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Sustainable process for the production of methanol from CO₂ and H₂ using Cu/ZnO-based multicomponent catalyst

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Abstract

We have performed R&D project on methanol synthesis from CO₂ and hydrogen in order to contribute to CO₂ mitigation. High-performance Cu/ZnO based multicomponent catalysts were developed. The roles of metal oxides contained in Cu/ZnO-based catalysts were classified into two categories: (1) Al₂O₃ or ZrO₂ improves the dispersion of copper particles in the catalyst; (2) Ga₂O₃ or Cr₂O₃ increases the activity per unit copper surface area of the catalyst. The long-term stability of Cu/ZnO-based catalysts during methanol synthesis from CO₂ and hydrogen was improved by adding a small amount of silica to the catalysts. Silica added to the catalysts suppressed the crystallization of ZnO contained in the catalysts. The catalysts were found to be highly active and extremely stable in methanol synthesis from CO₂ and hydrogen. In the next step, a bench plant with a capacity of 50 kg day⁻¹ of CH₃OH, which was equipped with facilities for recycling unreacted gases and gaseous products, was successfully operated. 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%.

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Keywords: CO₂, Methanol, catalytic hydrogenation; copper, ZnO

1. Introduction

Development and integration of carbon consuming processes in chemical industry and new energy production is becoming a serious option to stop accumulation of carbon dioxide and other greenhouse gases in the atmosphere. We have jointly developed a new process for the transportation of non fossil energy combined with methanol synthesis from CO₂ hydrogenation [1-4]. The key technologies to be developed in this system were membrane separation of CO₂ emitted from stationary sources, H₂ production by water electrolysis using electric power derived from non-fossil energy and methanol synthesis by the catalytic hydrogenation of CO₂. A joint research project conducted by Research Institute of innovative technology for the earth (RITE) has been

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performed for developing a novel technology for methanol synthesis from CO₂ and hydrogen. From both basic and practical points of view, methanol synthesis from CO₂ 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 the operation of a small bench plant for gas-phase methanol synthesis.

2. Experimental methods

All multicomponent Cu/ZnO-based catalysts were prepared by precipitation method using metal nitrates and sodium carbonate [1]. Further details about preparation methods and characterization can be found in our previous related publications [2-4]. A conventional fixed-bed flow reactor was used for both 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 was used for investigating practical methanol synthesis operations (figure 1). The make-up gas composed of CO₂ 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 N₂O 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.

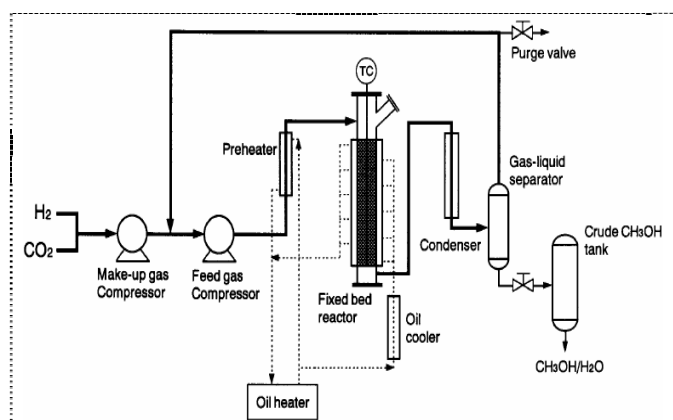
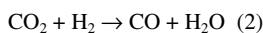


Fig. 1. Schematic diagram of a bench-scale methanol synthesis plant with a capacity of 50 kg day⁻¹. Reactor size: 3.84 mm i.d.x 4 m long; catalyst volume = 3 l.

3. Results and discussion

In the present paper we will mainly focus on the results obtained from bench plant. However, we have pointed out the main results obtained in previous steps in our methodology.

The main products of CO₂ 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 selectivity to the by-products was less than 0.1%. Methanol and CO were formed simultaneously at low conversions of CO₂ by the following two reactions:



The activity of the multicomponent catalyst was proportional to the surface area of copper, which was considered to be the main active site for the hydrogenation of CO_2 . The addition of Al_2O_3 or ZrO_2 to Cu/ZnO increased the surface area as well as the dispersion of Cu particles on the surface, while the association of Ga_2O_3 to the binary catalyst increased the activity per unit of Cu surface area (figure 2).

