

HYDROGENATION OF CARBON DIOXIDE OVER Fe-ZnO/HY COMPOSITE CATALYST

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INTRODUCTION

Fe-based catalysts are often used for various fields of catalytic reactions. F-T (Fischer-Tropsch) reaction is a representative example. It is well known that the Schulz-Anderson-Flory law determines the distribution of hydrocarbons in F-T reaction. To overcome this limitation, the composite catalysts comprised of Fe-based catalyst and zeolite have been examined (1). Although these composite catalysts produced branched hydrocarbons and improved the selectivity of hydrocarbons, the distribution was essentially restricted by the Schulz-Anderson-Flory law in almost cases.

We have already reported (2,3) that hydrocarbons were obtained efficiently from carbon dioxide and hydrogen over another type of the composite catalysts which are prepared by the physical mixing of Cu-based catalysts and zeolite (4). This catalytic system combining methanol synthesis and MTG (Methanol-to-Gasoline) reaction presents a novel method for hydrocarbon synthesis which is free from the Schulz-Anderson-Flory law. We recently found (5) that, in the hydrogenation of carbon dioxide, Fe-ZnO/HY composite catalyst produced hydrocarbons with a similar distribution to the composite catalysts comprised of Cu-Zn-chromate and zeolite (3), while Fe-ZnO catalyst (6) acted as a typical F-T catalyst to afford hydrocarbons with the Schulz-Anderson-Flory distribution. This presentation describes the entire studies of the hydrogenation of carbon dioxide over Fe-ZnO/HY.

EXPERIMENTAL

Fe-based catalysts were prepared by the coprecipitation of the corresponding nitrates using sodium hydroxide. The precipitate was washed five times, dried at 120°C for 6 h and calcined at 350°C for 3 h. The composite catalysts were obtained by the physical mixing of equal amounts of Fe-based catalyst and zeolite. HY [JRC-Z-HY4.8(2)] and NaY [JRC-Z-Y4.8] were provided from the Reference Catalyst of the Catalysis Society of Japan.

The hydrogenation of carbon dioxide was carried out using a pressurized flow-type fixed-bed reactor (2). The two stage reactor reaction was carried out using two separate stainless-steel reactors in series with the same diameter which were heated at the same temperature by the respective furnaces. The carbon monoxide adsorption and dissociation were carried out on a pulse reactor. TPR (Temperature-programmed reduction) measurement was carried out as follows; the catalyst (0.5 g) was heated (temperature increase rate: 10°C/min) in a glass tube reactor under a 10% H₂/He gas flow (31 ml/min). The consumption of the mass number 2 was monitored by an on-line quadrupole mass spectrometer. As the composite catalyst used for the hydrogenation of carbon dioxide was not suitable for this measurement because of carbon remained on the catalyst, Fe-ZnO(4:1)/HY pretreated by pure hydrogen at 350°C for 6 h, calcined at 350°C in air to re-oxidize was employed as a model used composite catalyst.

RESULTS AND DISCUSSION

The drastic differences of the catalytic behaviors of Fe-based catalysts were observed between sole catalysts and the corresponding composite catalysts with HY as shown in Table 1. Especially, the difference between Fe-ZnO(4:1) and Fe-ZnO(4:1)/HY is remarkable. From the hydrocarbon distribution shown in Fig. 1, it seems that Fe-ZnO(4:1) worked as a F-T catalyst and Fe-ZnO(4:1)/HY acted as the composite catalyst which was made of methanol synthesis catalyst and zeolite. The high selectivity of the branched hydrocarbons (For example: iso-C₄/n-C₄=5.5) in the case of this composite catalyst also suggested that these hydrocarbons cannot be produced by F-T reaction and that MTG reaction over zeolite was responsible for this formation. It is also noteworthy that ethylene and propylene were yielded in good selectivities. Most of studies on the composite catalysts for the hydrogenation of carbon oxides were unsatisfactory in the olefin formation so far (1,2). It is also paid attention that the yield of hydrocarbons decreased (from 9.8 to 0.7 C-mol%) over Fe catalyst by the mixing of HY. Fe/HY produced carbon monoxide exclusively, although the decrease of the total conversion of carbon dioxide was not serious (from 18.6 to 15.3%). In other cases such as Fe-Cr₂O₃ and Fe-Al₂O₃, the yields of hydrocarbons were very low. Cobalt catalyst was also studied because it is well known as an active F-T catalyst. In the absence of HY, Co-ZnO (4:1) produced methanol, and hydrocarbons obtained were only methane. Carbon monoxide was formed exclusively over the corresponding composite catalyst. Methanation was decisively inhibited and the hydrocarbon formation by the combination of methanol synthesis and MTG reaction was not observed in this case. Therefore, the noticeable change of the catalytic behaviors of Fe-based catalyst from F-T reaction to methanol synthesis was observed only in Fe-ZnO.

