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Development of a new low-temperature methanol synthesis process

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Abstract

A new reaction route of methanol synthesis at low temperature from CO_2-containing syngas with Cu/ZnO catalyst and the aid of alcohols has been developed in a batch and a flow-type semi-batch reactors. The use of alcohols as catalytic solvents realized methanol synthesis at 443 K with formate as an intermediate. The activity of methanol synthesis depends on types and structures of alcohols. Among all alcohols, 2-alcohol exhibited the highest activity. With the aid of 2-butanol, the one-pass 47.0% conversion and 98.9% selectivity were achieved at a mild condition, 443 K and 50 bar. The new reaction route of methanol synthesis is a practical method for near future technology.

Keywords: Methanol synthesis; Syngas; Alcohol; Formate; Cu/ZnO catalyst

1. Introduction

Methanol is a fundamental chemical, alternatively clean transportation fuel, and direct fuel for fuel cell. It is commercially produced from syngas containing few amount of carbon dioxide, with the scale of 30–40 million tons per year around the world under high temperature and high pressure (523–573 K and 50–100 bar) with Cu/ZnO catalyst. The reaction path was well known by the following fundamental steps:

$$CO + H_2O = CO_2 + H_2$$

$$CO_2 + 3H_2 = CH_3OH + H_2O$$

$$CO + 2H_2 = CH_3OH$$

Under the reaction condition, one-pass conversion of the process using H_2-rich syngas ($H_2/CO = 5$) is limited to 15–25% due to the thermodynamic limitation of the highly exothermic reaction [1–3]. The recycle of unreacted syngas is necessary to enhance the syngas conversion, leading to the production cost higher. The recycling process can be omitted if one-pass conversion is high enough. Consequently, developing a high one-pass conversion process at lower temperature which is of the thermodynamic favor will greatly lower the cost of production. Air can be used instead of pure O_2, in the reforming process to produce syngas resulting in the lower cost of methanol production [3].

Brookhaven National Laboratory (BNL) in USA has developed the synthesis based on a homogeneous process in a flow-type semi-batch reactor using a strong base catalyst (a mixture of NaH, alcohol, and metal acetate). It was operated at temperature of 373–403 K and pressure of 10–50 bar. Although its high conversion and selectivity is very attractive but a remarkable drawback of this process is the quick deactivation of catalysts. The basic catalyst is easy to be deactivated by trace amount of CO_2 and H_2O in the feed gas or reaction system [4,5], implying the higher cost from the complete syngas purification and the catalyst reactivation. Therefore, the commercialization of such a process is now impractical.

Methanol synthesis from pure CO and H_2 via methyl formate formation has been studied based on the two main reactions. The carbonylation of methanol in the first step following by the hydrogenation of methyl formate results in net methanol formation [6–13]

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$$\begin{array}{c}\mathrm{CO + CH_3OH \overset{RONa}{=} HCOOCH_3}\\ \mathrm{HCOCH_3 + 2H_2 \overset{solid\ cat.}{=} 2CH_3OH}\\ \hline \mathrm{CO + 2H_2 = CH_3OH}\end{array}$$

However, the deactivation of the basic RONa catalysts by CO_2 and H_2O is still the main problem, similarly to BNL method. The complete purification of syngas makes it difficult to be commercialized.

The present authors proposed a low-temperature methanol synthesis by which methanol was synthesized from CO_2 and H_2 using a conventional Cu-based oxide catalyst in ethanol as a catalytic solvent. This process was operated in a batch reactor at mild condition (443 K and 30 bar) [14]. The new process consists of three steps: (1) a synthesis of formic acid from CO_2 and H_2; (2) a formation of ethyl formate from an esterification of formic acid and ethanol; and (3) a formation of methanol from a hydrogenation of ethyl formate. Considering the fact that the water–gas shift reaction (WGSR) is easy to conduct on Cu/ZnO catalysts at low temperature [15–25], therefore a new process for methanol synthesis from CO_2-containing syngas is proposed as the following steps:

$$\mathrm{CO + H_2O = CO_2 + H_2} \tag{1}$$

$$\mathrm{CO_2 + 1/2\ H_2 + Cu = HCOOCu} \tag{2}$$

$$\mathrm{HCOOCu + ROH = HCOOR + CuOH} \tag{3}$$

$$\mathrm{HCOOR + 2H_2 = CH_3OH + ROH} \tag{4}$$

$$\mathrm{CuOH + 1/2\ H_2 = H_2O + Cu} \tag{5}$$

$$\mathrm{CO + 2H_2 = CH_3OH} \tag{6}$$

Reactions (2) and (3) were suggested where Cu represents the catalytic site of Cu-based catalysts since formic acid was not detected in the products. In the new process, the high conversion and selectivity were achieved under low temperature (423–443 K). In this present work, a typical batch reactor was particularly used for preliminary study of methanol synthesis at temperature range of 423–443 K and pressure range of 30–50 bar. Methanol was synthesized from CO_2-containing syngas with the aid of different alcohols as catalytic solvents and Cu/ZnO as a catalyst. A flow-type semi-batch reactor was employed to further study the total process such as catalyst lifetime when the product accumulation and pressure drop were avoided.

