Hydrogenation of Carbon Dioxide over Fe-ZnO/Zeolite Composite Catalysts

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(Received May 22, 1995)

The hydrogenation of carbon dioxide was studied over the composite catalysts comprised of Fe catalysts and HY zeolite. In the case of Fe-ZnO/HY, the distribution of hydrocarbons showed that hydrocarbons were obtained by methanol to gasoline reaction, not by Fischer-Tropsch reaction.

Hydrocarbon synthesis from carbon oxides free from Schulz-Flory distribution law as the decisive limitation of F-T (Fischer-Tropsch) reaction[1] is a desirable process in catalysis chemistry. Composite catalysts composed of two different catalysts have recently been utilized.[2-5] Two approaches of the composite catalysts have been studied. One involves the combination of F-T reaction and the reforming reaction of hydrocarbons.[2,3] Fe catalyst was often applied to this type of composite catalyst.[3] Although branched and aromatic hydrocarbons could be produced, the distribution of hydrocarbons were essentially restricted by the Schulz-Flory distribution law.[1] Another approach is the combination[4,5] of methanol synthesis and methanol to gasoline (MTG) reaction.[6] This method is advantageous to produce hydrocarbons with unique distributions. In this composite catalyst, Cu catalyst[7] was mainly employed.[4,5]

It is well known that the addition of reducible metal enhances the catalytic activity of Fe catalyst.[8] On the other hand, Fe catalysts promoted by metal oxides were found to produce methanol from carbon dioxide and hydrogen under high pressure. It is expected that some Fe catalysts would be effective as methanol synthesis catalyst of the composite catalyst. In this paper, we wish to describe the hydrogenation of carbon dioxide over the composite catalysts composed of Fe-metal oxide (Fe-MO_n) with zeolite. It was found that Fe-ZnO/HY behaved as the composite catalyst combining methanol synthesis and MTG reaction, although Fe-ZnO catalyzed F-T reaction.

All Fe catalysts were prepared by coprecipitation of the corresponding metal nitrate using sodium hydroxide. The paste obtained was washed, dried at 120 °C for 6 h, and calcinated at 350 °C for 3 h. The composite catalysts were obtained by physical mixing of equal amounts of Fe-MO_n and zeolite (HY).[9] The catalytic test was performed using a pressurized flow-type fixed-bed reactor.[5] Pretreatment was carried out at 250 °C for 12 h using 1%H_2/N_2.

Table 1 summarizes the results of the hydrogenation of carbon dioxide over Fe-MO_n. Hydrocarbons were obtained with Schulz-Flory distribution in all cases. The characteristics of Fe-MO_n depended on the added metal oxides. Although C_{2+} hydrocarbons were formed in good selectivity over Fe catalyst (**M1**), all Fe-MO_n, especially Fe-ZnO (**M2**), gave methane as the predominant hydrocarbon. On the other hand, methanol could be obtained over all Fe-MO_n (**M2-7**), but not over Fe catalyst.

Table 2 shows the catalytic performances of various composite catalysts made of Fe-MO_n and HY zeolite. The formation of carbon monoxide was predominant over all composite catalysts. The yields of hydrocarbons were strictly influenced by the added metal oxides. Fe/HY, Fe-Cr_2O_3/HY, Fe-Al_2O_3/HY, Fe-ZrO_2/HY, Fe-MgO/HY and Fe-La_2O_3/HY were not effective for hydrocarbon synthesis (**C1,3-7**). The predominant formation of methane indicated that F-T reaction proceeded mainly in almost cases. On the other hand, it is noteworthy that hydrocarbons were obtained in a good yield with a high C_{2+} hydrocarbon selectivity over Fe-ZnO/HY (**C2**). Moreover, ethylene was formed in good selectivity. In general, olefin synthesis over the composite catalyst has been regarded to be difficult, although Cu-Zn-chromate/HY composite catalysts was recently reported.[10]

Figure 1 shows the distributions of hydrocarbons over Fe-ZnO/HY (**C2**) and Fe-ZnO (**M2**). A typical Schulz-Flory distribution was observed in the reaction over Fe-ZnO [Figure 1(**B**)], clearly demonstrating that F-T reaction occurred. On the other hand, the distribution of hydrocarbons over Fe-ZnO/HY was quite different and similar to that of Cu-Zn-chromate/HY composite catalysts reported before.[10] The selectivity of methane was very low and that of C_4 hydrocarbons was maximum [Figure 1(**A**)]. Moreover, ethylene and propylene were also observed. These olefins seem to be polymerized to give higher hydrocarbons. Therefore, it is suggested that over Fe-ZnO/HY hydrocarbons were produced by MTG reaction, not

Table 1. Hydrogenation of Carbon Dioxide over Fe-MO_n

Cat. No.	Fe-MO_n[a]	Conv. of CO_2/%	Convert to/C-mol% C_1	C_{2+}	MeOH	CO	C_2= Ratio[b]
M1	Fe	18.6	1.4	8.4	0.0	8.8	81
M2	Fe-ZnO	17.2	7.6	3.1	0.5	6.0	1
M3	Fe-Cr_2O_3	28.1	0.5	0.1	0.3	27.2	50
M4	Fe-Al_2O_3	19.5	3.2	1.6	0.5	14.2	2
M5	Fe-ZrO_2	18.2	1.3	1.3	0.6	15.0	29
M6	Fe-MgO	9.3	0.5	0.0	0.5	8.3	0
M7	Fe-La_2O_3	16.6	5.3	1.9	0.3	9.2	0

350 °C, 50 atm, SV=3000 ml/g-cat./h, H_2/CO_2=3. Results after 6 h. [a]Fe/M=4; molar ratio. [b]$C_2H_4/(C_2H_4+C_2H_6)$/%.

