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Conversion of CO_2 to Dimethylether and Methanol over Hybrid Catalysts

Jean-Luc DUBOIS, Kazuhiro SAYAMA, and Hironori ARAKAWA*
National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305

Combination of a CH_3OH synthesis catalyst (Cu-ZnO-Al_2O_3) with a solid acid, which promotes CH_3OCH_3 formation, creates a strong driving force for CO_2 conversion. At equilibrium higher yields and selectivities can be achieved: 24.3% yield in DME+CH_3OH with hybrid catalyst, compared to 11.6% with CH_3OH synthesis catalyst only, at 240 °C and 3 MPa. Zeolites were proved to be very efficient, with a yield of 17%.

Considerable attention is now focused on CO_2 hydrogenation into CH_3OH for environmental consideration, reaction (1). Unfortunately, CH_3OH yield is limited by thermodynamic equilibrium. The necessity to achieve high conversion and high selectivity per pass, to limit recycling cost, requires to work near the equilibrium. In order to achieve higher yields, the pressure can be raised1) or the reaction can be divided in two or more steps (e.g. CO formation and then CO hydrogenation) on different catalysts.2)

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \qquad \Delta H^\circ_{298} = -49.5 \text{ kJ/mol} \qquad (1)$$

To overcome the equilibrium limitation, a reaction can be added to move the equilibrium to more favorable yields and selectivities. During CO_2 hydrogenation CO is also produced by the reverse water gas shift reaction, reaction (2). This reaction reaches quickly its equilibrium, so a solution to improve the selectivity could be to add 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 In the mean time, if the CH_3OH could be withdrawn from the reaction media, it would create a strong driving force for CO_2 conversion.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 (3).

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad \Delta H^\circ_{298} = 41.2 \text{ kJ/mol} \qquad (2)$$

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \qquad \Delta H^\circ_{298} = -23.4 \text{ kJ/mol} \qquad (3)$$

Methanol is an important basic chemical and DME is a key intermediate in the MTG process,3) and in a novel acetic acid process.4) Thermodynamic calculations at 3 MPa and between 200 and 300 °C, show that much higher selectivity in oxygenates can be achieved, although CO_2 conversion is only slightly improved, Fig 1.

The use of hybrid catalyst for CO and CO_2 hydrogenation has already been reported.4-10) Nevertheless, in the case of CO_2 hydrogenation the expected products were hydrocarbons and not DME. This reaction is highly exothermic and will require expensive engineering to remove the heat of reaction. In addition, at the high pressure required for CO_2 hydrogenation, aromatics might be favoured over olefins.3,7) Finally, the high temperature requested for hydrocarbons formation are not compatible with the Cu-ZnO-Al_2O_3 catalyst; and indeed different type of catalysts have been used in those cases, e.g. Ref. 7.

The methanol synthesis catalyst used in this study is a CuO-ZnO-Al_2O_3 (32/66/2) catalyst prepared by the conventional coprecipitation method. 1.7 ml of SiO_2 (Davison 57), Silicalite (SiO_2/Al_2O_3 = 2100), γ-Al_2O_3

Table 1. Improvement of CO_2 hydrogenation over various hybrid catalysts [a)]

Solid acid	Weight	Conv. /%	Selectivities /%			Yield /%
1.7 ml	g	CO_2	CO	DME	CH_3OH	DME+CH_3OH
SiO_2 (Reference)	0.56	20.5	50.3	0.0	49.6	10.2
Silicalite	0.91	20.7	50.1	0.0	49.8	10.3
γ-Al_2O_3	1.00	21.6	46.1	16.9	36.7	11.6
SiO_2-Al_2O_3 (Neobead D)	0.94	21.5	44.0	17.2	38.8	12.0
SiO_2-Al_2O_3 (Silbead N)	1.58	23.6	34.4	47.1	18.4	15.5
6% WO_3/SiO_2	0.60	24.0	34.4	47.6	17.7	15.7
Y-Zeolite (TSZ-330HUA)	0.80	24.4	32.4	54.8	12.8	16.5
Mordenite (Zeolon 200H)	1.09	25.0	31.7	55.1	13.0	17.0
Nafion tested at 200 °C	1.87	10.8	30.9	55.0	11.9	7.2

a) With 1.2 ml (1 g) of Cu-$Zn0$-Al_2O_3 catalyst mixed with 1.7 ml of oxide at 3 MPa, 240 °C, 30 ml/min.

