DME synthesis from carbon dioxide and hydrogen over Cu–Mo/HZSM-5

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HZSM-5 supported copper–molybdenum oxide prepared by an impregnation method has been applied for the first time in the hydrogenation of CO_2. The effect of the loading of Mo, the reaction temperature and the stability of hydrogenation of CO_2 were investigated. The results indicate that adding a small amount of Mo (Mo/Cu = 1/2 wt) markedly enhances the catalytic activity. The highest DME selectivity was more than 70%. The change of species on the catalyst surface due to the addition of Mo was also investigated by *in situ* DRIFT.

KEY WORDS: DME synthesis; hydrogenation of carbon dioxide; Cu–Mo/HZSM-5; *in situ* DRIFT

1. Introduction

Considerable attention is now focused on CO_2 hydrogenation into CH_3OH or other chemicals for environmental consideration [1–6] (equation (1)). Unfortunately, CH_3OH yield is limited by thermodynamic equilibrium,

$$\begin{aligned} &CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \\ &H^0_{298} = -49.5\ \text{kJ/mol} \end{aligned} \tag{1}$$

To overcome the equilibrium limitation, a reaction can be added to move the equilibrium to more favorable yield and selectivity. During CO_2 hydrogenation, CO is also produced by the reverse water–gas shift reaction (equation (2)). This reaction reaches quickly its equilibrium, so a solution to improve the selectivity could be adding water in the feed, although it might also decrease the rate of methanol formation. In the mean time, if the CH_3OH could be withdrawn from the reaction medium, it would create a strong driving force for CO_2 conversion. Both goals can be achieved through the simultaneous production of CH_3OCH_3 (DME) by methanol dehydration on solid acids, reaction (equation (3)).

$$\begin{aligned} &CO_2 + H_2 \rightarrow CO + H_2O \\ &H^0_{298} = 41.2\ \text{kJ/mol} \end{aligned} \tag{2}$$

$$\begin{aligned} &2CH_3OH \rightarrow CH_3OCH_3 + H_2O \\ &H^0_{298} = -23.4\ \text{kJ/mol} \end{aligned} \tag{3}$$

DME is an important chemical and intermediate for production of gasoline, ethene, aromatics and chemicals. Growing attention is being paid to its application as a fuel or a fuel additive for vehicles and family uses [7–11].

In view of environmental protection, the substitution of DME for freons as an aerosol spray [12] and a refrigerant [13,14] is unavoidable, therefore, the demand for DME will rapidly increase.

To date, there are few reports describing the methods of DME synthesis directly from carbon dioxide and hydrogen [15,16]. The methods they used are similar. A feed (CO_2/$H_2 = 1:3$) was passed over a hybrid catalyst consisting of a methanol synthesis catalyst (Cu/Zn, Cu/Zn/Al, etc.) and a dehydration catalyst (γ-alumina or zeolites, etc.), under 220–300 °C, 30–60 bar and GHSV = 500–5000 h^{-1}. In most reports, the hybrid catalysts were made by mechanically mixing the two catalysts.

From the report mentioned above, we know that the catalysts used for the process of CO_2 hydrogenation to DME mostly consisted of a methanol-synthesis catalyst and a methanol-dehydration catalyst which is similar with the catalyst used for syngas to DME (STD). But few researchers devote themselves to developing a new catalyst system, or easier preparation method. In the present paper, we report a study of HZSM-5 supported copper–molybdenum oxide catalyst used for CO_2 hydrogenation, which showed high activity and DME selectivity.

2. Experiment

2.1. Catalysts preparation

The Cu/HZSM-5 catalyst was prepared by the conventional impregnation method. An appropriate amount of copper nitrate was dissolved in deionized water and HZSM-5 (Si/Al = 25–28 and 20–40 mesh) was then added to the solution. After stirring the solution for 4 h and evaporating the excess water at 353 K, we dried the slurry in air at 393 K for 4 h and calcined the remainder in air at 673 K for 4 h. The Mo/HZSM-5 catalyst was also prepared by the conventional