Different composite catalysts such as Fe-ZnO/NaY and Fe-ZnO/SiO₂ were also examined. Although the composite catalyst with NaY produced methanol and dimethylether in high selectivities, the yields of hydrocarbons were poor. The acidity of NaY is not enough to the conversion of methanol into hydrocarbons. However, the formation of dimethylether showed that methanol is obtained in considerable yield and is able to be transformed by acidic mechanism. In the case of Fe-ZnO/SiO₂, hydrocarbons were obtained in the Schulz-Anderson-Flory

distribution, indicating that F-T reaction took place. The acidic HY was required for this change of the catalytic behaviors of Fe-ZnO. In addition, two reactor reaction in series (Fe-ZnO and HY were packed in the first or the second reactor, respectively.) gave methane with high selectivity, and the distribution of hydrocarbons was completely different from the reaction over Fe-ZnO/HY. Therefore, it is evident that the function of Fe-ZnO/HY was not to combine F-T reaction over Fe-ZnO and the reforming reaction of hydrocarbons over zeolite.

Table 1. Hydrogenation of Carbon Dioxide over Fe-Based Catalyst^{a)}

Catalyst ^{b,c)}	Conv. of CO ₂ (%)	Convert to (C-mol%)			
		C ₁	C ₂₊	Oxy ^{d)}	CO
Fe	18.6	1.4	8.4	0.0	8.8
Fe/HY	15.3	0.3	0.4	0.0	14.6
Fe-ZnO	17.2	7.6	3.1	0.5	6.0
Fe-ZnO/HY	13.3	0.4	4.5	0.2	8.2
Fe-Cr ₂ O ₃	28.1	0.5	0.1	0.3	27.2
Fe-Cr ₂ O ₃ /HY	24.9	1.1	0.6	0.0	23.2
Fe-Al ₂ O ₃	19.5	3.2	1.6	0.5	14.2
Fe-Al ₂ O ₃ /HY	15.9	0.3	0.3	0.0	15.3
Fe-ZnO/NaY	6.0	0.1	0.6	3.0	2.3
Fe-ZnO/SiO ₂	11.6	3.9	1.1	1.1	5.5
Fe-ZnO+HY ^{e)}	11.2	2.1	2.0	0.0	7.1
Co-ZnO	7.3	1.0	0.0	2.1	4.2
Co-ZnO/HY	10.2	0.0	0.0	0.0	10.2

a) 350°C, 5 MPa, SV=3000 ml/g-cat./h, H₂/CO₂=3, results after 6 h. b) Fe/Metal=4 (atomic ratio). c) Equal amount of Fe-based catalyst and HY was physically mixed for the composite catalysts. d) MeOH+MeOMe. e) Reaction using two reactors in series; Fe-ZnO in the first reactor and HY in the second reactor, SV=6000 ml/g-cat./h.

The effect of the zinc content on the catalytic behaviors was next examined as shown in Fig. 2. In the case of composite catalysts, Fe/HY and Zn/HY gave hydrocarbons in very poor yields. However, Fe-ZnO/HY with various zinc contents produced hydrocarbons in up to 5% yields, and the selectivities of C₂₊ hydrocarbons in all hydrocarbons were high [Fig. 2.(A)]. Although the zinc content was not a crucial factor in the hydrocarbon synthesis, the best yield of hydrocarbons was observed in Fe-ZnO(4:1)/HY. Fe-ZnO of which zinc content was higher than 33% can be considered as methanol synthesis catalyst, because methanol was obtained in up to 3% yield and the formation of hydrocarbons including methane was very low. It is understandable that hydrocarbons were obtained via MTG reaction in the case of the corresponding composite catalysts. However, the catalytic behaviors of Fe-ZnO(4:1)/HY were not expectable. Fe-ZnO(4:1) was a typical F-T catalyst because of the distribution of hydrocarbons approximately following the Schulz-Anderson-Flory law. On the contrary, in the case of the corresponding composite catalyst, Fe-ZnO acted as a methanol synthesis catalyst rather than a F-T catalyst [Fig. 1.(A)]. It seems that only the solid-solid interaction between Fe-ZnO and HY we noticed before (2) can explain this modification of the catalytic behaviors.