(Harshow), silica-alumina (Neobead D, $SiO_2/Al_2O_3=10/90$) and (Silbead N, $SiO_2/Al_2O_3=98/2$), 6% WO_3/SiO_2 prepared by incipient wetness method and calcination in air at 400 °C for 2 h, Y-zeolite (TSZ-330HUA, $SiO_2/Al_2O_3=6$) or mordenite (Zeolon 200H, $SiO_2/Al_2O_3=10$) were mixed with 1.2 ml (1 g) of the methanol synthesis catalyst. Both, catalyst and solid acid, had been sieved in the 0.5-1.0 mm size. The reaction was carried out in a fixed bed microreactor and using a reaction mixture $Ar/He/CO_2/H_2$: 1.00/8.23/22.1/68.7. Analysis conditions have been described elsewhere.[9)] In all cases carbon balance was achieved within 2%. The choice of operating conditions (3 MPa, in the range of 200 to 280 °C) was dictated by previous experiments,[9)] and mainly the flow rate was set to ensure to reach the thermodynamic equilibrium. Small amount of hydrocarbons were always produced and for example with the zeolites, the hydrocarbon selectivity becomes over 3% at 280 °C.

By using solid acids at 240 °C and 3 MPa, the oxygenate yield (CH_3OH + DME) can be strongly improved while CO selectivity is decreased, Table 1. At 260 °C, with the addition of a solid acid one can move from one equilibrium (CH_3OH only) to the other (DME + CH_3OH), Fig. 1. It was noticed that Silicalite behaves like SiO_2, Neobead D like γ-Al_2O_3, 6% WO_3/SiO_2 like Silbead N, and mordenite like Y zeolite, from 220 to 280 °C. Nafion (perfluoronated sulfonic acid resin, NR 50, Aldrich) was tested at 200 °C only, because of its low stability. At this temperature, it already started to decompose poisoning the Cu-ZnO-Al_2O_3 catalyst. Nevertheless, large amounts of DME were produced, Table 1. Solid acids containing sulfur and halogens should be avoided as these elements are strong poisons for the methanol synthesis catalyst.

The dehydration of methanol on alumina and amorphous silica-alumina has already been studied (see Ref. 3 and references therein). Reaction over alumina involved surface methoxy groups. On the other hand, the reaction over silica-alumina involves concerted action of Bronsted acid and basic sites. Similar interpretation has been reported recently for dealuminated H-mordenite.[13)] DME would be formed by interaction of a surface methoxy group with a CH_3^+ generated on the acid site.[13)]

Nafion is known to be a Bronsted acid, γ-Al_2O_3 a Lewis acid, silica and Silicalite are only weakly acidic, silica-aluminas and zeolites are both Bronsted and Lewis acids. The acidity of the 6% WO_3/SiO_2 is not known, but it was tested because in a previous study on WC, the produced DME was attributed to the formation of oxide on the surface.[14)] The acidity of γ-Al_2O_3 seems to be insufficient for methanol dehydration in our conditions. At higher temperature or pressure, the classification of solid acids reported in Table 1 is subjected to modifications.

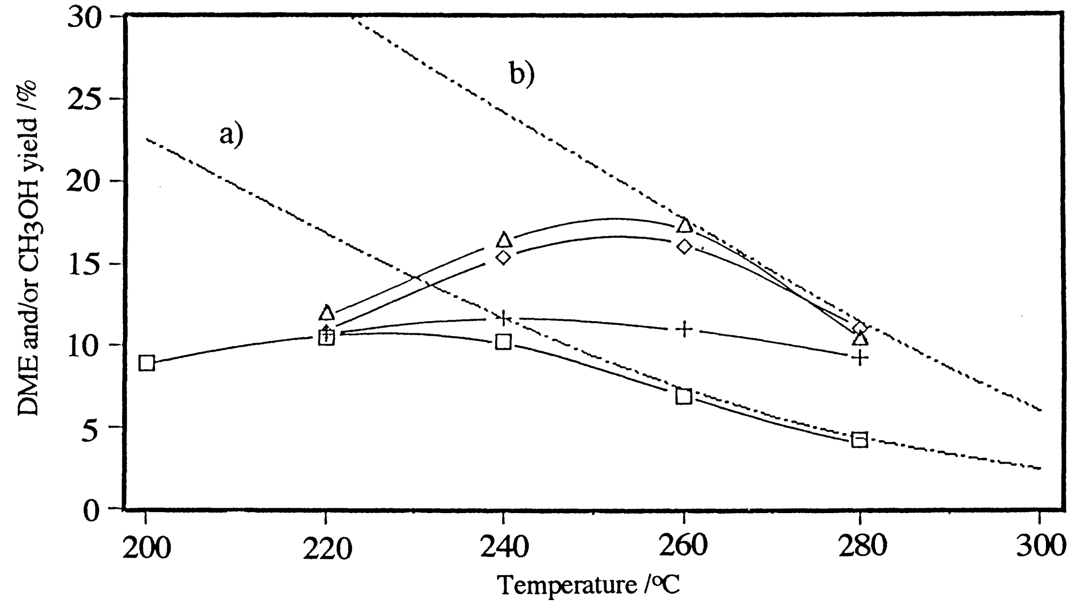

Fig. 1. Oxygenates yield at 3 MPa, $H_2/CO_2 = 3$.