2. Experiment

2.1. Materials

Copper(II) nitrate trihydrate (>77% purity, $Cu(NO_3)_2$), zinc nitrate hexahydrate (>99% purity), sodium carbonate (>99% purity), hexane (>96% purity) and alcohols (>99% purity) purity were purchased from Kanto Chemical and used as received. γ-Al_2O_3 (140 m^2/g) was purchased from Nikki Chemical. Pure gas and syngas were purchased from Takachiho Chemical Industrial. The gas contents of syngas were calibrated by the manufacturer and further purified by an activated carbon filter.

2.2. Catalyst preparation

The Cu/ZnO catalyst was prepared by the conventional co-precipitation method in aqueous solution. An amount of 300 ml copper and zinc nitrates (each 0.13 M, Cu/Zn in molar ratio = 1) and 300 ml sodium carbonate (0.47 M) used as a precipitant were simultaneously added to 300 ml water under rapid stir at 338 K and pH range of 8.3–8.5 and aged overnight. The precipitate was filtered and washed several times with distillated water. The drying process was conducted at 383 K for 24 h followed by calcination in the air at 623 K for 1 h. The reduction of oxide solid was taken at 473 K for 13 h by flowing 5% H_2 in N_2 and passivated by 2% O_2 in Ar. The homemade catalyst, molar ratio Cu/Zn of 1, is denoted as Cu/ZnO (A). No sodium impurity was found in the finished catalyst, determined by XRD (Rigaku RINT 2400) and EDX (Shimadzu Rayny EDX-700). The BET surface area of catalyst was 60 m^2/g and the Cu-specific surface area, determined by N_2O adsorption method, was 30.1 m^2/g [26].

The commercial ICI catalyst (ICI 51-2, Cu:Zn:Al = 62:35:3 wt.% determined by EDX) was reduced by the same pretreatment, denoted as Cu/ZnO (B) was used. The BET surface area of the catalyst was 20 m^2/g. In some experiments, Cu/Al_2O_3 (10 wt.% Cu) was also used together with Cu/ZnO (B) in a physical mixture form at the weight ratio of 1. The impregnation method was used to prepare Cu/Al_2O_3 using copper nitrate aqueous solution on γ-Al_2O_3 followed by the same treatment as that of Cu/ZnO (A). The BET surface area of Cu/Al_2O_3 was 113 m^2/g.

2.3. Methanol synthesis

A batch reactor with 80 ml inner volume and a stirrer were used to study the effect of solvent, reaction time, molar ratio of Cu/Zn, and reactant gas composition. The catalyst and solvent were firstly loaded in the reactor. The air inside was purged by the reactant gas, $CO/CO_2/H_2/Ar$ = 32/5/60/3,

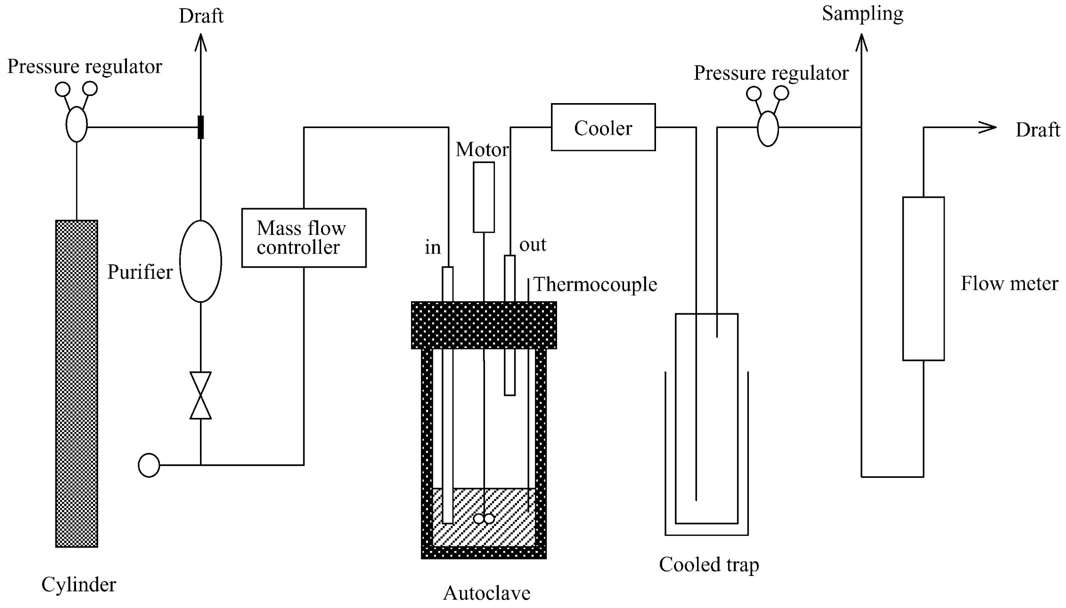

Fig. 1. The flow-type semi-batch apparatus for methanol synthesis.

then the reactor pressure was raised to 30 bar and the reaction took place at the set temperature for 2 h. The stirring speed was fixed at 1260 rpm and carefully checked to prevent the diffusion-controlled regime. The total pressure was calculated to 55 bar at the reaction temperature of 443 K including 10 bar of solvent vapor pressure when 20 ml ethanol was used [27]. The GC–MS (Shimadzu GCMS 1600) was used to confirm all products. Two GCs and TCD (Shimadzu GC-320) were used to analyze gas products and FID (Shimadzu GC-8A) was used to analyze liquid products.

