molar ratio in a batch reactor. Temperature = 443 K, initial pressure = 30 bar, reaction time = 2 h, mass of catalyst = 0.20 g, and volume of ethanol = 10 mL.

Table 1. Cu/ZnO Catalyst Properties with Different Cu/(Cu + Zn) Molar Ratios[a]

Cu/(Cu + Zn) molar ratio	BET surface area (m^2/g)	Cu^0 area by N_2O method (m^2/g)
0.1	38	3.6
0.3	44	12.2
0.5[b]	60	30.1
0.7	48	16.1
0.9	22	1.5

[a] Homemade Cu/ZnO catalysts prepared by coprecipitation method with Na_2CO_3. [b] Cu/ZnO(A)

Continuous Synthesis of Methanol and Reaction/Separation Effect. In Figure 3 is shown the time-on-stream activity change of the reaction during 40 h on Cu/ZnO (A). The analysis on the effluent gas after the trap exhibited only the presence of CO, CO_2, and H_2 existed and that of no other gas. The conversions

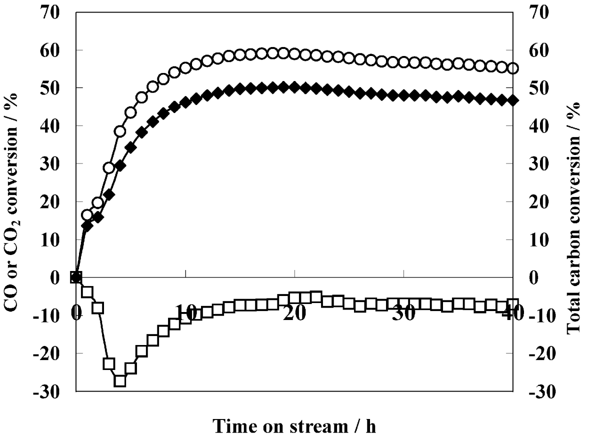

Figure 3. Variations of CO, CO$_2$, and total carbon conversions with time on stream for the continuous methanol synthesis from CO/CO$_2$/H$_2$. Temperature = 443 K, pressure = 50 bar, mass of Cu/ZnO (A) = 3.00 g, volume of 2-butanol = 20 mL, stirring speed = 1260 rpm, feed gas CO/CO$_2$/H$_2$/Ar = 32.59: 5.16:59.21:3.05, flow rate = 20 mL/min; (○) CO%, (□) CO$_2$%, and (◆) total carbon %.

were very low at initial stage due to the dead volume of the reactor and trap filled by the feed gas. The conversions were gradually increased and became steady stage at 12 h from the start. The low-temperature methanol synthesis showed a very high CO conversion at about 60%, while a small amount of CO$_2$ was formed about −8%. The total carbon conversion was about 47%. The negative CO$_2$ conversion meant that a very little part of CO in the feed gas converted to CO$_2$ via the water−gas shift reaction, indicating that the CO/CO$_2$ ratio of the feed gas should be adjusted carefully to optimize the methanol synthesis. Furthermore, at the initial 10 h, the CO$_2$ conversion dropped to a minimum of −29% and then increased again to about −8%. Considering the dilution effect of the initial gas in the dead volume, the real CO$_2$ conversion at the initial stage should be more negative than the apparent one, even if the absolute CO$_2$ concentration was not so high, because the concentration of CO$_2$ in the feed gas was limited.

According to the time-on-stream of the conversions above, CO was converted to CO$_2$ first through the water−gas shift reaction, step 4, and then CO$_2$ converted to methanol through the designed routes, steps 4−8. It should be noted that, if no alcohol was used as solvent, for example, in the case where hexane was used instead as alcohol solvent, no activity was observed. The added alcohol, 2-butanol, allowed a low-temperature methanol synthesis process, via a new reaction path, implying that the accompanying alcohol was a promoter. As the used alcohol containing some water (<0.5 vol %), this process used syngas containing CO$_2$ and H$_2$O, in fact.

It is considered that, at the initial stage, the water−gas shift reaction, step 4, was very quick, while steps 5−7 were slower. Consequently, CO$_2$ became rich in the gas and CO$_2$ conversion exhibited the lowest conversion. After 12 h, the balance between CO$_2$ formation and formate formation was reached. The ratio of the catalytic site number for these two directions might be adjusted during the reaction.

