Gas Phase Synthesis of Dimethyl Ether from Syngas

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1. Introduction

Dimethyl ether (DME) is used primarily as an aerosol propellant because of its attractive physical properties and its environmentally benign characteristics. Growing attention is being paid to its applications as a fuel or a fuel additive for vehicles and family uses[1-3]. DME can be burned at the same efficiency in a diesel engine with a modified fuel system and can be handled like liquefied petroleum gas (LPG). DME combines good fuel properties with low exhaust emissions and low combustion noise. DME's greenhouse emissions, measured from cradle-to-grave, are lowest among all transportation fuel alternatives. Amoco Production Company believes the development of this clean-burning fuel will provide competition for diesel and gasoline in a variety of engine markets. Therefore, the demand for DME will rapidly increase, and large scale production of DME will be a interesting topic in near future. Commercially DME has been produced by catalytic dehydration of methanol over acidic porous materials as catalysts. But it is more advantageous to use synthesis gas as a starting material and synthesize DME in a single step with hybrid catalysts. DME synthesis from syngas has the potentiality of giving much higher syngas conversion and DME yield than that of methanol synthesis because its limits might be overcome by the conversion if methanol to DME and water as shown in Fig.1.[4]

Fig.1 shows the equilibrium $(CO+H_2)$ conversion of the two DME synthesis reaction formulas. In each reaction, the equilibrium conversion has its maximum peak when the H_2/CO ratio reaches the reaction's stoichiometric value. The 2nd reaction formula in Fig.1 has an advantage compared with the 1st reaction formula when coal gasification gases are employed for DME synthesis because usually H_2/CO ratios of the gases are smaller than one.

In the present work, the direct conversion of syngas to DME was investigated using the physical mixture of methanol synthesis catalyst and methanol dehydration catalyst in a fixed bed reactor. The Cu-Zn-Al based catalyst and modified γ- alumina were used as a methanol

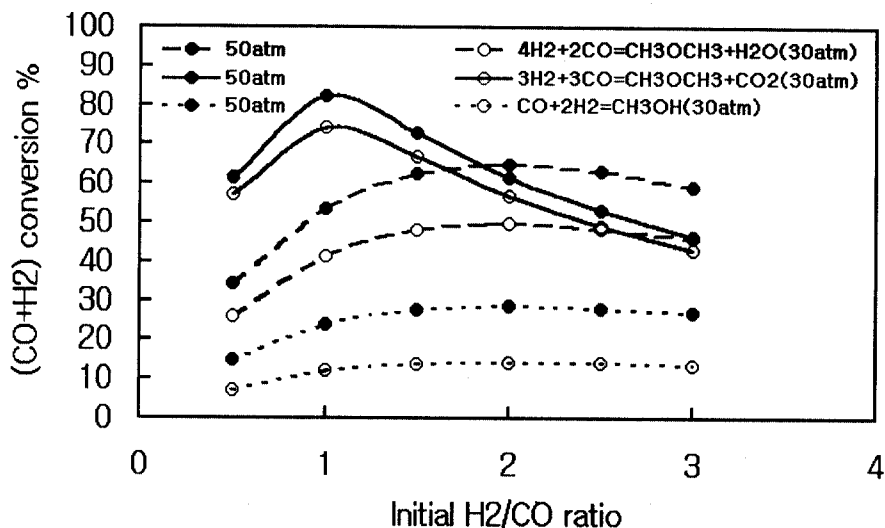synthesis catalyst and as a methanol dehydration catalyst separately.

Fig.1. Equilibrium (H_2 +CO) conversion to DME or methanol as function of pressure at 553K
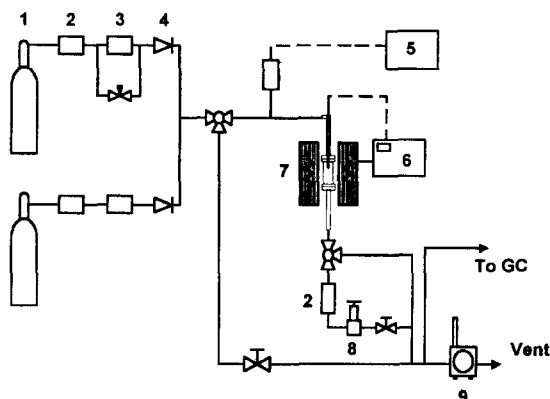
2. Experiments

2.1. Preparation of catalysts

The methanol synthesis catalyst (Cu-Zn-Al based catalyst) was prepared by a conventional co-precipitation method. Aqueous solution of nitrates with each component were mixed and agitated with sodium carbonate at 85°C and pH 7±0.3. The precipitate was aged for 1hr, separated by filtering, washed, dried, and calcined at 350°C for 6hrs in air. The modified γ- alumina was prepared by the impregnation method of γ- alumina with aqueous copper acetate or copper nitrate solution. The γ- alumina was supplied by Strem Chemicals and the copper loading in modified γ- alumina was 5 and 10% by weight. Catalysts prepared in this work were characterized by the surface area, their XRD pattern using CuKα radiation (RIKAKU; D/MAX-III model), SEM(Philips model XL-30). The specific surface area was determined by the N_2 BET method on a Micrometrics constant volume adsorption system (Accusorb 2100E), as shown in Table 1.

Table 1 Catalysts prepared in this work.

