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Advances in joint research between NIRE and RITE for developing a novel technology for methanol synthesis from CO_2 and H_2†

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NIRE and RITE have jointly performed a national R&D project on methanol synthesis from CO_2 and hydrogen in order to contribute to CO_2 mitigation. In the first step, many attempts were made at developing high-performance catalysts for methanol synthesis. The roles of metal oxides contained in Cu/ZnO-based catalysts were classified into two categories: (1) Al_2O_3 or ZrO_2 improves the dispersion of copper particles in the catalyst; (2) Ga_2O_3 or Cr_2O_3 increases the activity per unit copper surface area of the catalyst. The long-term stability of Cu/ZnO-based catalysts during methanol synthesis from CO_2 and hydrogen was improved by adding a small amount of silica to the catalysts, and then calcining the catalysts at high temperatures around 873 K. Silica added to the catalysts suppressed the crystallization of ZnO contained in the catalysts, which was probably caused by the action of water produced together with methanol. Based on those two important findings, high-performance Cu/ZnO-based multicomponent catalysts ($Cu/ZnO/ZrO_2/Al_2O_3/SiO_2$ and $Cu/ZnO/ZrO_2/Al_2O_3/Ga_2O_3/SiO_2$) were developed. The catalysts developed were found to be highly active and extremely stable in methanol synthesis from CO_2 and hydrogen. In the next step, a bench plant with a capacity of 50 kg day^{-1} of CH_3OH, which was equipped with facilities for recycling unreacted gases and gaseous products, was successfully operated. The activity of the $Cu/ZnO/ZrO_2/Al_2O_3/SiO_2$ catalyst was 580 g h^{-1} of CH_3OH per liter of catalyst under the reaction conditions of 523 K, 5 MPa and SV = 10,000 h^{-1} in 1000 h on stream. The selectivity to methanol synthesis was as high as 99.7%, and the purity of crude methanol produced was 99.9 wt%, whereas the purity of crude methanol produced from syngas in a present-day commercial plant was reported as 99.6 wt%. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: methanol synthesis; CO_2 hydrogenation; Cu/ZnO-based multicomponent catalyst; bench plant operation

INTRODUCTION

Global warming mainly caused by the increase in CO_2 emission has been recognized as one of the most serious problems in the world. In order to contribute to CO_2 mitigation, a national R& D project entitled ‘Fixation and Utilization of Carbon Dioxide by Catalytic Hydrogenation’ has been performed by the joint research between RITE and three national institutes (NIMC, ONRI and NIRE) of MITI since 1990. The main purpose of the project is to develop three key technologies required for a

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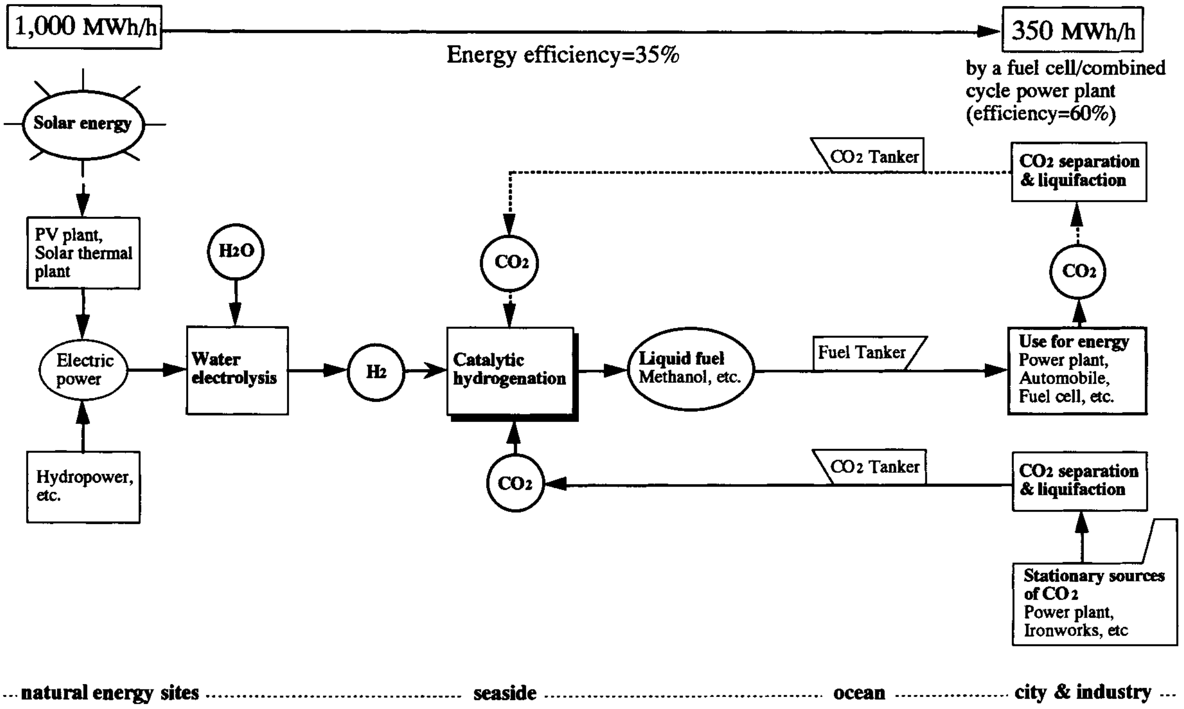