Different Alcohols Used as Solvent. In Table 2, no activity appeared when no solvent or cyclohexane, an inert solvent, was used. Methanol cannot be produced at a low-temperature such as 443 K without the aid of alcohol. The total carbon conversion of vapor phase 2-butanol is lower than that of liquid phase 2-butanol. As exhibited in Table 2 above, in case of a nonalcoholic system, the reaction never proceeded at 443 K in cyclohexane and/or a nonsolvent system. The reaction route, in alcohol-free medium, was the same as that of the ICI commercial process. But 443 K was too low to realize a reaction, leading to the necessity of alcohol solvent, a kind of catalyst. As indicated in Table 2, the reaction rate of the vapor-phase reaction was slower than that of the liquid-phase reaction. It seems that amount of ROH was important to step 6, the rate-determining step.

In Table 3, the effects of various types of alcohols on the continuous low-temperature methanol synthesis were studied where the reaction time was 20 h. Due to the dilution influence of the initial feed gas in the dead volume, the total carbon conversion was the equal to the average conversion of the last 10 h, when conversions were very stable. For Cu/ZnO (A), it is clear that the selectivity of methanol was very high, up to 98−100%, in all types of alcohol, indicating that the hydrogenolysis of HCOOR, step 7, was very fast under reaction conditions. In the reaction of 2-butanol, no 2-butyl formate was detected from the accumulated liquid products in the cold trap. Because of its higher boiling point, it was not easy for 2-butyl formate, the intermediate, to escape from the autoclave while the exit was cooled. The effect of reaction−separation acted very well here. Methyl formate might be formed through the transesterification between HCOOR and the formed methanol or through the same reaction as above, while the methanol itself played the role of the accompanying alcoholic solvent.

In the reaction where methanol was used as solvent, it was indeed true that the weight and mole number of total methanol after the reaction increased correspondingly.

It is observed that methanol, acting as the solvent, exhibited a higher activity than the activities of the other 1-alcohols. This is in accordance with the rate sequence of different 1-alcohols in the esterification reaction,[23] providing the evidence that step 6 was rate-determining. Beause the concentration of the ester, HCOOR, was so low, step 7 was believed to be quicker than step 6.

For the alcohols with the same carbon number but different structure, as shown in the cases of 1-butanol, *iso*-butanol, and 2-butanol in Table 3, 2-butanol exhibited the highest conversion. Different alcohol types affected step 6 by both their electronic and spatial effects. For 1-butanol, the electron density of the oxygen atom in ROH is lower. As a result, ROH attacked the carbon atom of HCOOCu more slowly. However, the spatial obstacle of 1-butanol is the smallest among all butanols, and this is favorable to the nucleophilic attack in the esterification reaction. On the other hand, *iso*-butanol has a high electronic density in its oxygen atom and this should accelerate the reaction. However, its large molecular volume becomes a severe spatial ob-

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Table 2. Methanol Synthesis in Batch Reactor with Various Solvents on Cu/ZnO(A)[a]

solvents	yield of MeOH/%	yield of MF/%	yield of HCOOR/%	total carbon conversion/%	selectivity of MeOH/%	selectivity of MF/%	selectivity of HCOOR/%
none	0	0	0	0	0	0	0
cyclohexane	0	0	0	0	0	0	0
2-butanol[b]	11.3	0	10.2	21.5	52.6	0.0	47.4
2-butanol[c]	8.4	0.1	0.1	8.6	97.7	1.2	1.1

[a] Temperature = 443 K, initial pressure = 30 bar, total reaction time = 2 h, catalyst = 1.00 g; solvent = 20 mL, feed gas $CO/CO_2/H_2/Ar$ = 32.6:5.2:59.2:3.0, stirring speed = 1260 rpm. [b] Liquid phase of 2-butanol. [c] Vapor phase of 2-butanol.

