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Methanol synthesis from CO_2 and H_2 in a bench-scale test plant†

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A small-scale test plant with a methanol production capacity of 50 kg day^{-1} has been designed and constructed in order to examine the performance of a previously developed Cu/ZnO-based catalyst under practical reaction conditions. The reaction model for methanol synthesis over the developed catalyst is presented. In addition, the methanol production rates measured in the test plant were found to fit the rates calculated based on the kinetic equations. A 4000 t day^{-1} methanol synthesis plant from CO_2 and H_2 was designed based on the kinetic equations and the selectivity to methanol over the developed catalyst. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: hydrogenation catalyst; methanol synthesis; CO_2 hydrogenation; copper zinc oxide catalyst

INTRODUCTION

RITE and three national institutes (NIMC, NIRE and ONRI) of MITI have been jointly carrying out an R & D project 'CO_2 Fixation and Utilization Using Catalytic Hydrogenation Reaction'. In this project, methanol synthesis from CO_2 and H_2 is one of the key technologies to be developed. According to a model system proposed in the project, an 8000 t day^{-1} methanol synthesis plant is required for converting 60% of CO_2 emitted from a 1000 MW coal firing power plant into methanol. Our group has developed several high performance Cu/ZnO-based catalyst.[1,2] Furthermore, the addition of a small amount of silica to the catalyst was found to improve the long-term stability of the catalyst. In addition, calcining the catalyst at high temperatures of 873 K also improved stability.[3,4]

A small-scale test plant with a methanol production capacity of 50 kg day^{-1} was constructed 3 years ago. The objects of the test plant are to evaluate the catalysts developed under practical reaction conditions and establish the optimum operation conditions for methanol synthesis from CO_2 and H_2. The catalyst developed has high activity under the practical reaction conditions, and the purity of methanol produced is extremely high.[5,6]

In the present study, a large-scale methanol synthesis plant from CO_2 and H_2 was designed based on the reaction kinetics and the selectivity to methanol over a developed catalyst.

EXPERIMENTAL

The catalyst developed ($Cu/ZnO/ZrO_2/Al_2O_3/SiO_2$) was prepared by a conventional coprecipitation method. The catalyst was pelletized to a cylindrical shape of 3 mm diameter by 3 mm high. The stability and the selectivity of the catalyst developed was measured by a 50 kg day^{-1} test plant with 3 l of catalyst.

Before the reaction, the catalyst fixed at the reactor was reduced in a gas mixture of 5% of H_2 and 95% of N_2 at a space velocity (SV) of 1000 h^{-1}. The reduction of the catalysts was performed in three steps: (1) the temperature was maintained at

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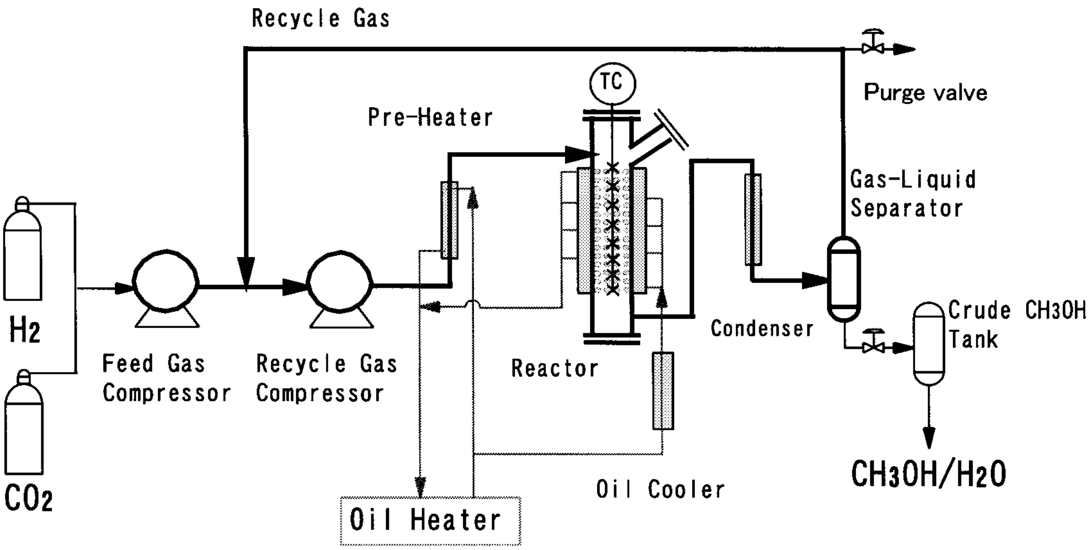

