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Co-production of dimethyl ether and methanol from CO_2 hydrogenation: development of a stable hybrid catalyst†

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Efforts have been made aimed at the development of an active active and stable catalyst in the co-production of dimethyl ether (DME) and methanol from CO_2–H_2. The stabilities of ZSM-5 catalysts and Cu–ZnO-based methanol synthesis catalysts were investigated separately under water-rich conditions. By combining each stable catalyst, a relatively stable hybrid catalyst, Cu–ZnO–Al_2O_3–Cr_2O_3 + H–ZSM-5 (SiO_2/Al_2O_3 = 80), has been developed. After losing about 5% of its original activity in 120 h, the catalyst exhibited no significant reduction in activity until 350 h in the reaction at 523 K and 3.0 MPa. Also, the catalytic activity was satisfactory at the steady state: the total yield of DME and methanol was higher than 26% with over 90% DME selectivity, but the total yield of hydrocarbons was lower than 0.25%. Copyright © 2001 John Wiley & Sons, Ltd.

Keywords: carbon dioxide; catalyst stability; Cu/ZnO-based catalysts; dimethyl ether; hybrid catalyst; methanol; ZSM-5

1 INTRODUCTION

The hydrogenation of CO_2 to methanol has attained great importance in recent years owing to its potential use for CO_2 mitigation. However, methanol formation from the hydrogenation of CO_2 is thermodynamically unfavorable under operating conditions of interest and thus gives very limited yield even under high pressure. The thermodynamic constraint can be lessened and the one-pass conversion can be largely increased by adding the reaction of turning methanol into dimethyl ether (DME), which is achieved by using the hybrid of a methanol synthesis catalyst and a solid acid catalyst in the CO_2 hydrogenation.[1–3] Furthermore, the production of DME from CO_2–H_2 may provide the opportunity for a new CO_2 utilization technology because DME has a great deal of potential use as a clean alternative fuel for diesel engines.[4] Although some results have been reported on the co-production of DME and methanol from CO_2–H_2, no results on the catalyst stability have yet been reported. In our previous work, we found that many of the hybrid catalysts were easily deactivated in the CO_2 hydrogenation to DME, e.g. a hybrid catalyst of Cu–ZnO based catalyst and Y zeolite loses more than 10% of the original activity in 30 h.[5] In the DME production, more water is produced because the methanol conversion to DME produces another molecule of water in addition to water formed with methanol formation and CO formation from CO_2–H_2, as shown in Eqns [1]–[3]:

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

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

$$2CH_3OH \Leftrightarrow CH_3OCH_3 + H_2O \qquad [3]$$

The high concentration of water would probably lead to the deactivation of the hybrid catalyst. Indeed, water is known to play a key role in the deactivation of methanol synthesis catalyst and affects the acidity of solid acids.[6,7] In the present study, efforts have been made to develop a stable

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hybrid catalyst for the oxygenates (DME + methanol) co-production from CO_2 hydrogenation.

2 EXPERIMENTAL

Cu–ZnO-based catalysts with and without promoters were prepared by the conventional coprecipitation. An aqueous solution of copper, zinc and promoter-metal nitrates and an aqueous solution of sodium carbonate were simultaneously added to warm water (338–343 K) with constant stirring; pH was maintained between 6.8 and 7.0. After the completion of coprecipitation, the pH was adjusted to 7.0 and the suspension was kept for 1 h in the mother liquid, then followed by filtration and washing. The precipitate was dried at 393 K overnight and calcined at 623 K for 12 h.

As solid acid catalysts, three kinds of H–ZSM-5 were used with various Si/Al ratios: the three zeolites were labeled ZSM-5(30), ZSM-5(50) and ZSM-5(80), where the numbers in parentheses denote SiO_2/Al_2O_3 ratios. The raw powder of commercial H–ZSM-5 zeolites (Zeolyst International) was mixed with an adequate amount of $Si(OH)_4$ sol-solution as a binder to be 5 wt% of SiO_2 in catalyst, then dried at 393 K overnight, crashed into small particles and calcined at 773 K for 4 h.