Catalysts	Surface area (m^2/g)	Pore volume(cc/g)	Particle size
Cu/ZnO/Al$_2$O$_3$ (57:33:10)	73.9	0.46	6.1μm
γ-alumina	148.1	0.42	24.2μm

1. Gas, 2.Filter, 3.Mass flowmeter, 4.Check valve , 5. Pressure tranducer & Indicator, 6. Temperature controller & Indicator, 7. Reactor & Heater, 8.Back pressure regulator, 9. Gas meter

Fig.2 Experimental apparatus.

2.2 Experimental apparatus

All reactions were conducted in a fixed catalyst bed under pressurized conditions, as shown in Fig.2.   Typically, 0.5g of the mixture of Cu-Zn-Al based catalyst and modified γ-alumina was loaded in the reactor, and reduced with pure hydrogen at 250°C for 16hrs before experiment.   After reduction of catalyst, the reactor was heated up to the desired temperature and pressurized to the desired pressure (up to 30 atm) with feed gas (CO/H$_2$ = 1/2), and maintained by back pressure regulator (TESCOM 26-1724-24).   The feed gas flow rate was regulated by mass flow controller (Brooks 5850TR).   Reaction products were analyzed by   on - line gas chromatography equipped with a Porapk T and a Molecular sieve 5A packed column.   The gas line from the reactor to gas chromatography was heated to 80°C in order to avoid condensation of the product.   Reaction conditions are shown in Table 2.   Carbon monoxide conversion was calculated from the carbon balance in the produced gas.   The selectivity was defined as the ratio of the mole of the desired material to the mole of material produced.   Also, space time yield (*l*-DME/g/hr) was defined as the volume of

DME at standard state (gas phase) per g of catalyst.

Table 2. Experimental conditions

Reaction temperature (° C)	220, 250, 280
Reaction pressure (kg/cm^2)	30
Catalyst loading (g)	0.25, 0.5
H$_2$/CO ratio of mixed gas	2/1
GHSV(h^{-1})	3,600~7,200

*GHSV(gas hourly space velocity)=feed gas volume at STP / catalyst volume/hr.

3. Results and Discussion

3.1 Effect of modified γ- alumina on product distribution

The rate of methanol synthesis on the Cu-Zn-Al alone increases with the increase in the temperature to reach the maximum up to 280°C, and decrease with the temperature increase, because of the thermochemical limitation. In case of hybrids catalysts, the rate of DME synthesis increase at 280C while giving small amount of methanol and carbon dioxide. Also, the amount of other hydrocarbons formed was quite small, and most of them are methane, as shown in Table 3.

Table 3. Comparison of methanol and DME synthesis at 30atm, H$_2$/CO=2:1, catalyst loading 0.5g, A/B=80:20.

Temperature (°C) Yield(%)	220	250	280	Cu-Zn-Al alone* 250	280
CO conversion %	2.4	8.8	27.2	4.2	4.9
Selectivity (%)					
DME	83.9	78.0	78.1	4.3	21.1
CH$_3$OH	8.4	4.8	2.5	95.3	77.5
CO$_2$	7.0	16.6	18.8	-	-
CH$_4$	0.7	0.6	0.7	0.4	1.4

* Catalyst loading 0.25g

In order to improve the selectivity of the γ- alumina in methanol dehydration, aqueous copper acetate and copper nitrate solution were used to modify the γ- alumina. Modified γ-alumina increased the yield of DME slightly while keeping the methane yield higher than the unmodified catalyst. The Hybrid catalyst with modified γ- alumina using copper acetate

showed the good characteristics at 250°C, and both the DME yield and CO conversion are increased with an increase in the amount of Cu in case of modified γ- alumina using copper acetate. However, at 280°C, modification did not improve CO conversion and DME yield.

3.2 Effect of catalyst mixing ratio

Based on conversion yield, 10% modified γ- alumina with copper acetate was selected as dehydrogenation catalyst. Cu-Zn-Al based catalyst and modified γ-alumina were physically mixed in different proportions to yield essentially any desirable combination of DME and methanol in the product stream. The proportion of catalysts was determined based on the maximum methanol equivalent productivity . The experimental data obtained from the catalyst with 3 different mixing ratios are given in Table 4.

Table 4. Effect of hybrid catalyst composition on DME synthesis.

A/B ratio (weight ratio)	CO conversion (%)	Selectivity (%)			
		DME	CH_3OH	CH_4	CO_2
1:1	17.4	92.9	3.3	3.6	0.2
7:3	27.3	82.9	3.6	0.6	12.9
8:2	27.2	78.1	2.5	0.7	18.8

A: Cu-Zn-Al catalyst, B: modified γ-alumina with 10% copper acetate solution.
Reaction condition: 280°C, $H_2/CO=2:1$, 30atm, GHSV=7,200

The 1:1 mixing ratio did not give sufficient active site for methanol synthesis. The best mixing ratio of Cu-Zn-Al and modified γ-alumina was 7:3 in weight. So, optimized weight proportion of the catalyst mixture was 70% to 30%.

4. Conclusion

Hybrid catalyst with modified γ- alumina using copper acetate showed the good characteristics at 250°C, and both the DME yield and CO conversion are increased with an increase in the amount of Cu in case of modified γ- alumina using copper acetate. However, at 280°C, modification did not improve CO conversion and DME yield. The Cu-Zn-Al based catalyst and modified γ-alumina were physically mixed in different proportions to yield essentially any desirable combination of DME and methanol in the product stream. . Optimized weight proportion of the catalyst mixture was 70% to 30%.

5. References

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