Figure 1 Flow diagram of a 50 kg day^{-1} test plant for methanol synthesis.

413 K for 5 h; (2) the temperature was raised to 543 K in 2 h; (3) the temperature was maintained at 543 K for 2 h.

Figure 1 shows a flow diagram of the test plant, which was equipped with facilities for recycling unreacted gases. The make-up gas (mixture of CO_2 and H_2) supplied from gas cylinders was compressed along with recycled gases, and then fed into the reaction tube through a pre-heater. The stainless-steel reactor was of tubular type with 38.4 mm ID and 4000 mm L in length. The reactor was surrounded by a heat exchanger divided into four parts to facilitate isothermal operation. The temperature profile along the bed was measured by means of eight thermocouples situated at the central axis of the reactor. The temperature difference along the reactor was less than 2 K. The pressure was controlled within 0.1 MPa by changing the total flow rate of the make-up gas, in which the H_2/CO_2 ratio was adjusted with the flow controllers. The flow rate of the inlet gas to the reactor was controlled by the flow controller placed just after the recycle gas compressor. Reaction products were cooled down, and then the mixture of methanol and water was separated at the gas–liquid separator from unreacted gases. Unreacted gases and gaseous products, such as CO, methane and so on, excluding small amounts of purge gas, were recycled back to the reactor. The mixture of methanol and water was taken out of the plant and stored in a container.

The make-up gas, the inlet and outlet gases of the reactor and the recycle gas were analyzed with an on-line gas chromatograph. The gas chromatography was employed for analysis of the reaction products; H_2, CO and CO_2 were analyzed by thermal-conductivity detector (TCD); methanol, dimethyl ether, methyl formate and hydrocarbons were analyzed by the flame ionization detector (FID).

A space time yield of methanol and the CO_2 conversion to methanol were calculated from the weight of crude methanol produced and the flow rate of the inlet gas. Selectivity and CO_2 conversions to methanol and by-products, excluding methane and ethane, were calculated from the material balance between the inlet gas and the outlet gas of the reactor. The material balance was determined from the analysis data obtained using gas chromatographs. Selectivity and CO_2 conversions to methane and ethane were calculated from the difference between concentrations at different purge flow rates, because their concentration differences between the inlet gas and the outlet gas of reactor were so small that CO_2 conversions to them could not be calculated correctly. A long-term test for methanol synthesis from CO_2 and H_2 over the developed catalyst was carried out using the test plant. A continuous operation was carried out for 1000 h under the reaction conditions of 523 K, 5 MPa and SV of 10,000 h^{-1}. After the continuous run, the operations were intermittently performed under various reaction conditions up to

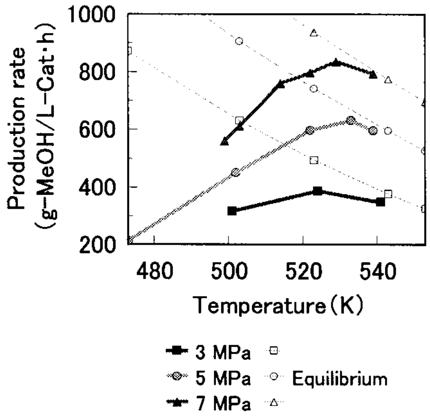

Figure 2 Production rate of methanol under various reaction conditions. Reaction conditions: SV = 10,000 h^{-1}; purge rate, 0.5% of the inlet gas, catalyst, $Cu/ZnO/ZrO_2/Al_2O_3SiO_2$.