A continuous flow-type reaction apparatus with a fixed bed reactor, made of a stainless steel tube with an inner diameter of 7.7 mm, was employed at pressurized conditions. Prior to CO_2 hydrogenation, a methanol synthesis catalyst or a hybrid catalyst, which is a mixture of the methanol synthesis catalyst and ZSM-5 in 1:1 weight ratio (size: 60–80 mesh), was placed in the reactor and reduced at 523 K for 6 h in H_2–N_2 mixture (10% H_2). CO_2 hydrogenation and methanol dehydration were carried out at 523–533 K and 3.0 MPa. Effluent gas from the reactor was heated electrically on-line to avoid the condensations of methanol and water, and analyzed by an on-line gas chromatograph equipped with Carbosphere column connected to a thermal conductivity detector for CO_2 and CO and with Porapark T column connected to a flame ionization defector for methanol, DME and hydrocarbons.

3 RESULTS AND DISCUSSION

First, the activity changes of the hybrid catalysts of $Cu/ZnO/Al_2O_3$ and HZSM-5 zeolites with time on stream were investigated under the following conditions: $H_2/CO_2 = 3$, 3.0 MPa, 533 K and SV = 6600 ml g^{-1} h^{-1}. The initial activities and the activity changes of the hybrid catalysts are summarized in Table 1. With three zeolite catalysts bearing different Si/Al ratios, the total yield of oxygenates was in order ZSM-5(50) > ZSM-5(30) > ZSM-5(80). However, after a time on stream of 70 h, the order of activity change was ZSM-5(30) > ZSM-5(50) > ZSM-5(80), showing that the deactivation of hybrid catalysts is dependent on the SiO_2/Al_2O_3 in ZSM-5, and the rates of DME yield loss were obviously higher than the rates of total oxygenates yield loss. These results suggest that the decrease in the total yield is in considerable part due to the deactivation of ZSM-5. It is likely that the activity change of ZSM-5 is due to hydrothermal dealumination, which would be

Table 1 The stability of ZSM-5 catalysts with different SiO_2/Al_2O_3 ratios in DME synthesis from CO_2 hydrogenation[a]

ZSM-5 SiO_2/Al_2O_3 mole ratio	SV[b] (ml g^{-1} h^{-1})	Temp. (K)	Yields (C-mol%) Time on stream = 6 h DME	Oxygenate[c]	Time on stream = 70 h DME	Oxygenate	Yield change rate[d] (%) DME	Oxygenate
80	6600	533	6.80	8.40	6.40	8.10	−5.9	−3.6
50	6600	533	8.50	10.40	7.30	9.10	−14.1	−12.5
30	6600	533	7.90	9.60	6.60	8.40	−16.5	−12.5
80	1500	523	12.50	14.50	10.90	13.60	−12.8	−6.2

[a] Conditions: feed gas = CO_2 (25%) + H_2 (75%), pressure = 3.0 MPa, catalyst = Cu–ZnO–Al_2O_3 + ZSM-5.
[b] Space velocity based on weight of MeOH synthesis catalyst.
[c] Methanol + DME.
[d] 100 − 100 × Yield (70 h)/Yield (6 h).

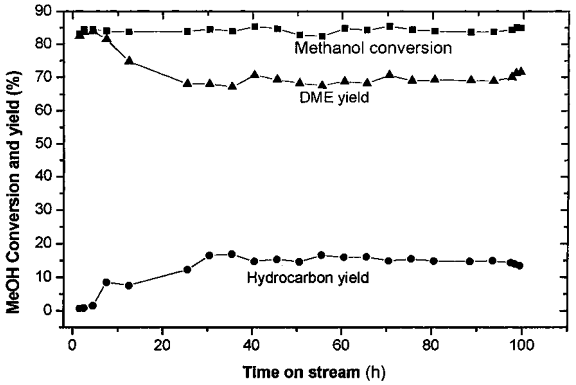

Figure 1 Catalytic activity change of ZSM-5(80) in the methanol conversion to DME. Conditions: feed gas is methanol (2.75%) + H_2O (2.75%) + CO_2 (23.75%) + H_2 (71.25%), 3 MPa, 523 K.