A continuous methanol synthesis was conducted using an 85 ml flow-type semi-batch reactor. The high-pressure gas flow controller and pressure regulator were set upstream and downstream of the reactor as shown in Fig. 1. The ice-cooled trap of liquid product and water cooler used to prevent the possible escaping of solvent from the reactor were set at the exit of reactor. The 3.0 g of catalyst and 20 ml of alcohol (purity > 99.5%) were poured into the reactor, and then the reactor was closed. After that, the temperature of water cooler was set at 273 K and the reactor was purged by reactant gas, $CO/CO_2/H_2/Ar = 32/5/60/3$ (Ar was used as an internal standard.) The pressure was raised to 50 bar followed by raising the temperature to 443 K within 20 min at the constant stirring speed (1260 rpm). The effluent gases were automatically analyzed by an online TCD and the liquid products were analyzed by FID equipped with a methanator after the reaction was completed. Total carbon conversion was calculated as follows:

$$\text{total carbon conversion} = \left[\text{CO conversion} \times \frac{a}{a+b}\right] + \left[\text{CO}_2\text{ conversion} \times \frac{b}{a+b}\right]$$

where a, b were the contents of CO, CO_2 in the feed gas.

The average yields of liquid products (methanol and formate), P_i yields, were calculated and obtained as follows:

$$P_i\text{ yield} = 100 \times \frac{P_i\text{ C-mol number}}{\text{total mol of carbon in the feed gas in total time}}$$

It should be noticed that carbon in the solvent, ROH, was not counted in the calculation to ensure proper selectivities of the reacted CO and CO_2. The selectivities of the liquid products, P_i selectivities, were calculated as follows:

$$P_i\text{ selectivity} = 100 \times \frac{P_i\text{ yield}}{\sum Pi\text{ yield}}$$

3. Results and discussion

3.1. Batch reactor

Fig. 2 shows an effect of ethanol, a catalytic solvent, on the conversion or yield of methanol synthesis. In this experiment, a physical mixture of CuZnO (B) and Cu/Al_2O_3 was utilized. The reaction did not proceed at low temperature as 423 K in cyclohexane, alcohol free medium. This reaction route could be the same route as a conventional process, ICI commercial process. The hydrogenation could not directly proceed at a temperature lower than 483 K informing that the catalyst showed no activity. The activity of catalyst existed at low temperature only when ethanol was used as a solvent. The alcohol significantly lowered the reaction temperature and accelerated the reaction, but did not effect the stoichiometry of the overall reaction (6). In reaction (1), the WGSR is easily conducted on Cu catalysts at low temperature. The reaction between acid and alcohol, known as an

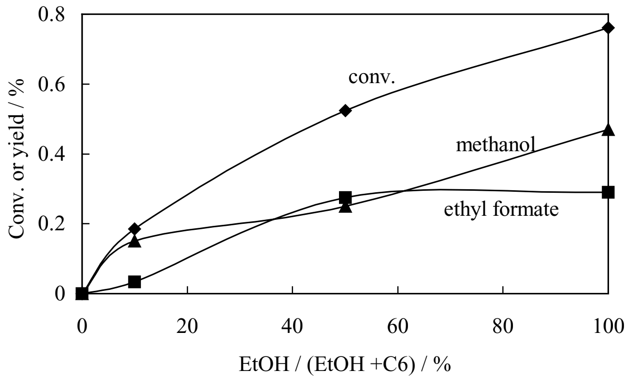

Fig. 2. Role of ethanol for methanol synthesis in a batch reactor. Temperature = 423 K; initial pressure = 30 bar; Cu/ZnO (B) + Cu/Al_2O_3 = 0.2 g; reaction time = 2 h; total solvent amount = 5 ml.

esterification, can proceed at mild condition as in reaction (3). The hydrogenolysis of ester in reaction (4) to methanol is an industrial process. The methanol can be easily produced in the overall reaction using Cu/ZnO catalyst and the aid of ethanol. The increased ethanol amount gradually increased both conversion and yield. Ethyl formate seemed to be the only intermediately by-product.