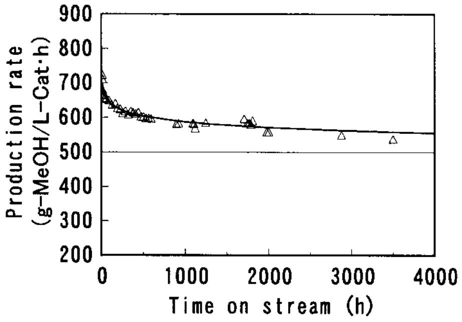

Figure 3 The production rate of methanol as a function of time. Reaction conditions: 523 K, 5 MPa, SV = 10,000 h^{-1}; catalyst, $Cu/ZnO/ZrO_2/Al_2O_3/SiO_2$. The line is to regression curve.

the total operation period of 3500 h. The experiments for examining the effects of reaction conditions on the product selectivity were carried out under the following reaction conditions: temperature: 503–543 K; total pressure: 3–7 MPa; SV: 5000–20,000 h^{-1}; feed gas composition: CO_2 (26%)/H_2 (74%).

RESULTS AND DISCUSSION

Figure 2 shows the production rate of methanol at SV = 10,000 h^{-1} under different pressures as a function of reaction temperature ranging from 473 to 540 K. The production rate was 580 g h^{-1} of MeOH per liter of catalyst under the conditions of 523 K, 5 MPa and SV = 10,000 h^{-1}, which is 20% lower than that at reaction equilibrium. The production rate of methanol increased with increasing reaction pressure. The production rate of methanol at a given pressure approached the value at equilibrium with increasing temperature. The methanol synthesis reaction over the developed catalyst was found to attain equilibrium at 543 K. This methanol synthesis rate was almost the same as the value calculated from the kinetic equations proposed in another study by our group. The following reaction formulas were considered for deducing the reaction kinetics:

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

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

A long-term methanol synthesis test was performed using the test plant under the following reaction

Table 1 Composition of the make-up gas, and the inlet and outlet gases of the reactor and selectivities[a]

Component	Make up (%)	Inlet (%)	Outlet (%)	Selectivity (%)
H_2	73.8	74.8	68.5	
CO_2	26.2	22.2	19.5	
CO		2.7	3.0	
H_2O		0.0	4.3	
Methanol		0.2	4.6	99.7
Methane		*1100*[b]	*1200*[b]	0.025
Dimethyl ether		*60*	*88*	0.106
Methyl formate		*21*	*56*	0.167
Ethane		*10*	*11*	0.000

[a] Reaction conditions: catalyst, $Cu/ZnO/ZrO_2/Al_2O_3/SiO_2$; temperature, 523 K; pressure, 5 MPa; SV = 10,000 h^{-1}; H_2/CO_2 ratio in the make-up gas, 2.82; purge rate, 0.5% of the inlet gas.

[b] Units are parts per million.

Table 2 Compositions of liquid products at various reaction temperatures[a]

Compound		Composition (%) at the reaction temperature			
		473 K	503 K	523 K	543 K
Methanol	CH_3OH	64.2	63.7	63.8	64.0
Methyl formate	$HCOOCH_3$	*663*[b]	*472*[b]	*292*[b]	*326*[b]
Ethanol	C_2H_5OH	ND	*6*[b]	*22*[b]	*112*[b]
1-Propanol	1-C_3H_7OH	ND	*4*[b]	*10*[b]	*45*[b]
2-Propanol	2-C_3H_7OH	ND	ND	*8*[b]	*15*[b]
2-Butanol	2-C_4H_9OH	ND	*3*[b]	*16*[b]	*45*[b]
CH_3OH/products except H_2O		99.90	99.92	99.95	99.91

[a] Reaction conditions: catalyst, $Cu/ZnO/ZrO_2/Al_2O_3/SiO_2$; pressure, 5 MPa; SV = 10,000 h^{-1}; H_2/CO_2 ratio in the inlet gas, 3; purge rate, 0.5% of the inlet gas.