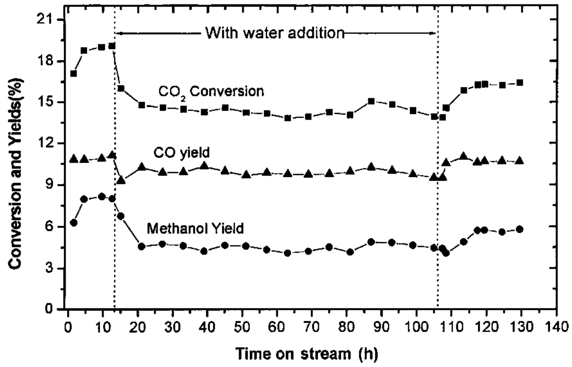

Figure 2 Catalytic activity change of methanol synthesis catalyst (Cu–ZnO–Al_2O_3-1) with water addition. Conditions: feed gas is CO_2 (25%) + H_2 (75%), pressure = 3.0 MPa, temperature = 523 K, SV = 6150 ml g^{-1} h^{-1}, P_{H_2O}/P_{total} during water addition = 0.024.

favored by the water-rich condition of CO_2 hydrogenation to DME. The order of activity change in the present results can be explained by the fact that the lower the Si/Al ratio in zeolite is, the easier the dealumination is.[8] By comparing the reaction at low space velocity (1500 ml g^{-1} h^{-1}) with that at high space velocity (6600 ml g^{-1} h^{-1}) on the same catalyst, the condition of low space velocity led to a higher activity loss. This is possibly due to higher water partial pressure in the reactor. The higher conversion at low space velocity would increase the water partial pressure, which could accelerate the deactivation of both components of the hybrid catalyst.

Separately from the hybrid catalysts, the stability of ZSM-5(80) itself in the methanol dehydration to DME has been investigated under conditions close to that for the co-production of DME and methanol: the mixture of water and methanol was pumped into the CO_2–H_2 flow through the pre-heater at a space velocity of 6150 ml g^{-1} h^{-1}. As shown in Fig. 1, the methanol conversion was almost unchanged during a period of 100 h, but the DME yield decreased by 13% and the yield of hydrocarbons increased during initial 30 h, indicating that relatively strong acid sites were formed. It seems that the formation of strong acid sites is due to dealumination of ZSM-5. After 30 h running, both yields maintained basically steady. This shows that ZSM-5(80) has a fairly good stability after the initial change in the selectivity. The initial change in the selectivity would contribute partly to the decrease of DME yield with increasing time on stream in the co-production of DME and methanol.

Also, the stability of methanol synthesis catalyst alone has been investigated. To simulate the water-rich condition of DME synthesis from CO_2–H_2, water was pumped into the reaction mixture through the pre-heater during the methanol synthesis reaction. From the results of CO_2 hydrogenation with and without water addition (see Fig. 2), we found that the methanol yield was decreased almost to 50% of initial yield after starting water addition and never recovered after stopping water addition. The methanol synthesis catalyst seems to be deactivated through the crystallization of the metal oxides, which is accelerated in the presence of a relatively large excess of water, as reported in previous studies.[7,9] To improve the water resistance of methanol synthesis catalysts, a modification was attempted by adjusting the composition of Cu–ZnO-based catalyst and the catalysts were tested in the reaction with water addition. From a number of trials, the representative results are listed in Table 2. The addition of B_2O_3, SiO_2, Cr_2O_3 and Ga_2O_3 into Cu–ZnO–Al_2O_3 made the catalysts less deactivated during the water addition. Among them, SiO_2 was the most effective additive for enhancing the stability. This is in agreement with the previous result that the SiO_2 modification resulted in the enhancement of the stability of Cu–ZnO-based catalyst in CO_2 hydrogenation.[9] Although the Cr_2O_3-modified catalyst showed a greater decrease in the activity after water addition than the SiO_2-modified one, it gave the highest methanol yield in the presence of excess water.