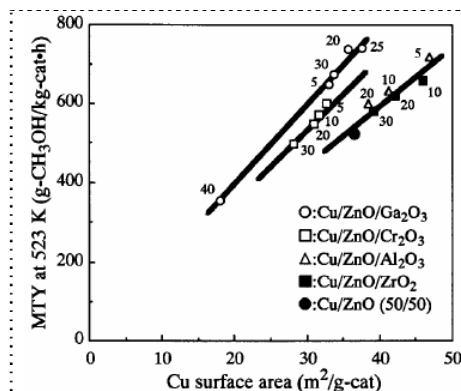


Figure 2. Methanol synthesis activity (MTY) of Cu/ZnO-based catalysts as a function of copper surface area. The catalysts and the contents of metal oxides are indicated in the figure. Copper content of the catalysts was 50 wt%. Reaction conditions: 523 K, 5 MPa, $\text{H}_2/\text{CO}_2 = 3$, $\text{F/W} = 18\ 000\ \text{ml-feed (g-cat h)}^{-1}$.

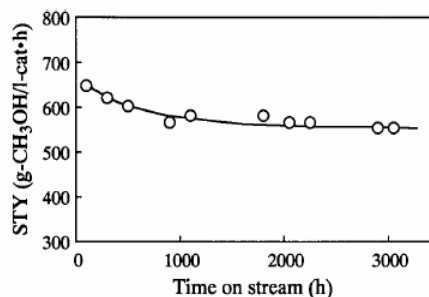


Figure 3. Change in the activity of a developed catalyst ($\text{Cu/ZnO/ZrO}_2/\text{Al}_2\text{O}_3/\text{SiO}_2$) during methanol synthesis in the bench plant. Reaction conditions: 523 K, 5 MPa, $10\ 000\ \text{h}^{-1}$.

The addition of small amounts of silica increased the stability of the catalyst [3]. Both Cu^+ and Cu^0 species were essential to catalyze the reaction and Ga_2O_3 regulated the optimal ratio of Cu^+/Cu^0 throughout the reaction. When a co-precipitated Cu/ZnO -based catalyst is used in the synthesis of methanol, ZnO has the following functions: (i) it favours the formation of appropriate precursors during the catalyst preparation, which leads to higher dispersion; (ii) in the presence of Al_2O_3 , it shows a refractory behaviour and attenuates the unavoidable agglomeration of Cu particles which takes place during a long-term operation; (iii) it improves the resistance of Cu particles to poisoning by feed gas impurities such as sulfides and chlorides and, (iv) ZnO, as a basic oxide, partially neutralizes the acidity of Al_2O_3 , preventing the transformation of methanol to dimethyl ether.

A small bench plant with a capacity of $50\ \text{kg day}^{-1}$ of CH_3OH , which was equipped with facilities for 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. A previously developed $\text{Cu/ZnO/ZrO}_2/\text{Al}_2\text{O}_3/\text{SiO}_2$ 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 products and gaseous products as shown in Figure 3.

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, propanol 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 1.

Table 1. 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

Compound	Gas composition (%)			Selectivity ^b (%)
	Make-up gas	Inlet gas	Outlet gas	
H ₂	73.8	74.8	68.9	
CO ₂	20.2	22.2	19.6	
CO		2.65	2.97	
H ₂ O		0.00	4.30	
CH ₃ OH		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

^aReaction conditions: catalyst = Cu/ZnO/ZrO₂/Al₂O₃/SiO₂, 5 MPa, 523 K, SV=10,000 h⁻¹, H₂/CO₂ ratio in the make-up gas = 2.82, purge ratio = 0.5% of the flow rate of the inlet.

^bSelectivity (%) = (CO₂ converted to a given product except CO, mol) x 100/Sum of CO₂ converted to all products except CO, mol)

Figure 4 shows the production rate of methanol under various reaction conditions. The production rate of methanol increased with increasing reaction 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 around 530-540 K. The maximum production rate of methanol was obtained at around 530 K.