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impregnation method. An appropriate amount of ammonium molybdate was dissolved in deionized water and HZSM-5 (Si/Al = 25–28 and 20–40 mesh) was then added to the solution. After stirring the solution for 4 h and evaporating the excess water at 353 K, we dried the slurry in air at 393 K for 4 h and calcined the remainder in air at 773 K for 4 h. Cu–Mo/HZSM-5 composite catalysts were prepared by the same method. An apropriate amount of copper nitrate was dissolved in deionized water and Mo/HZSM-5 was then added to the solution. After stirring the solution for 4 h and evaporating the excess water at 353 K, we dried the slurry in air at 393 K for 4 h and calcined the remainder in air at 673 K for 4 h. The individual catalyst is denoted as xCu/HZSM-5. The Cu–Mo binary oxides catalysts are designated as xCu–yMo/HZSM-5, in which the x and y denote the weight percentages of copper and molybdenum metal with respect to the weight of support, respectively.

2.2. Catalytic measurements

Catalytic activity measurements were carried out by using a high-pressure microreactor after introducing pretreatment gas (H_2) at 300 °C for 3 h; the reactant gas was passed through the catalyst bed (2 ml, 20–40 mesh) under a total pressure of 2.0 MPa and a space velocity of 1500 h^{-1}, at certain temperature. The tubing from the catalyst bed to the gas chromatograph was heated at 393 K so as to avoid any condensation of the products. All experimental data were obtained under steady-state conditions that were usually maintained for several hours before changing the reaction temperature to obtain another set of data. The products were analyzed using an on-line gas chromatograph with a thermal detector, in which two parallel connected columns Porapak-Q and TDX-01, were used to separate reaction products.

2.3. In situ DRIFT

In situ DRIFT was performed using catalyst weighing approximately 40 mg. The catalyst was contained in a low dead-volume infrared cell. The DRIFT spectra were collected using a Nicolet 560 FTIR spectrometer. *In situ* absorbance spectra were obtained by collecting 130 scans at 4 cm^{-1} resolution. Each spectrum was referenced to a spectrum of the sample collected at the same temperature under He flow as appropriate.

Prior to each experiment with a fresh sample of catalyst, the catalyst was reduced in 10% H_2/He flowing at 60 cm^3(STP)/min and 0.1 MPa. The reduction temperature was raised at 10 K/min from ambient to 573 K and maintained at 573 K for an additional 2 h. After that spectra of adsorbed CO_2/H_2 ($CO_2/H_2 = 1/3$) were taken by exposing the reduced samples to a CO_2/H_2 mixture flowing at 30 cm^3(STP)/min and 2.0 MPa at temperature between 373 and 673 K.

3. Results and discussion

3.1. The activity of DME synthesis over Cu–Mo/HZSM-5 for CO_2 hydrogenation

3.1.1. Effect of Mo loading on catalytic activity

DME was effectively synthesized from carbon dioxide and hydrogen at 513 K over the Cu–Mo/HZSM-5 catalyst prepared by the impregnation method (table 1). Table 1 clearly illustrates the promoting effect of Mo on Cu/HZSM-5 for hydrogenation of carbon dioxide. For instance, with addition of 3 wt% Mo, the conversion of CO_2 and selectivity of DME increase from 6.82 and 37.05 to 7.25% and 61.95%, respectively. When the addition of Mo is 6 wt% the catalyst (12Cu–6Mo/HZSM-5) has the highest activity and selectivity of DME.

3.1.2. Activity and DME selectivity at various temperatures

Table 2 summarizes the effects of reaction temperature on the CO_2 conversion. According to this result, the conversion of CO_2 increases with increasing reaction temperature. From table 2, it can be seen that

(i) The highest DME selectivity is obtained at 513 K, and then decreases as the reaction temperature increases.

(ii) Methane is produced when the reaction temperature is over 513 K.

(iii) The selectivity of methanol decreases as the temperature increases; in contrast, the selectivity of CO increases with increasing temperature.