Table 2. Hydrogenation of Carbon Dioxide over Fe-MO_n/HY Composite Catalysts

Cat. No.	Composite Catalyst[a]	Conv. of CO_2/%	Convert to/C-mol% C_1	C_{2+}	Oxy[b]	CO	C_2= Ratio[c]
C1	Fe/HY	15.3	0.3	0.4	0.0	14.6	92
C2	Fe-ZnO/HY	13.3	0.4	4.5	0.2	8.2	80
C3	Fe-Cr_2O_3/HY	24.9	1.1	0.6	0.0	23.2	79
C4	Fe-Al_2O_3/HY	15.9	0.3	0.3	0.0	15.3	80
C5	Fe-ZrO_2/HY	15.2	0.3	0.2	0.0	14.7	79
C6	Fe-MgO/HY	12.2	0.0	0.1	0.0	12.1	100
C7	Fe-La_2O_3/HY	11.2	2.3	0.9	0.0	8.0	5

350 °C, 50 atm, SV=3000 ml/g-cat./h, H_2/CO_2=3. Results after 6 h. [a]Fe/M=4; molar ratio. [b]MeOH+MeOMe. [c]$C_2H_4/(C_2H_4+C_2H_6)$/%.

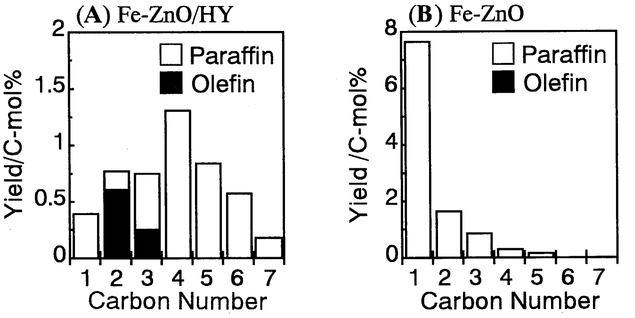


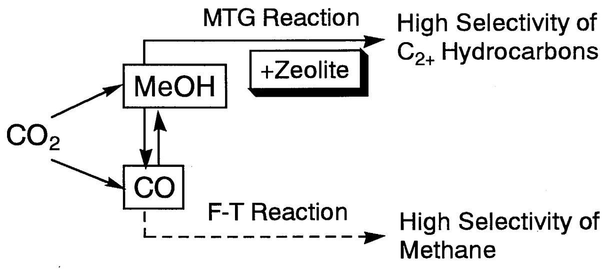
Figure 1. Hydrocarbon distribution of the hydrogenation of carbon dioxide (350 °C, 50 atm, 3000 ml/g-cat./h).

by F-T reaction.

It is well known that linear hydrocarbons are formed predominantly in F-T reaction. On the contrary, the reaction using F-T catalyst/zeolite[3] or methanol synthesis catalyst/zeolite composite catalyst[4] prefers the formation of branched hydrocarbons due to the acidic carbon-homologation by zeolite. The difference of the selectivities of iso-butane in all C_4 hydrocarbons was observed between Fe-ZnO (3%; **M2**) and Fe-ZnO/HY (83%; **C2**). This also indicated that the simple F-T reaction proceeded over Fe-ZnO (**M2**). On the other hand, the high selectivity of iso-butane over Fe-ZnO/HY (**C2**) supported that hydrocarbons were formed via methanol by MTG reaction.[6]

The effect of the increase of the space velocity (3000→30000 ml/g-cat./h) on the catalytic performances of Fe-ZnO (**M2**) was examined. Although the increase of space velocity scarcely changed the conversion of carbon dioxide (approximately 18%), the yield of hydrocarbons were decreased (12.4→10.6 C-mol%). On the contrary, both the yields of carbon monoxide (5.9→6.9 C-mol%) and methanol (0.4→0.8 C-mol%) increased. From these results, methanol and carbon monoxide are considered to be intermediates of the hydrocarbon formation. Carbon monoxide is the direct intermediate of F-T reaction, and methanol obtained from carbon dioxide also seems to be a resource of carbon monoxide by its decomposition.

Scheme 1 illustrates a plausible reaction path of the hydrogenation of carbon dioxide over Fe-ZnO/HY. C_{2+} hydrocarbons are formed via MTG reaction, while F-T reaction exclusively occurred with the decomposition of methanol to carbon monoxide in the case of Fe-ZnO. On the other hand, it was noteworthy that the yield of hydrocarbons drastically decreased by the addition of zeolite to Fe catalyst (9.8→0.7 C-mol%; **M1**→**C1**). We recently revealed that the solid-solid interaction between methanol synthesis catalyst and zeolite is an important factor to form the real composite catalysts.[5] It seems that the catalytic site of F-T reaction in Fe catalysts was preferentially deactivated by the coexistent zeolite. In the case of Fe-ZnO/HY (**M2**), the catalytic activity of Fe-ZnO for methanol synthesis was still effective even after the mixing of zeolite, exerting the hydrocarbon synthesis via MTG reaction.



Scheme 1. Reaction Path of the Hydrogenation of Carbon Dioxide over Fe-ZnO/HY.

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