Figure 1 Proposed system for fixation and utilization of CO_2 by catalytic hydrogenation (energy conversion/transportation system combined with CO_2 hydrogenation). The route drawn with solid lines emits CO_2 after methanol is used for energy, whereas the route drawn with dotted lines recycles CO_2 emitted after the use of methanol.

proposed system for the conversion/transportation of non-fossil energy combined with catalytic hydrogenation of CO_2, which is shown in Fig. 1.[1,2] The technologies to be developed are those for membrane separation of CO_2 emitted from stationary sources, for H_2 production by water electrolysis using electric power derived from non-fossil energy and for methanol synthesis by the catalytic hydrogenation of CO_2. A joint research between NIRE and RITE has been performed for developing a novel technology for methanol synthesis from CO_2 and hydrogen. From both basic and practical points of view, methanol synthesis from CO_2 and hydrogen has been extensively studied in our joint research. The present paper reports the advances in the development of practical high-performance catalysts and in the operation of a small bench plant for gas-phase methanol synthesis.

EXPERIMENTAL

All of the Cu/ZnO-based catalysts used in the present study were prepared by a conventional coprecipitation method.[3] An aqueous solution of mixed metal nitrates (total metal concentration 1 mol l^{-1}) and an aqueous solution of Na_2CO_3 (1.1 mol l^{-1}) were simultaneously added to stirred distilled water. Subsequently, the precipitates were filtered out, washed with distilled water, dried in air at 393 K overnight and calcined in air at a given temperature ranging from 623 to 873 K for 2 h. The calcined catalyst powder was pelletized, crushed and screened to sizes between 60 and 80 mesh.[1] In order to improve the long-term stability of the catalyst, a small amount of silica was added to the catalysts by using a colloidal silica supplied by Nissan Chemical Co. Two ways of adding silica to the catalysts were employed. In one way, colloidal silica was added to an aqueous solution of metal nitrates for coprecipitation. In the other way, the precipitates prepared were washed with distilled water containing colloidal silica. Both ways gave almost quantitative content of silica in the catalyst, suggesting that silica was incorporated into the catalyst by the adsorption of colloidal silica on the precipitates.

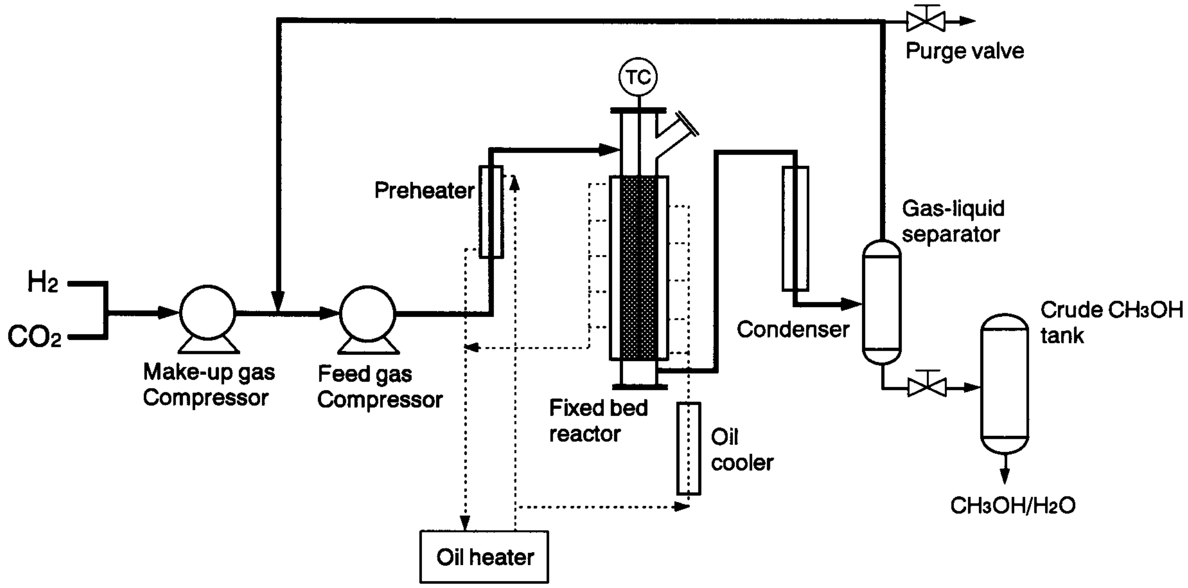

Figure 2 Schematic diagram of a bench-scale methanol synthesis plant with a capacity of 50 kg day^{-1}. Reactor size: 3.84 mm i.d. × 4 m long; catalyst volume = 3 1.

A conventional fixed-bed flow reactor was used both for short-term and long-term catalyst tests. The catalyst loaded in the reactor was reduced in a gas mixture of hydrogen (10%) and helium (90%) at 573 K with a total pressure of 5 MPa for 2 h, and then methanol synthesis was carried out under the given reaction conditions. The reaction products were analyzed by means of gas chromatographs directly connected to the reactor.