Curve a) methanol yield at equilibrium, if no DME is produced, reactions (1) and (2).

Curve b) methanol + DME yield at equilibrium, reactions (1), (2), and (3).

Experimental results with a flow rate of 30 ml/min, 1.2 ml (1 g) of methanol synthesis catalyst mixed with 1.7 ml of solid acid; □ : SiO_2, + : γ-Al_2O_3, ◇: Silbead N, △: Y-zeolite.

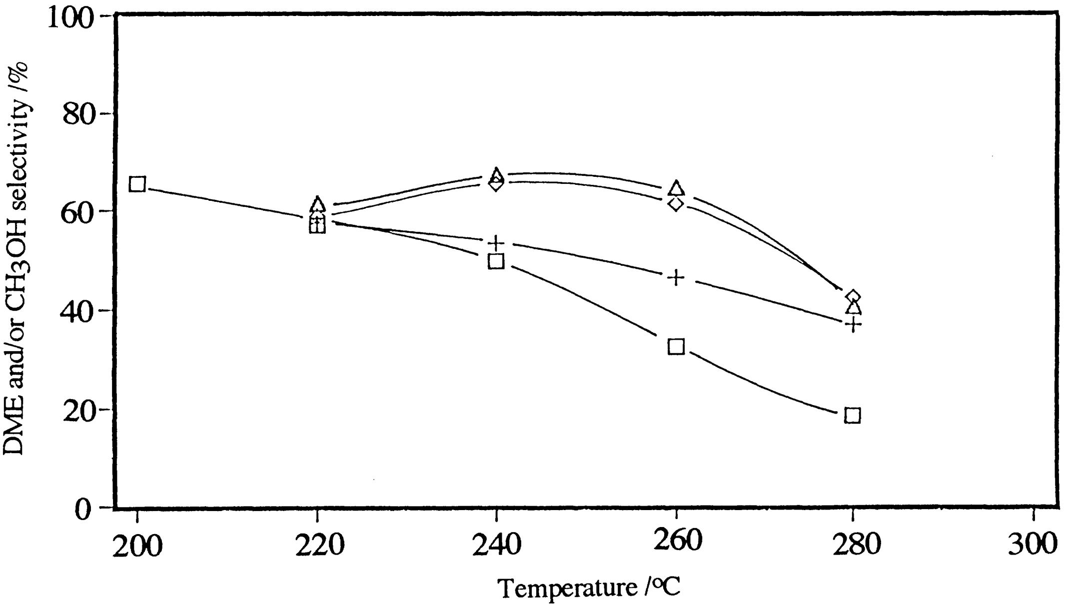

Fig. 2. Oxygenates selectivity at the same conditions as Fig. 1.

Table 2. Possible modifications of operating conditions by the use of an hybrid catalyst

Catalyst bed composition	Pressure	Temp	GSHV	CO_2 Conv.	Selectivity /%		Oxygenates	CO Sel.
	MPa	°C	h^{-1}	%	CH3OH	DME	Yield /%	%
Cu-ZnO-Al_2O_3-Cr_2O_3, 1g	7	250	3000	25.3	74.2	0.1	18.8	25.6
Cu-ZnO-Al_2O_3-Cr_2O_3, 1g	5	230	1800	20.0	67.3	0.0	13.5	32.4
Cu-ZnO-Al_2O_3,1g+Zeolon	3	240	620	25.0	13.0	55.1	17.0	31.7

The water-gas shift reaction is at the equilibrium in our operating conditions. This is not surprising as Cu-ZnO-Al_2O_3 catalysts are used for low temperature (200-250 °C) shift reaction. Although in syngas conversion excess CO_2 production is rather detrimental, it might become an advantage in CO_2 hydrogenation, if the reaction is operated near equilibrium conditions. The non selective hydrogenation of CO_2 into CO becomes limited, because CO is converted back to CO_2 and H_2 due to the large amount of water generated by the dehydration of methanol. In Table 1, it can be seen that as the DME selectivity is increasing the CO selectivity is decreasing. In addition, the oxygenate selectivity obtained at 240-260 °C, with the best solid acids, is comparable to the selectivity obtained at 200 °C with SiO_2 (Fig. 2), although the yield is strongly improved (Fig. 1).

Calculations on results obtained with mordenite showed that the dehydration reaction is near its equilibrium from 220 to 280 °C. This means that if the conversion is not higher at 240 °C, it is due to the poor activity of the catalyst and not to the acid strength. A strong synergistic effect was observed when a solid acid is mixed with a methanol synthesis catalyst. In Table 2, some results obtained with an other Cu-ZnO promoted catalyst of similar activity have been added for comparison, for more details on this catalyst see ref 1. Although the GHSV are fairly different, because one take into account the total volume of the catalyst bed, it can be noticed that the pressure can be significantly reduced, while selectivity and/or yield are maintained.

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