3.1.3. The stability of reaction

Furthermore, we used the 12Cu–6Mo/HZSM-5 catalyst to perform a long-term test at 513 K. The change of carbon

Table 1
Effect of Mo loading on catalytic activity for CO_2 hydrogenation.[a]

Catalyst	Conv. of CO_2 (mol%)	Selectivity (mol%)			
		CH_4	CO	CH_3OH	DME
12Cu–0Mo/HZSM-5	6.82	0	55.57	7.38	37.05
12Cu–3Mo/HZSM-5	7.25	0	24.08	13.97	61.95
12Cu–6Mo/HZSM-5	12.36	0.87	15.94	6.0	77.19
12Cu–9Mo/HZSM-5	8.08	1.50	40.91	5.51	52.08

[a] Reaction conditios: $T = 513$ K, $P = 2.0$ MPa, GHSV = 1500 h^{-1}, $CO_2/H_2 = 1/3$.

Table 2
Effect of temperature on activity and DME selectivity.[a]

Reaction temp. (K)	Conv. of CO_2 (mol%)	Selectivity (mol%)			
		CO	CH_4	CH_3OH	DME
493	7.63	13.52	0	19.54	68.74
513	12.36	15.94	0.87	6.00	77.19
533	14.76	30.46	2.35	6.20	60.99
553	18.61	49.48	3.44	5.56	41.52
573	22.91	61.20	6.59	4.67	27.54

[a] Reaction conditions: $P = 2.0$ MPa, GHSV = 1500 h^{-1}, $H_2/CO_2 = 3/1$.

dioxide conversion and selectivity of DME as a function of reaction time is displayed in figure 1. It clearly shows that both the CO_2 conversion and selectivity of DME are almost stable during the reaction for 10 h, which indicates that no significant deactivation of the catalyst is occurring.

3.2. In situ DRIFT

Figure 2 shows spectra collected at 513 K in H_2/CO_2 ($CO_2/H_2 = 1/3$) flowing at 30 cm^3(STP)/min over reduced Cu/HZSM-5 and Cu–Mo/HZSM-5. The total system pressure in both cases was 2.0 MPa. Spectra were collected after 1 h exposure to the feed. For Cu/HZSM-5 the peak at 1614 cm^{-1} is assigned to formate species (I) (HCOO–Cu) [17]. The peaks at 2177 and 2106 cm^{-1} are assigned to gas phase CO; those observed at 1463, 1061 and 1030 cm^{-1} are due to the methoxyl (CH_3O–Cu) [18,19].

For Cu–Mo/HZSM-5, the intensity of the peak at 1614 cm^{-1} (HCOO–Cu) decreases, but a new peak at 1596 cm^{-1} was produced, which is contributed to formate species (II) based on the reference [17,20,21]. The intensity of the peaks at 1463, 1061 and 1030 cm^{-1} increases markedly. At the mean time, the peak at 1540 cm^{-1} was produced. Schilke et al. [22] contribute the feature at 1560–1540 cm^{-1} to the bidentate carbonate on titania (b-CO_3–Ti) and the bidentate carbonate on zirconia (b-CO_3–Zr), respectively. Based on the above results, the peak at 1540 cm^{-1} is assigned to the bidentate carbonate on molybdenum (b-CO_3–Mo).

From the DRIFT results, it can be seen that adding of Mo not only produces the new adsorption species (1596 and 1540 cm^{-1}) but also increases the intensity of the species, which may be contributed to the hydrogenation of carbon dioxide.

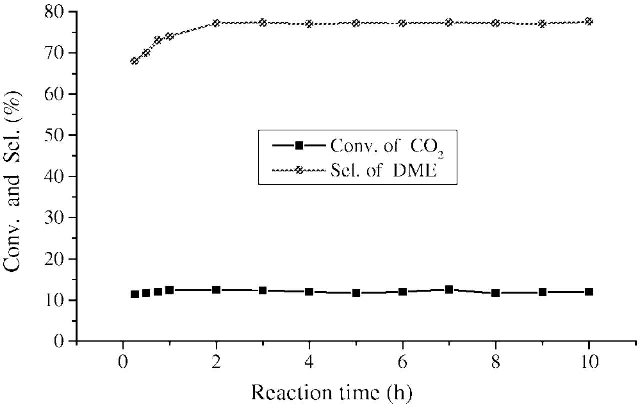

Figure 1. Conversion of CO_2 and selectivity of DME on stream of time over 12Cu–6Mo/HZSM-5 catalyst. Reaction conditions: $P = 2.0$ MPa, $T = 513$ K, GHSV = 1500 h^{-1}.