The activity of Cu/ZnO (B) was lower than that of Cu/ZnO (A). In order to enhance the conversion, Cu/Al_2O_3 was also used separately or physically mixed with Cu/ZnO (B). If only Cu/Al_2O_3 was used, only ethyl formate was formed and no methanol was observed. If both Cu/Al_2O_3 and Cu/ZnO (B) were used, the highest conversion was obtained, but selectivities of ethyl formate and methanol were the same as using Cu/ZnO (B) alone. It seems that Cu/Al_2O_3 catalyzed reactions (1)–(3), but the active site of the catalyst for reaction (4) was Cu–Zn–O structure. It seems that the main role of the added Cu/Al_2O_3 was increasing the rate of reaction (1).

The effect of reaction time on the conversion or yield at 443 K was shown in Fig. 3. The conversion and methanol yield linearly increased with the time of reaction. The yield of ethyl formate was nearly constant indicating that the reaction proceeded via the designed route where formate was the only intermediate.

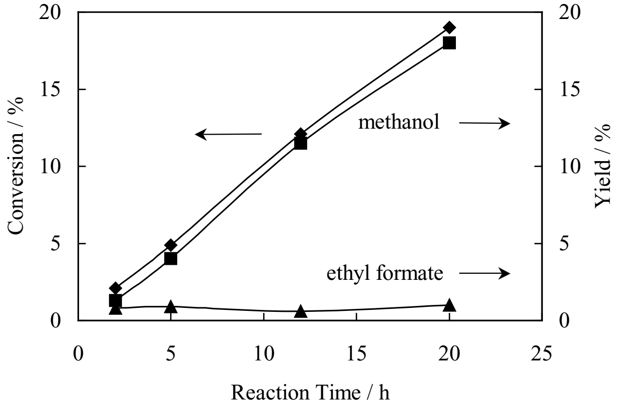

Fig. 3. Effect of reaction time on methanol synthesis in a batch reactor. Temperature = 443 K; initial pressure = 30 bar; Cu/ZnO (A) = 0.2 g; ethanol = 10 ml.

Table 1
The Cu/ZnO catalyst properties with different Cu/(Cu + Zn) molar ratio

Cu/(Cu + Zn) molar ratio	Cu^0 area by N_2O method (m^2/g)	BET surface area (m^2/g)
0.1	3.6	38
0.3	12.2	44
0.5[a]	30.1	60
0.7	16.1	48
0.9	1.46	22

[a] Cu/ZnO (A).

The reaction activity and its relationship with the chemical composition of Cu/ZnO in a closed reactor were shown in Fig. 4. It is clear that the Cu/Zn molar ratio of 1 (Cu/(Cu+Zn) = 50%) exhibited the best reaction activity, whereas large percentage of Cu or Zn was not favorable to the catalyst activity. At low total conversion, the selectivity of ethyl formate was high. When the conversion increased, the selectivity of methanol increased, indicating that ethyl formate was an intermediate in this low-temperature methanol synthesis.

As shown in Table 1, the BET surface area and Cu surface area were low when the Cu/Zn molar ratio was high or low. The active site, metallic Cu, was believed to be well dispersed in ZnO lattice, moderate Cu/Zn ratio was critical to ensure high catalytic activity. Cu/ZnO catalysts with various Cu/Zn ratios were prepared by different methods, for example, using oxalic acid solution in ethanol for co-precipitation besides the Na_2CO_3-contained co-precipitation reported here. It is found that the activity was almost proportional to Cu surface area of the obtained catalyst. It can be concluded that Cu was the active site for the reaction and it acted via a redox cycle, as shown in the reaction mechanism. Therefore, it is important to obtain high Cu surface area on ZnO in order to enhance the activity. Strong interaction between Cu and ZnO, which make reduction of Cu difficult, although the dispersion of Cu was increased. Incidentally, weak interaction between Cu and ZnO could not ensure high dispersion of Cu, leading to low Cu surface area.

Fig. 5 shows the effect of various alcohols on the conversion and yields. Alcohol-free solvent (cyclohexane and no solvent cases) showed no activity for methanol synthesis at 443 K. Considering 1-alcohols, the longer carbon chain, the lower the yield of methanol and corresponding ester. Ester was not found for 1-alcohols when there were more than three carbons. The result corresponds with the different 1-alcohols rate sequence in the esterification [28], supporting the fact that reaction (3) was a rate-determining step.

Among branched alcohols, which have the same amount of carbons but different structures, the 2-alcohol had the highest activity in both methanol and ester yields. 2-Propanol, the shortest carbon of 2-alcohol, showed the highest activity among 2-alcohols. The activity was lowered

