Single step synthesis of hydrocarbons from CO_2 and H_2 using hybrid catalyst

Kenta Serikawa, **Takahiro Yamaguchi, Yang Song, Ting Ma, Hiroyuki Imai, Xiaohong Li ***
Faculty of Environmental Engineering, The University of Kitakyushu, 1-1, Hibikino, Wakamatsu-ku, Kitakyushu, 808-0135, Japan
**Corresponding author. E-mail address: lixiaohong@kitakyu-u.ac.jp*

Abstract: The effect of solvent partial pressure on CO_2 hydrogenation to hydrocarbons over a hybrid catalyst composed of Cu-ZnO and Cu/ZSM-5 under near-critical condition was studied in a fixed bed reactor. Methanol was synthesized from CO_2 over Cu-ZnO. Subsequently, methanol as an intermediate was converted to hydrocarbons through the formation of dimethyl ether (DME) over Cu/ZSM-5. The conversion of CO_2 increased from 28 % to 45 % with increasing the partial pressure of n-hexane used as the solvent from 0 MPa to 1.5 MPa. The corresponding selectivity of DME and CO decreased with increasing the partial pressure of n-hexane.

Keywords: CO_2 to hydrocarbons, Near-critical phase, Hybrid catalyst, Solvent.

1. Introduction

Because of a drastic increase in worldwide energy consumption, the development of alternative hydrocarbon production processes from non-fossil fuel has been highly desirable. One major consideration is the gas to liquid (GTL) process. In particular, many efforts have been focused on using CO_2 that can be obtained easily as a raw material for the production of fuels and chemicals, and this is also beneficial to control greenhouse gas emissions. In this study, we investigated the catalytic activity of the hybrid catalysts composed of Cu-ZnO and Cu/ZSM-5 for the conversion of CO_2 to hydrocarbons via methanol in a near-critical n-hexane solvent.

2. Experimental

A hybrid catalyst was prepared by physically mixing the 224-355 µm pellets of a Cu-ZnO methanol synthesis catalyst of 0.5 g with those of a 7wt%Cu/ZSM-5 catalyst of 0.5 g, and packed in a pressurized type fixed-bed reactor.

The catalyst was first reduced in a flow of 5 vol% H_2 with 100 ml/min at atmospheric pressure and 573 K for 3 h. After the reduction of the catalyst, the catalyst was cooled down to room temperature, and then a mixture gas (72% H_2,24% CO_2,3% Ar) and n-hexane as a solvent were introduced into the reactor to pressurize it. The partial pressure of the mixture gas, $P_{mixture\ gas}$, of 2.5 MPa was retained, and the partial pressure of n-hexane, $P_{n\text{-}hexane}$, was varied from 0 MPa to 1.5 MPa, and He flow was used to keep the total pressure inside the reactor at 4.0 MPa. Finally, the reactor was heated up to 553 K to start the reaction. The ratio of catalyst weight to the flow rate (W/F) was 10.2 g-Cat/h/mol.

3. Results and discussion

A series of activity tests was conducted to investigate the effect of n-hexane solvent partial pressures on the catalytic performances of the hybrid catalyst for hydrocarbon production from CO_2 at 553 K and 4.0 Mpa. The results of CO_2 conversion and selectivity of products at different solvent partial pressure over hybrid catalyst were listed at Table 1. When n-hexane solvent was not used, CO_2 conversion was only 27.8 %, DME and CH_4 were the main products and gasoline fractions were not detected. That means there only conducted the synthesis reaction of DME via CH_3OH intermediate over Cu-ZnO catalyst. However, CO_2 conversions increased from 30.3 % to 44.6 % when the n-hexane were used and the partial pressures of it were increased from 0.75 to 1.5 MPa, respectively. Meanwhile, DME almost disappeared, and hydrocarbon products were obtained dominantly, especially of $C_{4\text{-}7}$. These suggest that DME can be further convert to high level hydrocarbon such as gasoline factions by introducing n-hexane solvent into the system, therefore CO_2 conversion can be improved. A possible reason is that introduction of n-hexane in near-critical which have unique properties such as superior solubility and transfer characteristics due to gas-like viscosity and diffusivity as well as liquid-like density was in favor of the dispersion of the hydrocarbons and could also suppress the formation carbon deposition on the surfaces of zeolite.

Table 1. Effects of partial pressure of n-hexane on catalytic properties of the hybrid catalyst composed of Cu-ZnO and 7wt%Cu/ZSM-5 in the conversion of CO_2 to hydrocarbons.

n-hexane partial pressure (Mpa)	CO_2 conversion (%)	Selectivity (%)				H.C. distribution (mol-C %)			
		CO	CH_4	DME	H.C.	C_1	C_2	C_3	C_{4-7}
0	27.8	25.2	0.54	40.9	33.9	75.0	25.0	0	0
0.75	30.3	27.4	17.8	1.7	70.9	42.3	4.7	15.5	37.6
1.5	44.6	14.2	10.8	0.4	85.4	35.6	4.0	9.3	51.1

4. Conclusions

The catalytic performances of a hybrid catalyst composed of Cu-ZnO and 7wt%Cu/ZSM-5 in the production of hydrocarbons from CO_2 in a near-critical n-hexane solvent have been studied. Utilization of the near-critical n-hexane solvent could significantly increase CO_2 conversion and hydrocarbon products could be obtained over the hybrid catalyst. In addition, the employment of the near-critical solvent could also suppress the formation of CO during the reaction.

References

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