The CO_2 hydrogenation to DME + methanol was conducted for 350 h over the hybrid catalyst

Table 2 The activities of various methanol synthesis catalysts with and without water addition[a]

Catalyst	Before water addition (time on stream = 23.5 h)		After water addition (time on stream = 47.5 h)		Yield change rate[d] (%)
	Y_{MeOH}[b] (%)	Y_{CO}[c] (%)	Y_{MeOH} (%)	Y_{CO} (%)	
$Cu–ZnO–Al_2O_3$	11.80	1.10	4.80	1.30	−59
$Cu–ZnO–Al_2O_3–B_2O_3$	11.18	2.27	7.35	−0.07	−34
$Cu–ZnO–Al_2O_3–SiO_2$	9.35	3.10	7.61	3.54	−19
$Cu–ZnO–Al_2O_3–Cr_2O_3$	13.07	0.53	10.10	1.87	−23
$Cu–ZnO–Al_2O_3–Ga_2O_3$	13.20	−0.21	9.77	2.10	−26
$Cu–ZnO–Al_2O_3–Cr_2O_3–CaO$	11.27	1.42	9.40	2.51	−17

[a] Reaction conditions: feed gas = CO (4%) + CO_2 (22.3%) + H_2 (73.7%), temperature = 523 K, pressure = 3.0 MPa, SV = 6150 ml g^{-1} h^{-1}, start time of water addition = 24 h, P_{H_2O}/P_{total} during water addition = 0.024.

[b] Methanol yield based on carbon dioxide.

[c] CO yield based on CO_2.

[d] $100 - 100 \times Y_{MeOH}(47.5\ h)/Y_{MeOH}(23.5\ h)$.

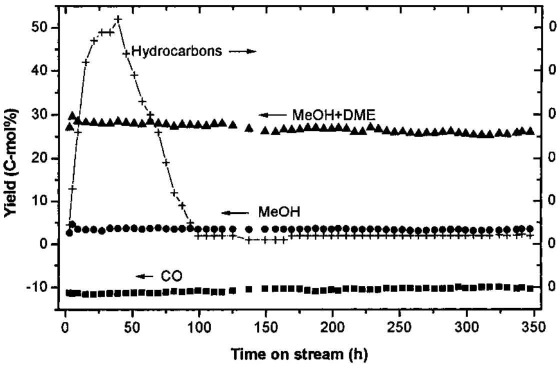

Figure 3 Catalytic activity change of the hybrid catalyst, $Cu–ZnO–Al_2O_3–Cr_2O_3$ + ZSM-5(80), for a long term. Conditions: feed gas is CO (4%) + CO_2 (22.3%) + H_2 (73.7%), pressure = 3 MPa, temperature = 523 K, SV = 1500 ml g^{-1} h^{-1}. Yields defined here refer to CO_2 concentration in the feed gas. The negative CO yield indicates that CO consumption takes place.

containing $Cu–ZnO–Al_2O_3–Cr_2O_3$ and ZSM-5(80) at 523 K, 3.0 MPa and SV = 1500 ml g^{-1} h^{-1}. As shown in Fig. 3, after losing about 5% of its original activity in 120 h, the catalyst exhibited no significant reduction in activity until 350 h. In addition, after 120 h reaction the formation of hydrocarbons was reduced, obviously showing that the relatively strong acid sites disappeared. The decrease in the total yield is probably due to the deactivation of ZSM-5. It seems that the strong acid sites formed initially are blocked by the coke formation while the reaction is going on. Consequently, some fraction of acid sites would be lost. At the steady state, the total yield of DME and methanol was higher than 26% with over 90% DME selectivity, but the total yield of hydrocarbons was lower than 0.25%.

In conclusion, the hybrid catalyst, $Cu–ZnO–Al_2O_3–Cr_2O_3$ + ZSM-5(80), developed in this work has both relatively high activity and stability.

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