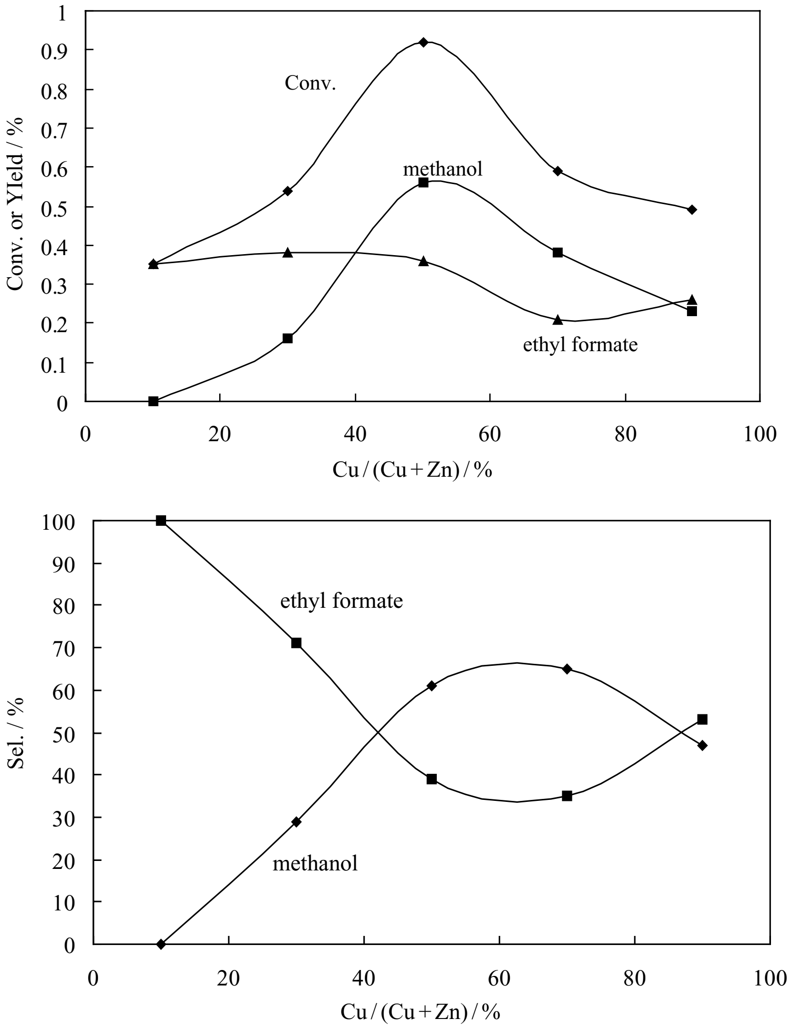

Fig. 4. The reaction performances of Cu/ZnO catalysts with different Cu/(Cu + Zn) molar ratios in a batch reactor. Temperature = 443 K; initial pressure = 30 bar; Cu/ZnO = 0.2 g; reaction time = 2 h; ethanol 10 ml.

due to the spatial obstacle from the branching in *iso*-butanol, *tert*-butanol, and cyclopentanol. However, the yields to ester in the batch reactor were high when 2-alcohols were used, especially 2-pentanol, referring that reaction (4) was slow if 2-alcohols were used. In other cases, the rate of reaction (4) was much faster than that of reaction (3), resulting the disappearance or small yield of the corresponding esters. The results on the effect of different alcohols might not be clear enough in the batch reactor to strongly conclude that reaction (3) was the rate-determining step. Therefore, the experiments were further investigated in the flow-type semi-batch reactor in order to confirm the rate-determining step. Furthermore, ethylene glycol and benzyl alcohol showed no activity. It can be concluded that the rate and reaction path of reaction (3) solely depended on the nature of alcohols, the electron density and spatial effect.

Although low electron density of the oxygen atom in 1-butanol which made it slowly attack formic salt, the nucleophilic attack in the esterification was favorable due to the smallest spatial obstacle. On the contrary, the large spatial obstacle, which retarded the nucleophilic attack, lowered the esterification rate; even though, the electronic density of the oxygen atom in *tert*-butanol was high. Consequently, *tert*-butanol exhibited the lowest activity. As a result of the balance between electronic factor and spatial obstacle effects, among all butanols, 2-butanol showed the highest activity.

In order to demonstrate the mechanism, the hydrogenation of ester was conducted in a batch reactor. The mixture of 1.5 ml of ethyl formate and 18.5 ml of cyclohexane was poured into the reactor. Methanol was easily produced through the hydrogenation of ethyl formate under 30 bar of the total initial pressure, in which H_2/N_2 molar ratio of 2 was used instead of syngas. The total conversion of ethyl formate and the yield of methanol at 443 K was 98.2 and 83.7%, respectively. The two by-products were methyl formate and CO. The methyl formate could be produced from the *trans*-esterification between ethyl formate and methanol product. CO might be derived from the ethyl formate decomposition.