[b] Units are parts per million by weight.

conditions: 523 K, 5 MPa and SV = 10,000 h^{-1}. Although the production rate was over 700 g h^{-1} of MeOH per liter of catalyst initially, it gradually decreased with reaction time. The production rate at 1,000 h on stream was around 580 g h^{-1} of MeOH per liter of catalyst, and decreased by less than 10 g h^{-1} of MeOH per liter of catalyst in the next 1,000 h. The extrapolation of the regression curve estimates that the production rate will be more than 500 g h^{-1} of MeOH per liter of catalyst in 3 years on stream. This finding clearly indicates that the developed catalyst is extremely stable under practical reaction conditions (Fig. 3).

The inlet gas of the reactor was composed of the recycle gas and make-up gas. The components, excluding CO_2 and H_2 in the inlet gas and the outlet gas of the reactor, were produced during the methanol synthesis reaction. The selectivity to various products under the reaction condition of 5 MPa, 523 K, SV = 10,000 h^{-1} are shown in Table 1. The selectivity to methanol in the products was over 99.7%, except for CO and water. The main by-products were CO, dimethyl ether (DME), methyl formate (MF), methane and ethane. The concentration of CO among the products was almost constant through the test, and nearly equal to the CO concentration at equilibrium of the reverse water-gas shift reaction at the reaction temperature. The concentration of each component in the outlet gas had no direct relation with its selectivity. The concentration of methane at the outlet of the reactor was larger than that of DME and MF, but the selectivity of methane was smaller than that of DME and MF.

Table 2 shows the composition of the liquid products obtained from the operation under different temperatures. The main compositions of the liquid products were methanol and water, but a very low concentration of MF, ethanol, higher alcohol and so on were observed as the by-products. The purity of the methanol produced at any reaction temperature tested was higher than 99.9 wt%. The purity of the methanol produced at 523 K was the highest, mainly because there was more production of MF at 473 K and more higher alcohols were formed at 543 K.

Figures 4, 5 and 6 show the selectivities to various products as a function of contact time, temperature and pressure respectively. The selectivity to methanol was found to increase with decreasing contact time, temperature and pressure. The selectivities to DME and methane changed more greatly with contact time and temperature than with pressure. The change in the selectivity to

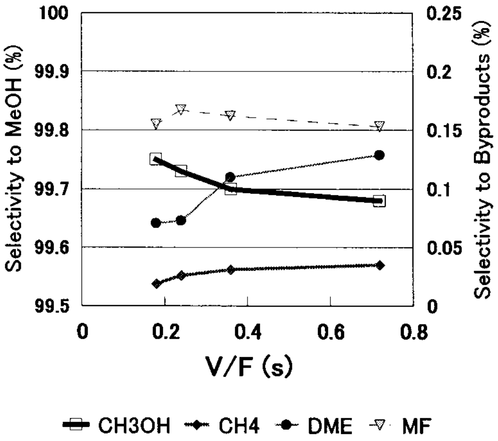

Figure 4 Selectivities as a function of contact time. Reaction conditions: 523 K, 5 MPa; catalyst, $Cu/ZnO/ZrO_2/Al_2O_3/SiO_2$.

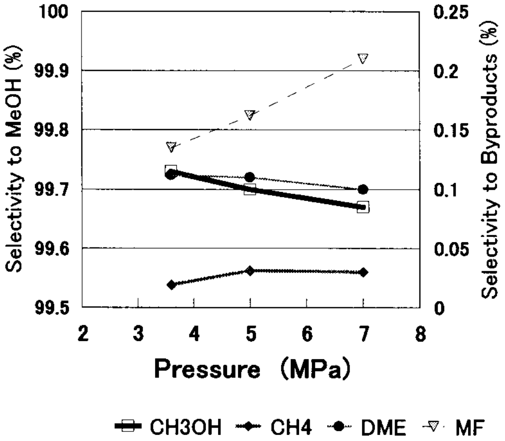

Figure 5 Selectivities as a function of pressure. Reaction conditions: 523 K, SV = 10,000 h^{-1}; catalyst, $Cu/ZnO/ZrO_2/Al_2O_3/SiO_2$.