A bench plant with a methanol synthesis capacity of 50 kg day^{-1}, the flow diagram of which is shown in Fig. 2, was used for investigating practical methanol synthesis operations. The make-up gas composed of CO_2 and hydrogen was mixed with a recycle gas mixture from a gas–liquid separator, which was composed of unreacted gases and gaseous products such as CO, methane, ethane and dimethyl ether. Then, the feed gas mixture was supplied to a fixed-bed reactor. The reaction products from the reactor were cooled at a condenser and sent to the gas–liquid separator, where crude methanol and water were separated from the unreacted gases and the gaseous products.

The surface areas of the catalysts were measured by a flow method employing nitrogen adsorption at 77 K. The copper surface areas of the post-reaction catalysts were measured by the technique of N_2O reactive frontal chromatography after re-reducing the post-reaction catalysts with hydrogen at 523 K. X-ray diffraction (XRD) measurements were performed for analyzing the structure of the catalysts.[3]

RESULTS AND DISCUSSION

Reaction paths for methanol synthesis

The main products of CO_2 hydrogenation over Cu/ZnO-based catalysts were methanol, CO and water. Methane, dimethyl ether and methyl formate were also detected in the reaction products, but the selectivities to the by-products were less than 0.1%.

Figure 3 shows the yields of methanol and CO as a function of reciprocal space velocity (1/SV). Methanol and CO were formed simultaneously at low conversions of CO_2 by the following two reactions:

$$CO_2 + 3H_2 = CH_3OH + H_2O \qquad [1]$$

$$CO_2 + H_2 = CO + H_2O \qquad [2]$$

The yield of CO increased with an increase in 1/SV and reached a maximum when reaction [2] nearly attained equilibrium, and then gradually decreased while reaction [2] remained at equilibrium. On the

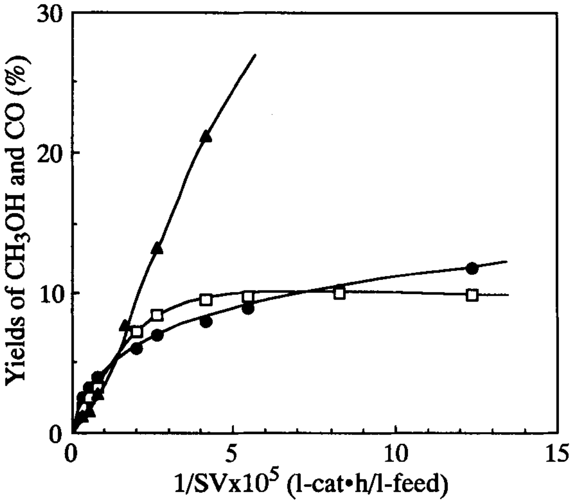

Figure 3 Yields of methanol (●, ▲) and CO (□) in methanol synthesis from $CO_2(25)/H_2(75)$ (●, □) and $CO(25)/CO_2(6)/H_2(69)$ (H) over a $Cu/ZnO/ZrO_2$ catalyst at 523 K and 5 MPa as a function of reciprocal SV.

other hand, the yield of methanol gradually increased with increasing 1/SV until reaction [1] reached equilibrium.[3]

Figure 4 shows the inhibitory effect of water on methanol synthesis and on CO formation, and also the effect of CO on methanol synthesis. Both water and CO suppressed methanol synthesis over Cu/ZnO-based catalysts, and the inhibitory effect of water was much stronger than that of CO. The inhibitory effects of water and CO can explain the finding that the rate of methanol synthesis greatly decreased with increasing 1/SV, as shown in Fig. 3.

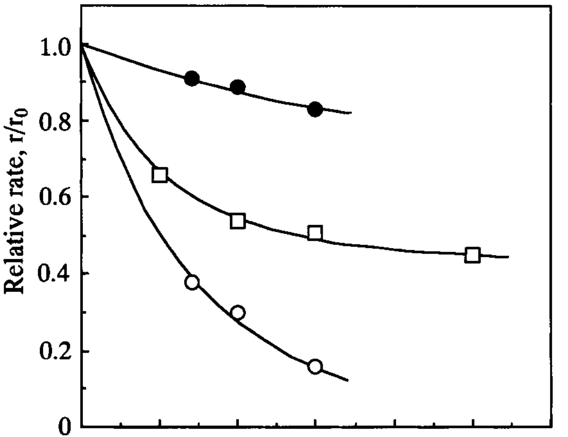

Figure 4 Inhibitory effects of H_2O (○) and CO (□) on methanol synthesis and of H_2O (●) on CO formation from $CO_2(25)/H_2(75)$ over a $Cu/ZnO/ZrO_2$ catalyst at 523 K. Reaction conditions: SV = 180 000 h^{-1}, pressure = 5 MPa for H_2O addition, and 3.5 MPa for CO addition. r_0 and r are the rates of methanol synthesis or CO formation without and with the addition of H_2O or CO to the feed respectively.

