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Effective Hydrogenation of Carbon Dioxide with Two-Stage Reaction System

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Carbon dioxide (CO_2) was effectively hydrogenated to methanol(MeOH) and hydrocarbons (H.C.) in the two-stage reaction system. In the first stage, CO_2 was converted to carbon monoxide by reverse CO shift reaction at 450 °C, then CO was converted to MeOH, C_2-C_5 hydrocarbons (LPG), or liquid H.C. in the second stage. Product yields were improved when the produced H_2O in the first stage was removed from upstream of the second reactor.

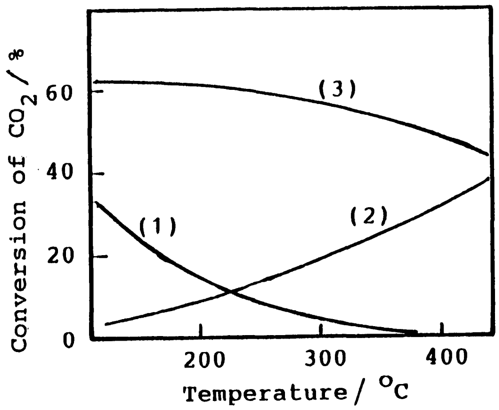
Carbon dioxide is one of the cheap and abundant carbon resources. At the same time, it is regarded as one of the cause materials of the green house effect. Thus the development of new technologies which suppress the exhaustion of CO_2 or convert it to usable materials has been intensively studied. Although the hydrogenation of CO_2 to organic compounds is an attractive process for its utilization, most of the reactions are thermodynamically unfavorable except the formation of hydrocarbon.1)

In order to overcome this problem, the present authors postulate and demonstrate a new method for utilizing CO_2, which comprises the conversion of CO_2 by H_2 to CO and the successive hydrogenation of the CO produced.1)

The catalysts used are commercially available Fe-Cr mixed oxide (BASF K6-10), Cu-Zn mixed oxide (BASF S3-85), a high silica Y-type zeolite (Tosoh Co,Ltd., SiO_2/Al_2O_3=11 mole ratio), and a home-made Co+La/SiO_2 catalyst. The details of the catalyst preparation, compositions and activation were described elsewhere.2,3)

The reaction apparatus was a fixed bed, flow type one which was equipped with two reactors in series and was operated under pressurized conditions. If necessary, a cold trap with ice was set between two reactors to remove water from the effluent of the first reactor. All the products were analyzed by gas chromatographs.

Figure 1 shows the equilibrium conversion of CO_2 to CO, MeOH, and butane. It should be noted that while the equilibrium conversion of CO_2 to MeOH and butane decreases with the increase in reaction temperature, that to CO increases with increasing temperature. This means that hydrogenation of CO_2 to organic compounds via CO consists of a high temperature favorable reaction ($CO_2 \rightarrow CO$) and low temperature favorable reactions ($CO \rightarrow$ H.C. etc.). Two-stage reaction system will have its advantages from this point of view.



Initial ratio : $CO_2/H_2=1/2$

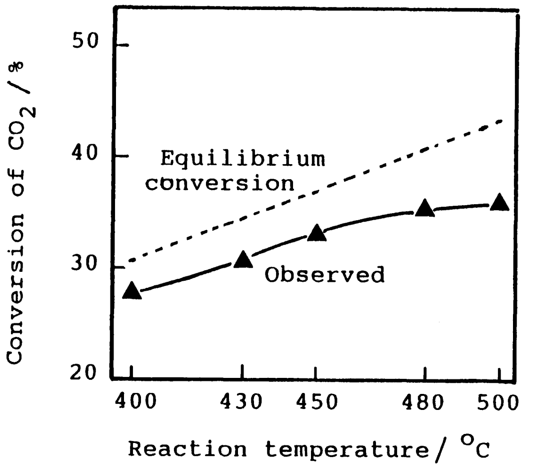
Pressure : 20 kg/cm^2

(1) $CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$

(2) $CO_2 + H_2 \rightleftharpoons CO + H_2O$

(3) $4CO_2 + 13H_2 \rightleftharpoons C_4H_{10} + 8H_2O$

Fig. 1. Equilibrium conversion of CO_2.



20 kg/cm^2, W/F 10 g-cat h/mol

Fe-Cr catalyst (BASF K6-10)

Fig. 2. Activity change on reverse CO shift reaction.

Figure 2 shows the CO_2 conversion on a Fe-Cr catalyst as a function of temperature. The CO_2 conversion increased with increasing reaction temperature and achieved 91% of equilibrium conversion at 450 °C. Carbon monoxide was the sole product at 450 °C or below, and small amount of methane was also formed as by product at 480 °C. In the first stage, Fe-Cr shift catalyst showed constant catalytic activity mentioned above for more than 20 hours at 450 °C. When the feed gas composition was $CO_2:H_2=0.50:1$, effluent gas composition was $CO_2:H_2:CO:H_2O=0.41:1:0.22:0.22$. After passing through the ice-cooled trap, the composition changed to $CO_2:H_2:CO = 0.41:1:0.23$. Reaction conditions in the first stage was 450 °C, 20 kg/cm^2, W/F=10 g-cat•h/mol in all the experiments tested.

Table 1 shows the results of methanol synthesis from CO_2 (or CO) and H_2 with a two stage reactor, which contained a Fe-Cr catalyst (BASF K6-10) in the first stage and a methanol synthesis catalyst (BASF S3-85) in the second stage. Table 1 summarizes the results of the second stage reactor. Inlet gas composition, contact time of mixture gas, and other reaction conditions changed accordingly as mentioned above and dependently whether shift converter and ice-cooled trap were used or not.