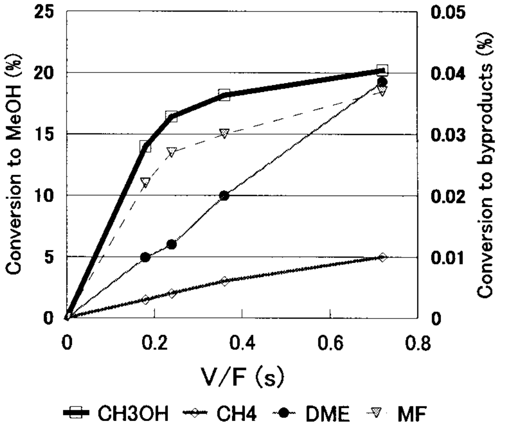

Figure 7 CO_2 conversions as a function of contact time. Reaction conditions: 523 K, 5 MPa, catalyst, $Cu/ZnO/ZrO_2/Al_2O_3/SiO_2$.

MF was smaller than to DME and methane with a change in contact time or temperature, but larger with a change in pressure.

Figure 7 shows CO_2 conversions to methanol and by-products excluding CO under the reaction conditions of 5 MPa and 523 K as a function of contact time. CO_2 conversions to by-products were much smaller than that to methanol. The CO_2 conversions to methanol increased and finally reached the equilibrium value with increasing contact time.

CO_2 conversions to DME and methane rise in proportion to a rise in contact time. The CO_2 conversion to ethane was always 1% of methane. This finding suggests that the production rates of DME and methane should be much smaller than that of methanol. On the other hand, the CO_2 conversion to MF increased with increasing CO_2 conversion to methanol. The concentration of MF at the outlet of the reactor was close to the value calculated from the equilibrium constant of the carbonylation of methanol from MF.

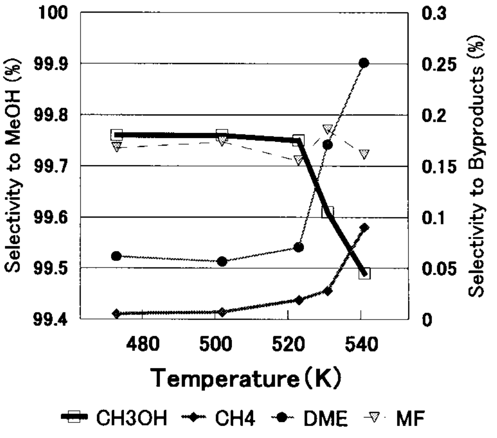

Figure 6 Selectivities as a function of temperature. Reaction conditions: 5 MPa, SV = 10,000 h^{-1}, catalyst, $Cu/ZnO/ZrO_2/Al_2O_3/SiO_2$.

After the purge valve was closed, a change in the flow rate of the gas from zero to 0.5% at the inlet led to a gradual increase in the concentrations of the methane and ethane. They became steady after 50 h at a level higher than before the purge valve was closed as shown in Fig. 8. On the other hand, the concentrations of CO and MF at the outlet of the reactor were independent of the purge flow rate, probably because their concentrations were controlled by the equilibrium of their formation reactions. The concentrations of DME and methane remained at some steady level even when the purge flow rate was zero. Probably some of them were dissolved in the crude methanol containing H_2O and MF and discharged from the gas–liquid separator. Since the steady concentration of the inert gases, such as methane and ethane, is so low, the inert gases should not inhibit the methanol synthesis reaction. The purging operation must be unnecessary in this process for methanol synthesis from CO_2 and H_2, unlike methanol synthesis from syngas.