When using a feed gas mixture containing a higher amount of CO and a lower amount of CO_2, which is normally used in industrial processes for methanol synthesis from natural gas, the yield of methanol increased almost linearly with increasing 1/SV, as shown in Fig. 3. This finding can be explained as follows: methanol and water are formed via reaction [1] and then the water formed reacts with CO to produce CO_2 and hydrogen via the reverse of reaction [2]. Accordingly, methanol is apparently produced from CO and hydrogen in the feed gas mixture, and a very small amount of water, which slightly suppresses the rate of methanol synthesis, is formed.[3]

Development of practical catalysts for methanol synthesis

As a first step, the effects of various metal oxides contained in Cu/ZnO-based ternary catalysts ($Cu/ZnO/M_xO_y$) on their activities for methanol synthesis from CO_2 and hydrogen were investigated. Al_2O_3. Ga_2O_3, ZrO_2 and Cr_2O_3 were found to increase the activity of a Cu/ZnO catalyst. Figure 5 shows the methanol synthesis activity of Cu/ZnO-based ternary catalysts containing Al_2O_3, Ga_2O_3, ZrO_2 and Cr_2O_3 on varying the content from 5 to 40 wt% as a function of copper surface area.[3] Figure 5 strongly suggests that the role of metal oxides contained in Cu/ZnO-based catalysts should be classified into two categories: (1) Al_2O_3 or ZrO_2 improves the surface area of copper, i.e. the dispersion of copper particles in the catalyst; (2) Ga_2O_3 or Cr_2O_3 increases the specific activity, i.e. the activity per unit Cu surface area of the catalyst.

In the second step, Cu/ZnO-based multicomponent catalysts were designed by selecting adequate metal oxides on the basis of the role of metal oxides described above. Figure 6 shows the activities of the multicomponent catalysts developed ($Cu/ZnO/ZrO_2/Al_2O_3$ and $Cu/ZnO/ZrO_2/Al_2O_3/Ga_2O_3$), catalyst and a Cu/ZnO catalyst as a function of the temperature of pretreatment in hydrogen ranging from 523 to 723 K.[3] Figure 6 clearly indicates that

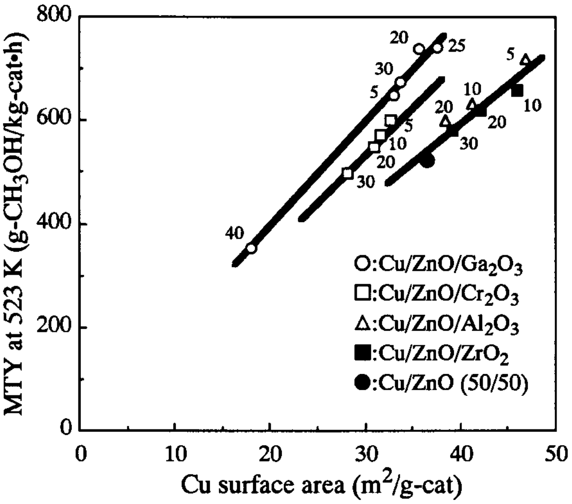

Figure 5 Methanol synthesis activity (MTY) of various Cu/ZnO-based ternary catalysts as a function of copper surface area. The catalysts and the contents of metal oxides in the catalysts are indicated in the figure. Copper content of the catalysts was 50 wt%. Reaction conditions: 523 K, 5 MPa, $H_2/CO_2 = 3$, F/W = 18 000 ml-feed (g-cat h)$^{-1}$.

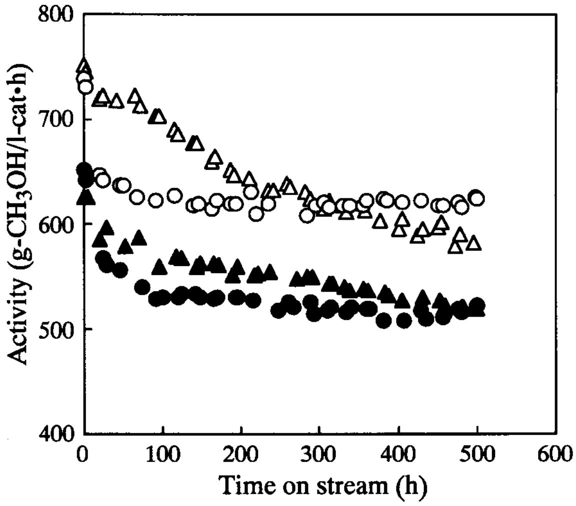

Figure 7 The effect of a small amount of silica added to a Cu/ZnO/ZrO_2/Al_2O_3 catalyst on its long-term stability during methanol synthesis. Catalyst: (△) without SiO_2, calcined at 873 K; (▲) without SiO_2, calcined at 623 K; (○) with 0.6 wt% SiO_2, calcined at 873 K; (●) with 0.6 wt% SiO_2, calcined at 623 K. Reaction conditions: 523 K, 5 MPa, SV = 10,000 h^{-1}, $CO_2/CO/H_2 = 22/3/75$.

the multicomponent catalysts are more active than the ternary or binary catalysts. Furthermore, the multicomponent catalysts were found to be highly active even after the treatment of the catalysts in flowing hydrogen at 723 K, indicating that their thermal stabilities are extremely high.