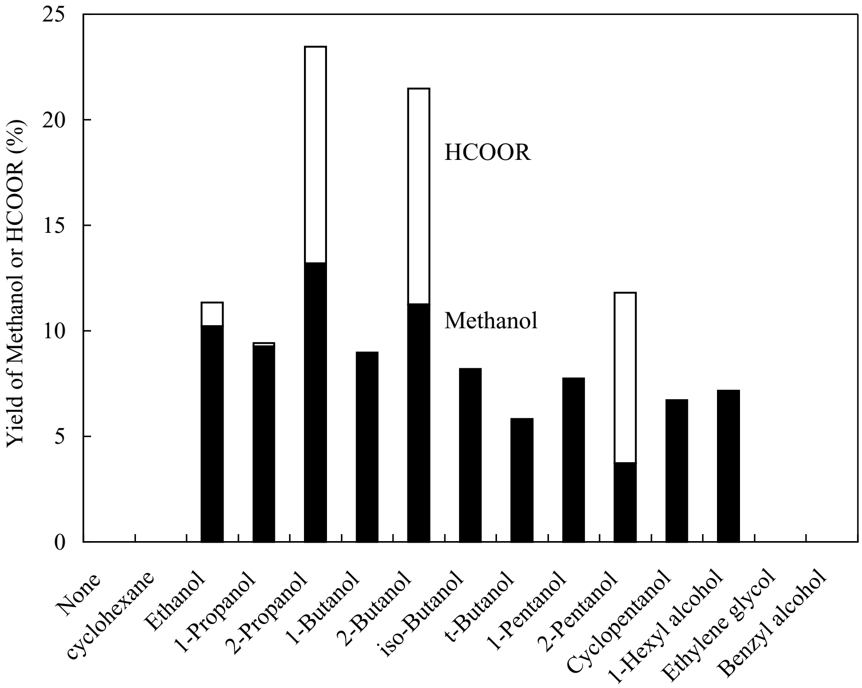

Fig. 5. Effect of different alcohols on methanol synthesis in a batch reactor. Temperature = 443 K; initial pressure = 30 bar; Cu/ZnO (A) = 1.0 g, reaction time = 2 h; alcohol = 20 ml.

The effect of reactant gas composition was shown in Table 2. No reaction was observed when pure CO was used, indicating that the direct carbonylation of alcohol to ester was impossible. Ethyl formate was produced without methanol product when pure syngas ($CO + H_2$), CO_2-free syngas, was used. The formation of ester or reaction mechanism is not clear, as its formation via an insertion of CO into ethanol was excluded. The one possibility of its formation is the WGSR of water containing in ethanol (100–150 ppm). The WGSR between CO and water to form CO_2 possibly proceeded the reactions (1)–(3). The increase in CO_2 content enhanced the total reaction rate when CO_2-containing syngas was used. It was implied that the reaction rate of methanol synthesis from $CO_2 + H_2$ was faster than that of $CO + H_2$; therefore, the designed reaction route was confirmed.

Table 2
Effect of reactant gas on methanol synthesis in a batch reactor

Experiment no.	Partial pressure (bar)			Yield (%)		
	CO	H_2	CO_2	Ethyl formate	Methanol	Total
1	10	0	0	0	0	0
2	10	20	0	0.30	0	0.30
3[a]	9.6	18	1.5	0.28	0.15	0.43
4	7.5	18	4.5	0.43	0.17	0.60
5	0	22.5	7.5	0.55	0.40	0.95

Temperature = 423 K; initial pressure = 30 bar; Cu/ZnO (B) = 0.2 g; reaction time = 2 h; ethanol = 5 ml.

[a] Argon = 0.9 bar.

In Fig. 6, the total carbon conversion and methanol yield increased when the reaction temperature increased. The selectivity of methanol gradually increased with the increase in temperature as well. As a result of the low investigated temperature, the limitation from thermodynamics did not occurred.

Furthermore, water added in order to study the reaction behavior and catalyst activity did not effect the reaction under studied reaction conditions. The additional water was an intermediate in the reaction mechanism, similarly to the role of CO_2, while they severely deactivated the catalysts in other low-temperature methods.

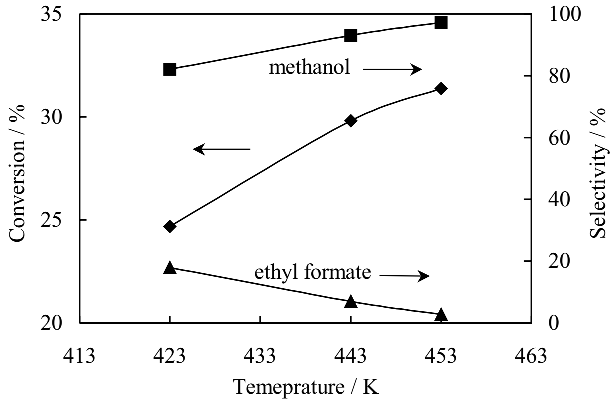

Fig. 6. Effect of reaction temperature on methanol synthesis in a batch reactor. Initial pressure = 30 bar; Cu/ZnO (A) = 1.0 g; reaction time = 2 h; ethanol 20 ml.