Table 1. Methanol Synthesis from CO_2, CO, and H_2 on Cu-Zn catalyst

Run	Feed Gas	First reactor	H_2O removal	Conv./% CO_2 (CO)	Product Yield/% CO	MeOH	H.C.
1a)	CO_2 H_2	no	no	7.8	4.6	3.2	---
2b)		yes	no	28.3	18.1	8.7	1.5
3c)		yes	yes	30.0	16.7	9.8	2.5
4d)	CO H_2	---	---	(10.5)	---	10.5	---

250 °C, 15 kg/cm^2, a) W/F=3.3 g-cat•h/mol, CO_2:H_2=0.50:1.
b) W/F=3.3 g-cat•h/mol, CO_2:H_2=0.50:1. c) W/F=3.8 g-cat•h/mol, CO_2:H_2=0.50:1.
d) W/F=1.5 g-cat•h/mol, CO:H_2:CO_2=1.97:1:0.16.

In the reaction of CO_2 and H_2 (run 1), main product was CO, which was produced on the Cu-Zn catalyst (BASF S3-85). After conducting reverse CO shift reaction (run 2), methanol yield drastically increased to the yield shown in the case of CO and H_2 (run 4), in which methanol yield reached the equilibrium one.2) Moreover, when produced H_2O was removed at the exit of the first stage (run 3), methanol yield increased, however CO yield decreased, and a certain amount of hydrocarbons (mainly CH_4) was produced.

Table 2. Hydrocarbon Synthesis from CO_2, CO, and H_2 on hybrid catalyst

Run	Feed Gas	First reactor	H_2O removal	Conv./% CO_2 (CO)	Product Yield/ % CO	C_1	C_2-C_5	C_6^+	MeOH	DME	CO_2
5a)	CO_2 H_2	no	no	13.0	11.7	0.1	---	---	1.2	---	---
6b)		yes	no	29.9	18.7	3.4	7.2	0.4	0.2	---	---
7c)		yes	yes	28.0	18.2	1.0	8.0	0.6	0.3	---	---
8d)	CO H_2	---	---	(71.7)	---	1.1	33.3	1.3	4.3	1.0	30.7

300 °C, 20 kg/cm^2, a) W/F=3.3 g-cat•h/mol, CO_2:H_2=0.50:1.
b) W/F=3.3 g-cat•h/mol, CO_2:H_2=0.50:1. c) W/F=3.8 g-cat•h/mol, CO_2:H_2=0.50:1.
d) W/F=3.4 g-cat•h/mol, CO:H_2=0.50:1, Cat. Cu-Zn 1 g + DAY 1 g.

Table 2 shows the product distribution from CO_2 or CO and H_2 on the hybrid catalyst of the methanol synthesis catalyst and the Y-type zeolite. This catalyst system, in which methanol was converted to hydrocarbons, is free from the equilibrium limitation of methanol formation, and thus, this system achieves high CO conversion as shown in the case of CO and H_2 (run 8).1) The Cu-Zn catalyst showed a certain activity to produce CO from CO_2

and H_2 (run 5). However, only a small amount of methane is the produced hydrocarbon in this case. After the feed gas passed through the first reactor (run 6), the yield of hydrocarbon increased drastically, while the main product was methane (excluding CO). When H_2O was removed from the feed of the second reactor (run 7), methane production was effectively suppressed while keeping the hydrocarbon yield at a similar level.

Two stage reaction system has another advantage, that is, H_2O, which adsorbed strongly on the catalyst to inhibit its methanol synthesis activity,[1] can be removed.

Table 3. Hydrocarbon Synthesis from CO_2, CO, and H_2 on Cobalt catalyst

Run	Feed Gas	Shift converter	H_2O removal	Conv./% CO_2 (CO)	Product Yield/% CO	C_1	C_2-C_5	C_6-C_{11}	C_{12}^+
9[a]	CO_2 H_2	no	no	6.7	0.2	4.9	1.2	tr.	---
10[b]		yes	no	12.1	0.3	3.2	4.5	3.8	0.3
11[c]		yes	yes	16.0	0.2	3.6	5.5	6.0	0.3
12[d]	CO H_2	---	---	(24.4)	---	4.9	4.6	13.2	1.7

240 °C, a) $CO_2:H_2=0.50:1$, W/F=10 g-cat•h/mol, 20 kg/cm^2. b) $CO_2:H_2=0.50:1$ W/F=10 g-cat•h/mol, 20 kg/cm^2. c) $CO_2:H_2=0.50:1$, W/F=11.6 g-cat•h/mol, 20 kg/cm^2. d) $CO:H_2=0.50:1$, W/F=10 g-cat•h/mol, 10 kg/cm^2
Catalyst; Co+La/SiO_2(ID) (20:6:87 by weight)

Table 3 shows the effect of the pre-hydrogenation of CO_2 and the removal of water on the Fischer-Tropsch synthesis. Co+La/SiO_2(ID), one of the conventional Fischer-Tropsch synthesis catalysts, selectively produces C_6-C_{11} hydrocarbons from CO and H_2 with high conversion.[3] However, the direct hydrogenation of CO_2 on the catalyst showed low conversion and the produced hydrocarbon composed of almost methane (run 9). This phenomena should be attributed to the low CO/H_2 ratio in the feed. The reverse shift reaction increased the conversion of CO_2 and the average molecular weight of product hydrocarbons (run 10). Removal of H_2O increased the chain growth probability of the products (run 11).

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