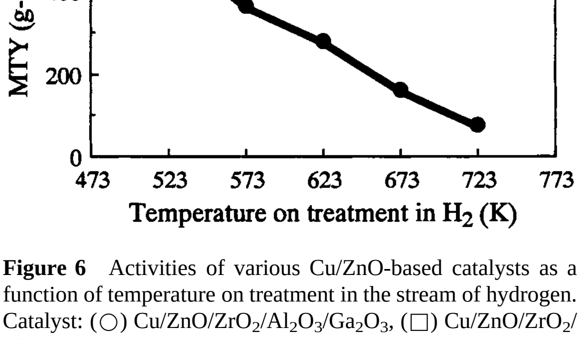

Figure 6 Activities of various Cu/ZnO-based catalysts as a function of temperature on treatment in the stream of hydrogen. Catalyst: (○) Cu/ZnO/ZrO_2/Al_2O_3/Ga_2O_3, (□) Cu/ZnO/ZrO_2/Al_2O_3, (▲) Cu(50)/ZnO(45)/Al_2O_3(5), (●) Cu(50)/ZnO(50). Reaction conditions were the same as shown in Fig. 5.

In the third step, many attempts were made at improving the long-term stability of Cu/ZnO-based multicomponent catalysts during methanol synthesis.[4,5] Finally, a small amount of silica incorporated into the catalysts by the adsorption of colloidal silica on the precipitates prepared by coprecipitation was found to improve greatly their long-term stabilities. Calcining the catalyst at high temperatures around 873 K is also important for stabilizing the catalyst activity.[5,6] The activity of a Cu/ZnO/ZrO_2/Al_2O_3 catalyst containing 0.6 wt% of silica and calcined at 873 K decreased by 10% of its initial activity in 40 h of methanol synthesis, but after that time no significant decrease in the activity was observed until 500 h, as shown in Fig. 7. On the other hand, the activity of the catalyst without silica decreased monotonously and did not become stable until 500 h. Table 1 shows both the surface area and copper surface area of the catalysts without and with silica as a function of time on stream in methanol synthesis. Both the surface area and the copper surface area changed in the same manner as the activity of the catalyst did. Figures 8 and 9 show the XRD patterns for the catalysts without and with silica respectively as a function of time on stream in

Table 1 Changes in the surface area and copper surface area of Cu/ZnO/ZrO_2/Al_2O_3 catalysts without and with silica during methanol synthesis from CO_2 and hydrogen

Catalyst[a]	Time on stream (h)	Surface area[b] ($m^2\,ml^{-1}$)	Cu surface area[b] ($m^2\,ml^{-1}$)	Activity[c] ($g\,h^{-1}$ CH_3OH)
Cu/ZnO/ZrO_2/Al_2O_3 without SiO_2	1	82.9	24.9	750
	141	75.2	23.6	679
	500	62.7	19.3	583
Cu/ZnO/ZrO_2/Al_2O_3 with 0.6 wt% SiO_2	1	85.3	27.9	721
	20	78.8	23.2	632
	90	76.9	22.1	607
	500	76.8	22.6	609
Cu/ZnO/ZrO_2/Al_2O_3 with 2.2 wt% SiO_2	1	73.3	20.0	636
	163	73.5	13.8	395

[a] Calcined at 873 K.
[b] Determined after the methanol synthesis reaction.
[c] Per liter of catalyst. Reaction conditions: 523 K, 5 MPa, SV = 10,000 h^{-1}, CO_2/CO/H_2 = 22/3/75.

methanol synthesis. The XRD peaks assigned to ZnO in the catalyst without silica increased greatly with an increase in time on stream, whereas those peaks for the catalyst containing 0.6 wt% of silica hardly changed. Furthermore, the effect of silica on the stability of a Cu/ZnO/Al_2O_3 catalyst was similar to that for a Cu/ZnO/ZrO_2/Al_2O_3 catalyst, although the activity of a Cu/ZnO/Al_2O_3 catalyst was around 20% lower than that of a Cu/ZnO/ZrO_2/

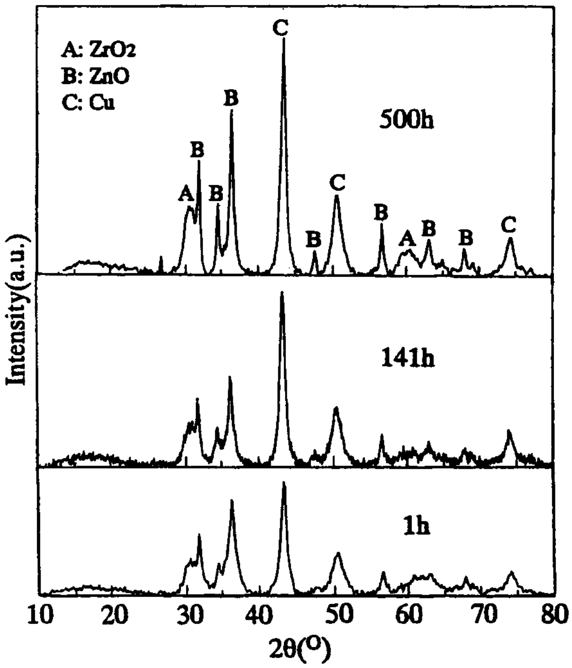

Figure 8 XRD patterns for a Cu/ZnO/ZrO_2/Al_2O_3 catalyst without silica as a function of time on stream in methanol synthesis.