Table 2 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. 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.

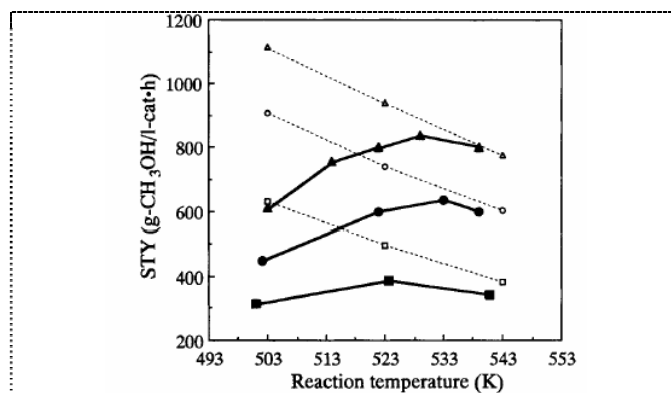


Figure 4. The activity of a Cu/ZnO/ZrO₂/Al₂O₃/SiO₂ catalyst for methanol synthesis in a bench plant. Reaction conditions: pressure (Δ, ▲)=7 MPa, (○, ●)=5 MPa, (□, ■)=3 MPa, SV=10,000 h⁻¹, purge ratio=0.5%; Δ, ○ represents STY at equilibrium

Table 2. 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 ^a	Commercial plant ^b
Methanol (wt%)	CH ₃ OH	99.95	99.59
Methyl formate	HCOOCH ₃	460	700
Higher alcohols (C2-C4) (ppm)	ROH	70	530
Hydrocarbons (C6-C10)	C _n H _m	-	50
Dimethyl ether (ppm)	(CH ₃) ₂ O	-	230

^aReaction conditions: catalyst = Cu/ZnO/ZrO₂/Al₂O₃/SiO₂, temperature = 523 K, total pressure = 5 MPa, H₂/CO₂ ratio in the make-up gas = 3.
^bICI methanol synthesis catalysts booklet, ICI CATALYSTS [5].

Another step in our research work is to apply the technologies developed in the present joint research to CO₂ mitigation and future industries especially automotive transport. In deed, according to our experimental estimations, the new developed process has an overall efficiency of 35%. If pure methanol is used in car engine, the overall efficiency can reach around 10% which is lower than that of gasoline engines (19%). However, taking into account the cost of environmental impacts and CO₂ taxes in global calculation, the methanol will become more comparable to fossil fuels knowing that the results are based on a price of around 1 euro per l at gasoline station.

Conclusion

New energy-efficient and eco-friendly process for the synthesis of methanol from CO₂ and H₂ was successfully developed at bench-scale level. The new process has been operated with rich carbon dioxide as raw material from chemical plant. A bench plant with a capacity of 50 kg day⁻¹ of CH₃OH was successfully operated using high performance catalysts for the production of clean methanol from CO₂ and renewable hydrogen. 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. According to the similar methodology, further process consuming rich CO₂ and using catalytic materials can be developed in Morocco especially for the production of high value chemicals and new energy sources by using phosphate derived materials.

References

- [1] M. Saito, M. Takeuchi, T. Watanabe, J. Toyir, S. Luo, J. Wu, Energy Convers. Mgmt. 38 (1997) 403.
- [2] S. Luo, J. Wu, J. Toyir, M. Saito, M. Takeuchi, T. Watanabe, Stud. Surf. Sci. Catal. 114 (1998) 549.
- [3] J. Wu, S. Luo, J. Toyir, M. Saito, M. Takeuchi, T. Watanabe, Catal. Toda45 (1998) 215.
- [4] M. Saito, J. Wu, S. Luo, J. Toyir, M. Takeuchi, T. Watanabe, Proc. 4th Int. Conf. Greenhouse Gas Control Technologies, 1999, Interlaken, Switzerland, P. Riemer, B. Eliasson, A. Wokaun (eds.) (Pergamon) pp 337–342.
- [5] ICI methanol synthesis catalysts booklet, ICI CATALYSTS.