Compared with methanol synthesis from syngas,[6] methanol synthesis from CO_2 and H_2 has such disadvantages as the low equilibrium conversion to

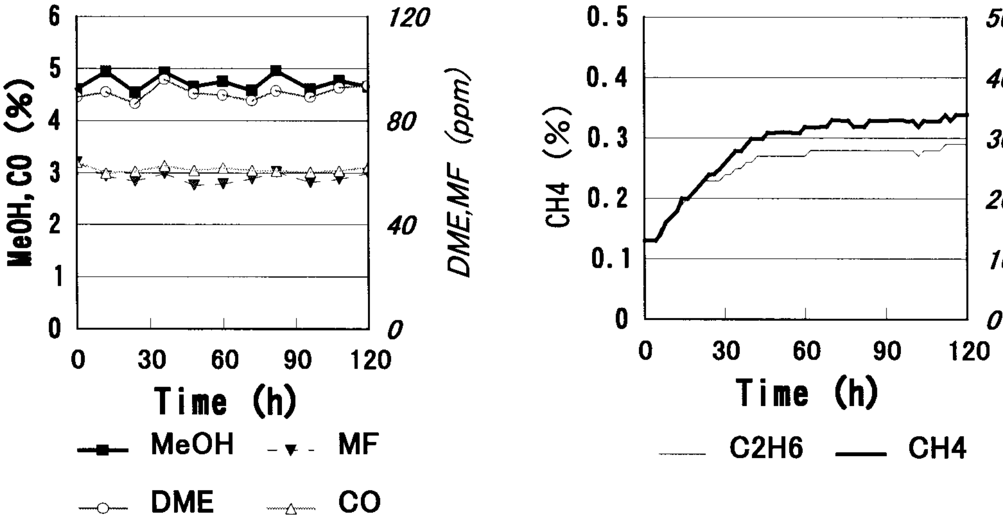

Figure 8 Concentration change of outlet gas of the reactor after stopping purge flow. Reaction conditions: 523 K, 5 MPa, SV = 10,000 h^{-1}; catalyst, $Cu/ZnO/ZrO_2/Al_2O_3/SiO_2$.