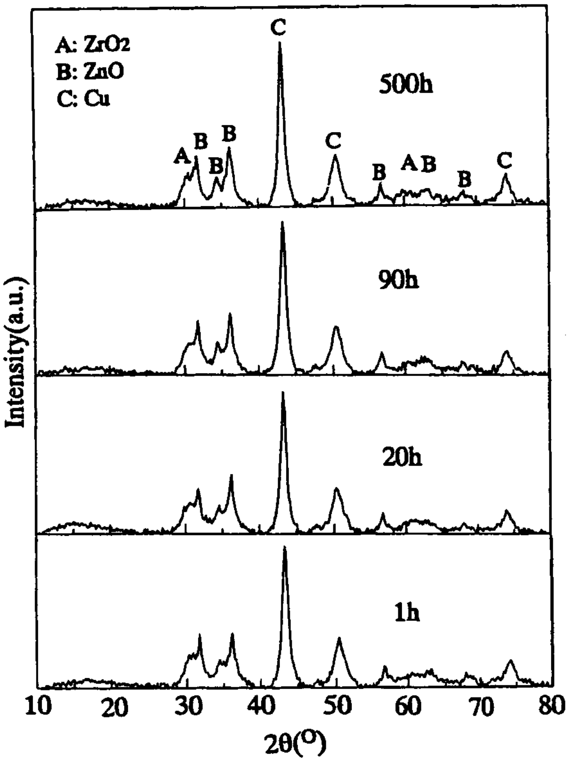

Figure 9 XRD patterns for a Cu/ZnO/ZrO_2/Al_2O_3 catalyst containing 0.6 wt% of SiO_2 as a function of time on stream in methanol synthesis.

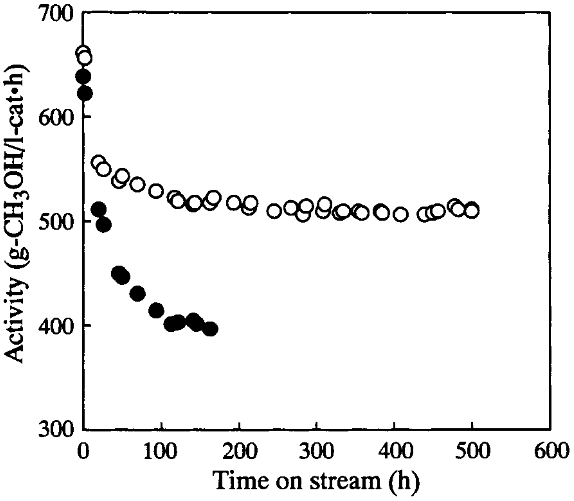

Figure 10 The effect of a larger amount of silica added to a Cu/ZnO/ZrO_2/Al_2O_3 catalyst on its activity change. Catalyst: (○) with 1.1 wt% SiO_2, calcined at 873 K, (●) with 2.2 wt% SiO_2, calcined at 873 K. Reaction conditions were the same as shown in Fig. 6.

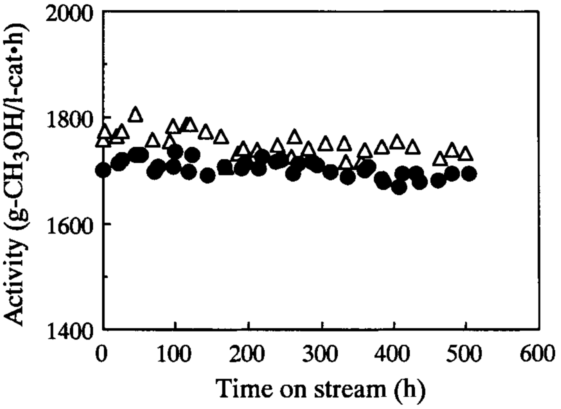

Figure 11 The long-term stability of a Cu/ZnO/ZrO_2/Al_2O_3 catalyst (△) and a Cu/ZnO/ZrO_2/Al_2O_3/SiO_2 catalyst (●) during methanol synthesis from a CO-rich feed (CO/CO_2/H_2 = 25/6/69). Reaction conditions: 523 K, 5 MPa, SV = 10,000 h^{-1}.

Al_2O_3 catalyst. The findings shown above strongly suggest that the catalyst deactivation in methanol synthesis could be caused by the crystallization of the metal oxides contained in the catalyst, especially ZnO, which leads to a reduction of the surface area and the copper surface area. These findings also clearly indicate that the silica added to the catalyst can suppress the crystallization of ZnO in the catalyst to improve the long-term stability of the catalyst during methanol synthesis from CO_2 and hydrogen.