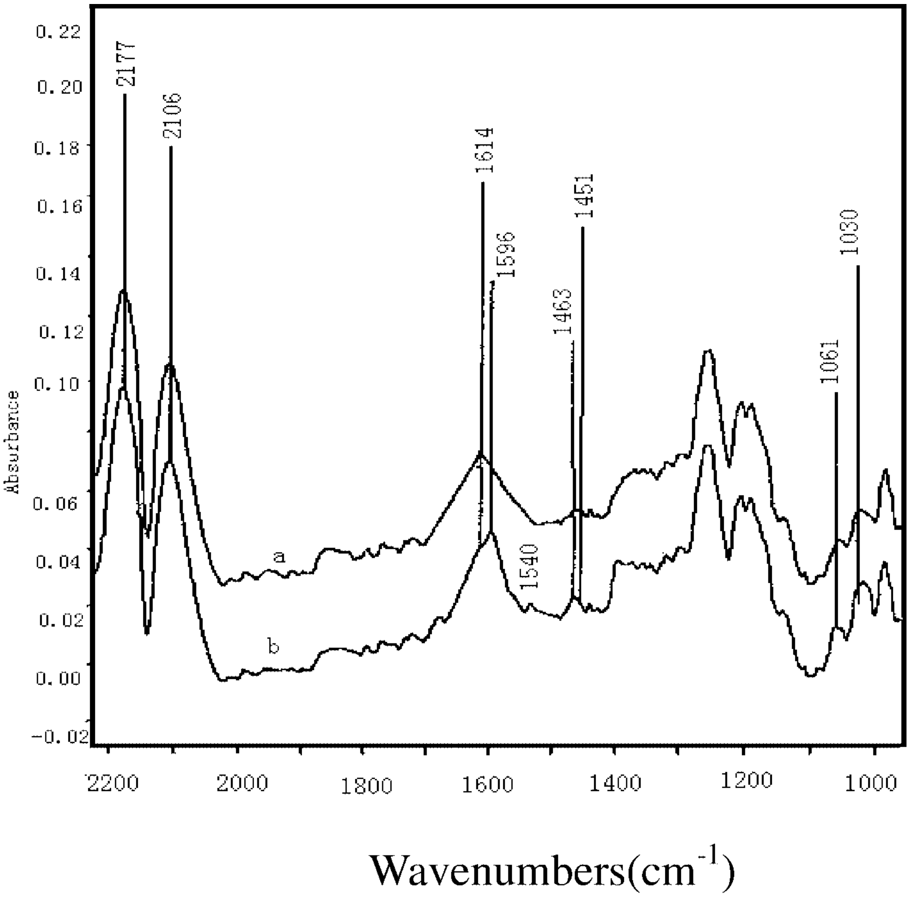

Figure 2. *In situ* DRIFT spectra of hydrogenation of CO_2 over 12Cu–6Mo/HZSM-5 catalyst at 2.0 MPa and 240 °C. (a) Cu/HZSM-5 and (b) Cu–Mo/HZSM-5.

4. Conclusions

(1) HZSM-5 supported Cu–Mo catalyst is highly active for the dimethyl ether (DME) synthesis from carbon dioxide and hydrogen. The results indicate that adding of a small amount of Mo (Mo/Cu = 1/2 wt) markedly enhances the catalytic activity. DME selectivity was more than 70%: (i) The highest DME selectivity is obtained at 513 K, and then decreases with increasing reaction temperature. (ii) Methane is produced when the reaction temperature is over 513 K. (iii) The selectivity of methanol decreases as the temperature increases; in contrast the selectivity of CO increases with increasing temperature.

(2) Adding of Mo not only produces the new adsorption species (1596 and 1540 cm^{-1}) but also increases the intensity of the species on the catalyst surface, which may be contributed to the hydrogenation of carbon dioxide.

(3) It clearly shows that both the CO_2 conversion and selectivity of DME are almost stable during the reaction for 10 h, which indicates that no significant deactivation of the catalyst occurs.

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