Table 3. Continuous Methanol Synthesis from $CO/CO_2/H_2$ with Various Alcohols on Cu/ZnO (A)[a]

solvents	yield of MeOH[b]/%	yield of MF/%	yield of HCOOR/%	total carbon conversion/%	selectivity of MeOH/%	selectivity of MF/%	selectivity of HCOOR/%
methanol	39.8	0.5	0	40.3	98.7	1.3	0
ethanol	33.0	0	0.5	33.5	98.5	0	1.5
1-propanol	34.5	0.0	0.7	35.2	98.1	0	1.9
1-butanol	34.3	0.1	0	34.4	99.8	0.2	0
2-butanol	46.5	0.2	0.3	47.0	98.9	0.4	0.7
iso-butanol	29.8	0.1	0	29.9	99.6	0.4	0
1-pentanol	34.1	0.1	0.0	34.2	99.7	0.3	0.0
1-hexanol	34.4	0.1	0	34.5	99.7	0.3	0
2-butanol[c]	28.5	0.1	0.5	29.1	98.0	0.4	1.6

[a] Temperature = 443 K, pressure = 50 bar, total reaction time = 20 h, catalyst = 3.00 g, alcohol = 20 mL, feed gas $CO/CO_2/H_2/Ar$ = 32.6:5.2:59.2:3.0, flow rate = 20 mL/min, stirring speed = 1260 rpm. [b] Average total carbon conversion in the last 10 h from on-line gas analysis. [c] Using Cu/ZnO (B).

Table 4. Continuous Methanol Synthesis from $CO/CO_2/H_2$ with Various Catalyst Weights and Amount of 2-Butanol on Cu/ZnO (B)[a]

catalyst/g	2-butanol/mL	yield of MeOH[b]/%	yield of MF/%	yield of HCOOR/%	total carbon conversion/%	selectivity of MeOH/%	selectivity of MF/%	selectivity of HCOOR/%
3.00[c]	20	28.5	0.1	0.5	29.1	98.0	0.4	1.6
6.00[d]	20	44.2	0.1	0.3	44.6	99.1	0.2	0.7
6.00[d]	40	43.1	0	0.2	43.3	99.5	0.0	0.5

[a] Cu/ZnO (B): temperature = 443 K, pressure = 50 bar, reaction time = 20 h, feed gas $CO/CO_2/H_2/Ar$ = 32.6:5.2:59.2:3.0, flow rate = 20 mL/min. [b] Average total carbon conversion in the last 10 h from on-line gas analysis. [c] Stirring speed = 1260 rpm. [d] Stirring speed = 1600 rpm.

stacle in the nucleophilic attack. Therefore, its esterification rate was low. As a balanced effect between electronic and spatial factors, 2-butanol exhibited the highest activity in the rate-determining step 6. As the opposite example, *tert*-butyl alcohol gave the total carbon conversion as low as 21% here.

For Cu/ZnO (B), the total carbon conversion of Cu/ZnO (B) was as low as 29%. The selectivity of Cu/ZnO (B) is nearly the same asthat of Cu/ZnO (A), but the activity was lower due to the lower surface area of the catalyst.

Increasing Catalyst Weight and Solvent Volume. In Table 4, the effects of catalyst weight and amount of solvent were studied using Cu/ZnO (B). Even if the activity of CuZnO (B) was lower than that of Cu/ZnO (A), the total carbon conversion still increased from 29% to 45% while the catalyst weight increased from 3.0 to 6.0 g. The conversion rate of low-temperature methanol synthesis can be improved by increasing the catalyst weight. This indicated that the increased catalyst weight increases the overall rate of reaction. However, in the case of high-temperature methanol synthesis, especially in the case of the gas-phase reaction, the increased catalyst weight cannot improve the conversion of methanol synthesis because of the thermodynamic limitation.

As in Table 4, the catalyst weight effect was studied, clearly indicating that most of our reactions were influenced by rate limitation, instead of equilibrium limitation. Only with the use of enough catalyst (weight) can the reaction reach an equilibrium limitation regime.

For the effects of amount of solvent, the total carbon conversion and selectivity of methanol were nearly the same when solvent amount was doubled. The amount of solvent was not influential on the total carbon conversion and selectivity because the amount of alcohol solvent used in this experiment, such as 20 mL, was enough.

Conclusions

The low-temperature methanol synthesis from $CO/CO_2/H_2$ using 2-butanol as solvent has exhibited very high activity and selectivity for methanol formation at a temperature as low as 443 K and with a pressure of 50 bar. Since the reaction employed a conventional solid catalyst, very mild reaction conditions, and syngas containing CO_2 and H_2O, it might be a promising practical method for methanol synthesis at low temperature. The total carbon conversion increased with the increasing of catalyst weight. The excess amount of solvent had no effect on total carbon conversion of methanol synthesis. The high conversion of methanol synthesis at low-temperature was produced from CO and H_2 containing small amounts of CO_2.

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