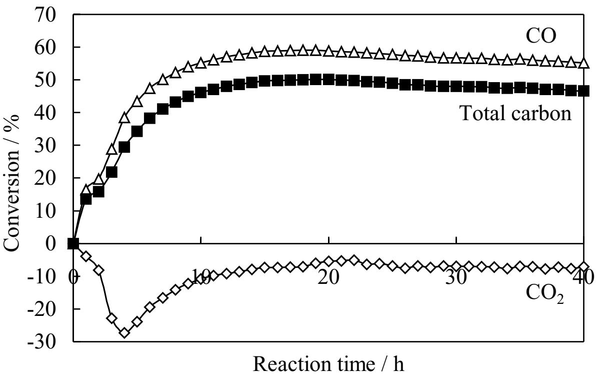

Fig. 7. Variations of conversions with time on stream for continuous methanol synthesis from CO/CO_2/H_2. Temperature = 443 K; pressure = 50 bar; Cu/ZnO (A) = 3.0 g; 2-butanol = 20 ml; flow rate = 20 ml/min.

3.2. Flow-type semi-batch reactor

The time-on-stream and activity change of continuous process was shown in Fig. 7. CO conversion gradually increased was nearly stable at approximately 60% conversion after 12 h from the beginning due to the dilution effect of the pressurized reactant gas. CO_2 conversion, on the other hand, dropped to −29% conversion and gradually increased to stabilize at approximately −8% conversion in the initial 10 h. The negative CO_2 conversion resulted from the excess CO_2 formed from WGSR of CO informed that the adjustment of CO/CO_2 ratio was required. As the absolute CO_2 content in the feed gas was very low, the CO_2 content was not so high even if it showed minus conversion. Total carbon conversion also gradually increased and became stable at about 47% conversion. The time-on-stream of conversion indicated that CO was initially converted to CO_2 via WGSR, reaction (1), and then, CO_2 converted to methanol via reactions (2)–(4).

Table 3 shows the effect of various alcohols on the continuous methanol synthesis during 20 h of reaction time. This low-temperature method, leading to the high selectivity of methanol, up to 98–100% selectivity, indicated the rapid hydrogenolysis of HCOOR, reaction (3). Methyl formate was another by-product formed through the *trans*-esterification between HCOOR and methanol product. Similarly to the batch process, 2-alcohols showed the highest conversion due to the balance between electronic factor and spatial obstacle effects. According to the sequence of the esterification rate, methanol, among 1-alcohols, showed the highest activity. It was believed that reaction (4) was faster than reaction (3) because of the low concentration of ester by-product, providing the evidence that reaction (3) was the rate-determining step.

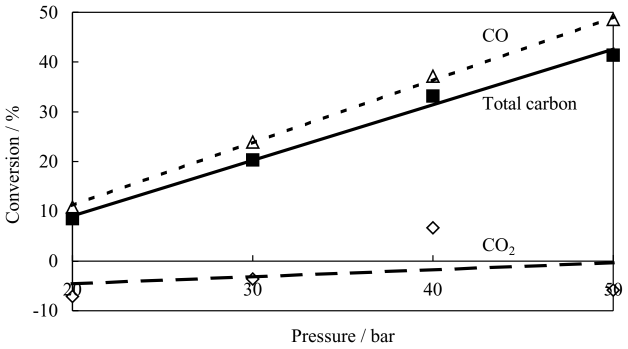

Fig. 8. Effect of reaction pressure on methanol synthesis in a flow-type semi-batch reactor. Temperature = 443 K; Cu/ZnO (A) = 3.0 g; reaction time = 20 h; 2-butanol = 20 ml; flow rate = 20 ml/min.

The effects of pressure and temperature were shown in Figs. 8 and 9, respectively. The total carbon conversion linearly increased with the increase in pressure and temperature without changing in the selectivity of methanol (>98%). The thermodynamic limitation did not occurred, as the investigated temperature here was low. Furthermore, the increase in the amount of catalyst linearly increased the conversion, proving the high efficiency of syngas mass transfer and unlimited thermodynamics in the reactor. Unlike the high temperature process, the conversion was thermodynamically limited.

The continuous process may have an excellent potential for commercialization where the high purity of syngas (CO+ H_2) was not necessary and the deactivation of catalyst by water and CO_2 can be solved.

Table 3
Continuous processes with various alcohols for methanol synthesis

Solvents	Selectivity (%)			Total carbon conversion (%)	Yield (%)		
	Methanol	MF	HCOOR		Methanol	MF	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
2-Propanol	44.0	0.1	0.3	44.4	99.0	0.3	0.7
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
2-Pentanol	43.3	0.1	0.6	44.0	98.4	0.3	1.3
1-Hexanol	34.4	0.1	0	34.5	99.7	0.3	0

Temperature = 443 K; pressure = 50 bar; Cu/ZnO (A) = 3.0 g; reaction time = 20 h; alcohol = 20 ml; flow rate = 20 ml/min.