The addition of a larger amount of silica to a Cu/ZnO/ZrO_2/Al_2O_3 catalyst gave slightly different results. Figure 10 shows the decrease in the activity of a Cu/ZnO/ZrO_2/Al_2O_3 catalyst containing a larger amount of silica (1.1 or 2.2 wt%) during methanol synthesis under the same reaction conditions as shown in Fig. 7. The initial decrease of its activity was much larger than that for the catalyst containing 0.6 wt% of SiO_2. In addition, as shown in Table 1, the surface area of the catalyst containing 2.2 wt% of SiO_2 did not change during the methanol synthesis for 160 h, whereas the copper surface area and the activity of the catalyst decreased by 31% and by 38% respectively. These findings suggest that some of the silica might move to and block the active sites on the copper surface to result in a large initial decrease in the activity of the catalyst with no change in the surface area of the catalyst. This could also explain the initial decrease in the activity of the catalyst containing 0.6 wt% of silica during the 40 h from the beginning of methanol synthesis, as shown in Fig. 7. The optimum amount of silica in the catalyst was determined to be 0.5 to 0.9 wt%.[6,7]

Figure 11 shows the change in the activities of the catalysts without and with silica with time on stream in methanol synthesis from CO-rich gas; this indicates that even the catalyst without silica was hardly deactivated. XRD measurements revealed that ZnO peaks for the catalysts scarcely increased during methanol synthesis for 500 h. Since only a small amount of water is produced in methanol synthesis from CO-rich gas as described before, the findings shown above strongly suggest that a larger amount of water produced should accelerate the crystallization of ZnO contained in the catalysts during methanol synthesis from CO_2 and hydrogen.

The Cu/ZnO/ZrO_2/Al_2O_3 catalyst containing 0.6 wt% of SiO_2 has been very stable during a long-term (about 1 year) operation for methanol synthesis from a feed gas containing a small amount of water and CH_3OH, the composition of which is similar to that of the feed gas to the reactor in the bench plant, as shown in Fig. 12.

Methanol synthesis in a bench plant

A small bench plant with a capacity of 50 kg day^{-1} of CH_3OH, which was equipped with facilities for

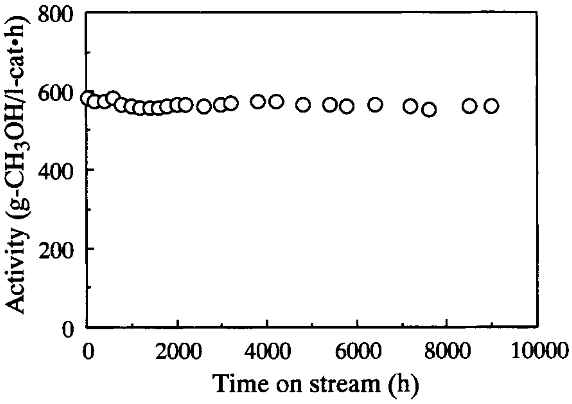

Figure 12 The long-term stability of a $Cu/ZnO/ZrO_2/Al_2O_3/SiO_2$ catalyst during methanol synthesis from a feed gas containing CH_3OH and H_2O. Reaction conditions: 523 K, 5 MPa, SV = 10,000 h^{-1}, $CO_2/CO/H_2$ = 22/3/75, partial pressure of CH_3OH = 11 kPa, partial pressure of H_2O = 6 kPa.

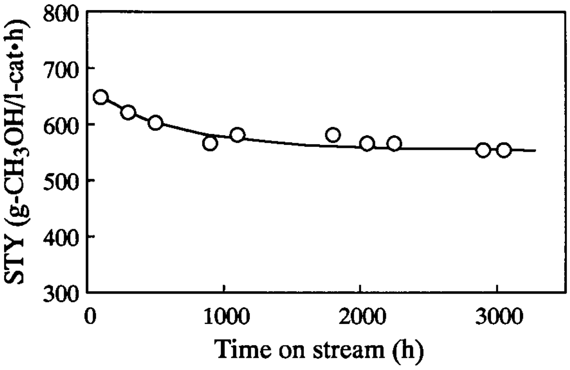

Figure 13 Change in the activity of a developed catalyst ($Cu/ZnO/ZrO_2/Al_2O_3/SiO_2$) during methanol synthesis in the bench plant. Reaction conditions: 523 K, 5 MPa, 10,000 h^{-1}.

recycling unreacted gases and gaseous products, was constructed for testing the multicomponent catalysts developed under practical reaction conditions for methanol synthesis from CO_2 and hydrogen. The present bench plant has been successfully operated so far.[8,9]

A previously developed $Cu/ZnO/ZrO_2/Al_2O_3/SiO_2$ catalyst was used for methanol synthesis operation in the bench plant. The catalyst was found to be very stable during long-term methanol synthesis in the bench plant recycling unreacted gases and gaseous products, as shown in Fig. 13.

The products of CO_2 hydrogenation at 473 to 543 K under a total pressure of 3 to 7 MPa in the bench plant were methanol, CO, water, methane, ethane, dimethyl ether, methyl formate, ethanol, propanols and butanol, but the yields of the products other than methanol, CO and water were very small. The selectivity to methanol in the products, except CO and water, was 99.7%, as shown in Table 2.

Figure 14 shows the production rate of methanol under various reaction conditions. The production rate of methanol increased with increasing reaction

Table 2 Compositions of the make-up gas and the gases at the inlet and at the outlet of the reactor, and the selectivity to various products in methanol synthesis in the bench plant[a]

	Gas composition (%)			
Compound	Make-up gas	Inlet gas	Outlet gas	Selectivity[b] (%)
H_2	73.8	74.8	68.9	
CO_2	26.2	22.2	19.6	
CO		2.65	2.97	
H_2O		0.00	4.30	
CH_3OH		0.22	4.61	99.72
Methane		0.11	0.12	0.025
Dimethyl ether		60 ppm	88 ppm	0.106
Methyl formate		21 ppm	56 ppm	0.150
Ethane		10 ppm	11 ppm	0.00

[a] Reaction conditions: catalyst = $Cu/ZnO/ZrO_2/Al_2O_3/SiO_2$, 5 MPa, 523 K, SV = 10,000 h^{-1}, H_2/CO_2 ratio in the make-up gas = 2.82, purge ratio = 0.5% of the flow rate of the inlet gas.
[b] Selectivity (%) = (CO_2 converted to each product except CO, mol) × 100/(Sum of CO_2 converted to each product except CO, mol).