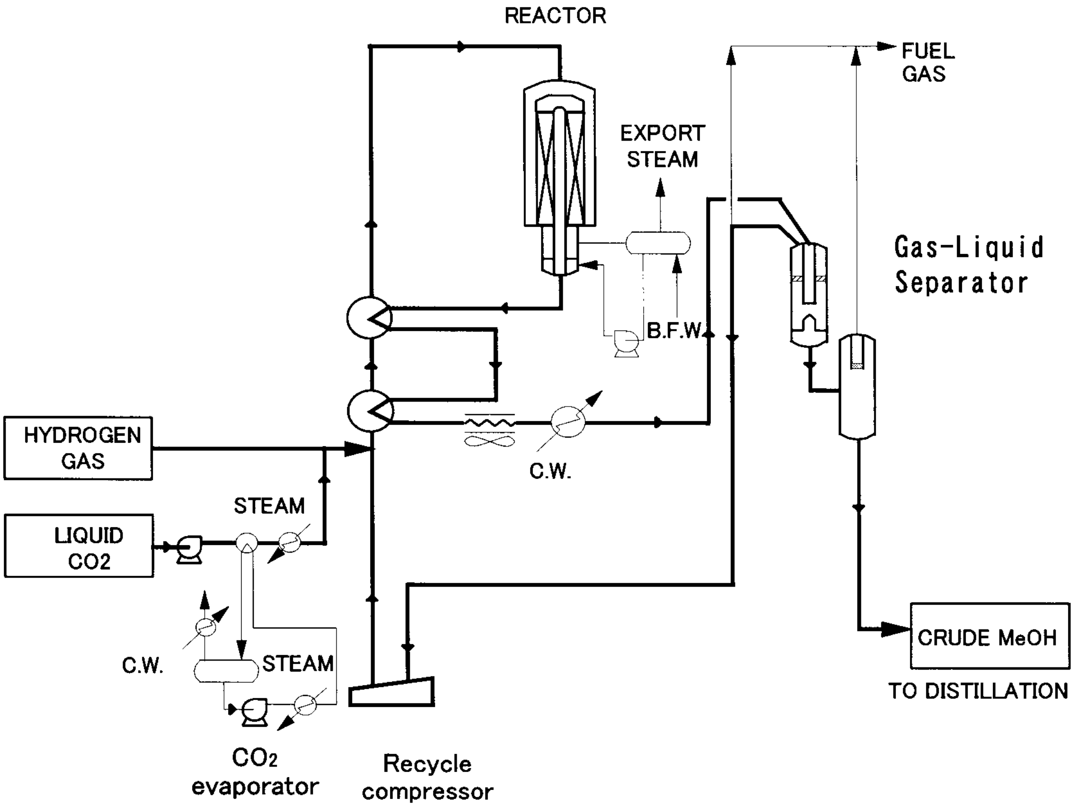

Figure 9 Process flow scheme for a 4000 t day^{-1} methanol plant from CO_2 and H_2.

methanol and the formation of a larger amount of H_2O. Nevertheless, the present study has revealed that methanol synthesis from CO_2 and H_2 has the following advantages.

(1) The selectivity to methanol in the CO_2 hydrogenation is extremely high.
(2) Higher alcohols and ketones, which are difficult to remove in the distillation stage of crude methanol, are very low in concentration.
(3) The methane formation is limited to such a low concentration that a purge operation is not necessary. Moreover, our developed catalyst is very stable in a long-term operation, although the higher amount of H_2O produced in the methanol synthesis from CO_2 and H_2 is unfavorable for the stability of the Cu/ZnO-based catalyst.

DESIGN OF A LARGE-SCALE PLANT

An 8000 t day^{-1} methanol synthesis plant from CO_2 and H_2 composed of two train facilities, each of which has a capacity of 4000 t day^{-1}, was designed based on the kinetic equations and the selectivity to methanol over the developed catalyst. The design of the methanol synthesis reactor was entrusted to Toyo Engineering Corporation (TEC). The process flow scheme for a 4000 t day^{-1} methanol plant is shown in Fig. 9. A multi-stage indirect cooling and radial flow (MRF-Z®) reactor was developed by TEC.[7] The size of reactor for methanol synthesis from CO_2 and H_2 is almost the same as an ordinary reactor for methanol synthesis from natural gas. The MRF-Z® reactor employs bayonet boiler tubes for the reaction heat removal together with radial flow of reaction gases across the catalyst bed in the shellside. A multi-stage indirect cooling system enables control of the reaction conditions along the path of the maximum reaction rate curve in order to achieve maximum conversion per pass and minimum catalyst volume per unit product. In addition, a radial flow system ensures the achievement of a higher heat transfer coefficient, less pressure drop and larger catalyst volume within the restricted manufacturing limit of a high-pressure vessel diameter. The MRF-Z® reactor was found one of the most promising reactors for methanol synthesis from CO_2 and H_2. The distillation system in a methanol synthesis plant from CO_2 and H_2 has some advantages over that in a methanol plant from syngas because the purity of crude methanol from CO_2 and H_2 is higher.

CONCLUSIONS

We have found that our Cu/ZnO-based multicomponent catalyst developed for methanol synthesis from CO_2 and H_2 has a high performance in the activity, the selectivity and the stability under practical reaction conditions. In addition, we have clarified the behavior of the by-products in the reactor, which could explain the effects of contact time, temperature and pressure on the selectivity to methanol. Furthermore, a 4000 t day^{-1} methanol synthesis plant from CO_2 and H_2 employing a radial gas flow reactor was designed based on the kinetic equations and the selectivity to methanol over the developed catalyst.

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