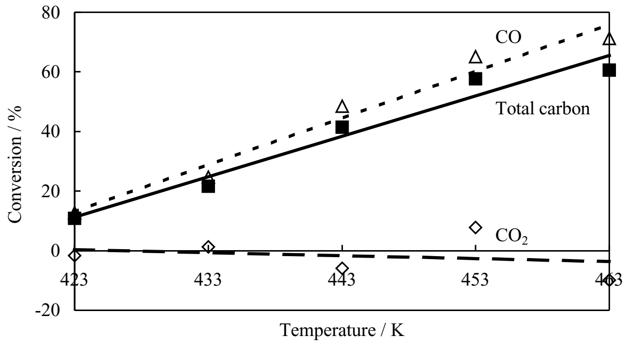

Fig. 9. Effect of reaction temperature on methanol synthesis in a flow-type semi-batch reactor. Pressure = 50 bar; Cu/ZnO (A) = 3.0 g; reaction time = 20 h; 2-butanol = 20 ml; flow rate = 20 ml/min.

4. Conclusions

Methanol was synthesized via a new reaction route with conventional solid catalyst and the aid of catalytic alcohol at low temperature from CO_2-containing syngas which purification of syngas was unnecessary. The new reaction route not only exhibited high activity, but also overcame the drawbacks of other low-temperature methods in terms of catalyst deactivation. Alcohols, as catalytic solvents, greatly lowered the reaction temperature and pressure. The nature of alcohol structure solely influenced the activity of methanol synthesis. Among the studied alcohols, 2-alcohols showed the highest activity. Additionally, no thermodynamic limitation occurred; therefore, the conversion was linearly increased when the amount of catalyst increased. The present methanol synthesis by continuous process is a promisingly practical method which may have the potential to be commercialized.

In the near future, a bubble-column reactor is considered for large-scale synthesis.

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References

[1] S. Lee, Methanol Synthesis Technology, CRC Press, Boco Raton, FL, 1990.
[2] I. Wender, Fuel Process. Technol. 48 (1996) 189.
[3] M. Marchionna, M. Lami, A.M. Raspolli Galletti, CHEMTECH, 27 April 1997.
[4] J. Haggin, Chem. Eng. News, 4 August 1986, p. 21.
[5] Brookheaven National Laboratory, US Patents 4 614 749, 4 619 946, 4 623 634, 4 613 623 (1986), 4 935 395 (1990).
[6] V.M. Palekar, H. Jung, J.W. Tierney, I. Wender, Appl. Catal. 102 (1993) 13.
[7] Kirk-Othmer Encyclopedia of Chemical Technology, vol. 13, 2nd ed., Wiley, New York, 1964, p. 390.
[8] V.M. Palekar, H. Jung, J.W. Tierney, I. Wender, Appl. Catal. 103 (1993) 105.
[9] O.T. Onsager, World Patent 86/03190 (1986).
[10] H. Zhang, H. Li, G. Lin, K.R. Tsai, Stud. Surf. Sci. Catal. 101 (1996) 1369.
[11] Y.Z. Chen, B.Z. Chung, C.R. Hsieh, Catal. Lett. 41 (1996) 213.
[12] M. Girolamo, M. Marchionna, Italian Patent MI92/A 002126 (1992).
[13] S. Ohyama, Topics Catal. 22 (2003) 337.
[14] N. Tsubaki, Y. Sakaiya, K. Fujimoto, Appl. Catal. 180 (1999) L11.
[15] C.S. Chen, W.H. Cheng, S.S. Lin, Catal. Lett. 68 (2000) 45.
[16] J. Yoshihara, C.T. Campbell, J. Catal. 161 (1996) 776.
[17] S. Fujita, M. Usui, H. Ito, N. Takezawa, J. Catal. 157 (1995) 403.
[18] S. Bailey, G.F. Fromont, J.W. Snoeck, K.C. Waugh, Catal. Lett. 30 (1995) 99.
[19] J. Yoshihara, S. Parker, A. Schafer, C.T. Campbell, Catal. Lett. 31 (1995) 313.
[20] S. Oki, J. Happel, M. Hnatow, Y. Kaneko, in: Proceedings of the Fifth International Congress on Catalysis, vol. 1, 1973, p. 173.
[21] S. Oki, R. Mezaki, J. Phys. Chem. 77 (1973) 447, 1601.
[22] R. Mezaki, S. Oki, J. Catal. 30 (1973) 488.
[23] G.G. Shchibrya, N.M. Morozov, M.I. Temkin, Kinet. Katal. 6 (1965) 1115.
[24] H. Uchida, N. Isogai, M. Oba, T. Hasegawa, Bull. Chem. Soc. Jpn. 40 (1967) 1981.
[25] T.M. Yureva, G.K. Boreskov, V.S. Gruver, Kinet. Katal. 10 (1969) 862.
[26] J.W. Evans, M.S. Wainwright, A.J. Bridgewater, D.J. Young, Appl. Catal. 7 (1983) 75.
[27] F. Perry, T. Chilton, Chemical Engineers' Handbook, 5th ed., McGraw-Hill, New York, 1975, Section 3, pp. 3–62.
[28] R.T. Morrison, R.N. Boyd, Organic Chemistry, Allyn & Bacon, Boston, MA, 1973 (Chapter 20).