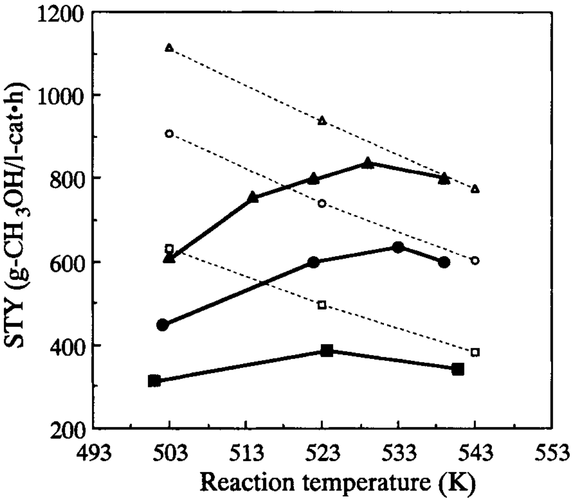

Figure 14 The activity of a $Cu/ZnO/ZrO_2/Al_2O_3/SiO_2$ catalyst for methanol synthesis in a bench plant. Reaction conditions: pressure (△,▲) = 7 MPa, (○,●) = 5 MPa, (□,■) = 3 MPa, SV = 10,000 h^{-1}, purge ratio = 0.5%; △, ○ and □ represents STY at equilibrium.

pressure. The production rate of methanol at a given pressure approached the value at reaction equilibrium with increasing temperature, and reached an equilibrium value at a temperature between around 530 and 540 K. The maximum production rate of methanol was obtained at around 530 K.

Table 3 shows the purity of crude methanol, except for water, produced in the bench plant, and this is compared with the purity of methanol produced in a present-day commercial plant for methanol synthesis from syngas.[10] The purity of crude methanol produced in the present work was 99.9 wt%, and is higher than that of the crude methanol from a commercial methanol synthesis from syngas. The CO concentration in the feed gas to the reactor for methanol synthesis from CO_2 and hydrogen is much lower than that for methanol synthesis from syngas. It is well known that CO is much more reactive with hydrogen to produce methyl formate, higher alcohols and higher hydrocarbons than CO_2. Therefore, it is strongly suggested that a lower CO concentration in the feed gas to the reactor should result in lower yields of by-products and a higher methanol purity.

Compared with methanol synthesis from syngas, the disadvantages and the advantages of methanol synthesis from CO_2 and hydrogen are summarized in the following.

Disadvantages: (1) the lower yield of methanol at equilibrium in CO_2 hydrogenation may result in a larger amount of recycle gas in a practical methanol synthesis process; (2) the larger amount of water produced in methanol synthesis from CO_2 and hydrogen reduces the rate of methanol synthesis and causes the deactivation of the catalyst.

Advantages: (1) the lower heat released by methanol synthesis from CO_2 and hydrogen which is around half of that by methanol synthesis from syngas, could lead to a simpler methanol synthesis process; (2) the higher selectivity to methanol in CO_2 hydrogenation might make the operation of purging some amount of recycle gas unnecessary, and lead to a simpler purification process.

CONCLUSIONS

The present joint research on methanol synthesis from CO_2 and hydrogen has led to the development of high-performance Cu/ZnO-based multicompo-

Table 3 Comparison of the purity of the methanol produced in our bench plant[a] with that of the methanol produced in a commercial plant for methanol synthesis from syngas[b]

Compound		Composition: This work	Composition: Commercial plant
Methanol (wt%)	CH_3OH	99.95	99.59
Methyl formate (ppm)	$HCOOCH_3$	460	700
Higher alcohols (C_2–C_4) (ppm)	ROH	70	530
Hydrocarbons (C_6–C_{10}) (ppm)	C_nH_m	—	50
Dimethyl ether (ppm)	$(CH_3)_2O$	—	230

[a] Reaction conditions: catalyst = $Cu/ZnO/ZrO_2/Al_2O_3/SiO_2$, temperature = 523 K, total pressure = 5 MPa, H_2/CO_2 ratio in the make-up gas = 3.
[b] Cited in Ref. 10.

nent catalysts ($Cu/ZnO/ZrO_2/Al_2O_3/SiO_2$ and $Cu/ZnO/ZrO_2/Al_2O_3/Ga_2O_3/SiO_2$) that are highly active and extremely stable.

A bench plant with a capacity of 50 kg day^{-1} of CH_3OH was successfully operated using the catalysts developed. The selectivity to methanol synthesis was 99.7%, and the purity of crude methanol produced was 99.9%, which was higher than that of crude methanol produced from syngas in a present-day commercial plant.

Our group greatly hopes that the technologies developed in the present joint research will contribute to CO_2 mitigation and future industries.

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