According to XRD measurement, Fe-ZnO with a zinc content lower than 33% prior to the reaction consisted of α -Fe₂O₃ and ZnFe₂O₄. In the catalyst used, the diffraction patterns of α -Fe₂O₃ disappeared completely and those of ZnFe₂O₄ remained. This suggested that α -Fe₂O₃ transformed to other iron species. As the active species for F-T reaction are generally obtained by the reduction of α -Fe₂O₃ via Fe₃O₄, the iron species derived from α -Fe₂O₃ seem to be the catalytic sites for F-T reaction. On the other hand, the diffraction patterns of ZnO and ZnFe₂O₄ were detected in Fe-ZnO with zinc contents higher than 33%. After the reaction, all peaks still remained only to become sharper. The catalytic activity for methanol synthesis of Fe-ZnO(1:2) was higher than that of ZnO as shown in Fig. 2. (A), indicating that not only ZnO (7) but also ZnFe₂O₄ are responsible for methanol synthesis. Fe-ZnO(2:1) can be regarded as pure ZnFe₂O₄, because its content of zinc and iron is similar to ZnFe₂O₄ and only the peaks of ZnFe₂O₄ were observed before the reaction by XRD measurement. However, ZnO as well as ZnFe₂O₄ were detected in the catalyst used. The spinel structure of ZnFe₂O₄ was destroyed during the reaction. Although evaluating the catalytic activity of pure ZnFe₂O₄ was unsuccessful, ZnFe₂O₄ is thought to be a significant component of Fe-ZnO to produce methanol. Moreover, in the case of the composite catalyst, it seems that some iron species from α -Fe₂O₃, which are deactivated not to be active for F-T reaction, promote this methanol synthesis, because the best yield of C₂₊ hydrocarbons was observed in Fe-ZnO(4:1) which is composed of α -Fe₂O₃ and ZnFe₂O₄.

The reaction of carbon monoxide, which is an important intermediate of F-T reaction, is also significant to reveal the influence of zeolite on the catalytic activity of Fe-ZnO. Carbon monoxide adsorption and dissociation experiments also show the change of the catalytic behavior of Fe-ZnO(4:1). The amount of adsorbed carbon monoxide can be related to the number of metallic sites active for F-T reaction. Furthermore, the amount of dissociated carbon monoxide was found to be correlated with the formation of C₂₊ species (8). Especially, this dissociation experiments at 300°C is advantageous so as to know the ability of the catalyst for F-T reaction, because the dissociation of carbon-oxygen bond in carbon monoxide is the first step of hydrocarbon formation in the conventional mechanism of F-T reaction. Table 2 shows the clear differences of the reaction manner of carbon monoxide between on Fe-ZnO and on Fe-ZnO/HY. In the case of Fe-ZnO, the adsorption of carbon monoxide was approximately the same as the reported one of α -Fe₂O₃ (9). The conversion of carbon monoxide at 300°C was very high, whereas only a limited part of carbon monoxide was involved in the Boudouart reaction, and the major part of converted carbon monoxide remained on the catalyst as surface carbon evidenced by carbon analysis. Thus, Fe-ZnO was very active for the dissociation of carbon monoxide to be an effective F-T catalyst. On the contrary, the ability of adsorbing carbon monoxide on Fe-ZnO/HY was extremely low, and the conversion of carbon monoxide at 300°C was lower than Fe-ZnO. From these results, it is obvious that the catalytic activity of Fe-ZnO for F-T reaction was diminished in the composite catalyst by the solid-solid interaction with HY.

Table 2. Adsorption and Reaction of Carbon Monoxide on Catalysts

Catalyst ^{a)}	Fe-ZnO (4:1)	Fe-ZnO (4:1)/HY
CO adsorption (μ mol) ^{b)}	15.4	1.2
CO reaction (%) ^{c)}	Total conv. of CO	78 (29) ^{d)}
	Carbon content (wt-%) ^{e)}	2 (<0.1) ^{f)}
		<0.1 (3.8) ^{f)}

a) Catalyst was pretreated by 20% H₂/N₂ for 5 h at 370°C. b) Measured by the pulse reaction of carbon monoxide (0.5 ml) at room temperature. Per 1 g of Fe-ZnO. c) Measured by the pulse reaction of carbon monoxide (0.5 ml) at 300°C. d) Boudouart reaction determined by the amount of carbon dioxide detected by TCD. e) After the nine pulses of carbon monoxide. f) Catalyst used for the hydrogenation of carbon dioxide.

The solid-solid interaction was confirmed by TPR (Temperature-programmed reduction) measurement as well. The first hydrogen consumption which is thought to be caused by the reduction of α -Fe₂O₃ to Fe₃O₄, was observed at 313°C in Fe-ZnO (4:1) and also in Fe-ZnO(4:1)/HY without pretreatment. However, the temperature of the first hydrogen consumption was detected at 337°C in Fe-ZnO/HY pretreated at 350°C. Furthermore, this temperature was shifted to 376°C in Fe-ZnO/HY pretreated at 400°C. The solid-solid interaction between Fe-ZnO and HY changed the reducibility of the Fe-ZnO. These results also show that zeolite crucially affects the characteristics of Fe-ZnO.

From all results discussed here, it is obvious that hydrocarbons are produced by F-T reaction over Fe-ZnO(4:1), and by the combination of methanol synthesis and MTG reaction over Fe-ZnO(4:1)/HY, respectively. Fe-ZnO(4:1) consists of α -Fe₂O₃ and ZnFe₂O₄ in XRD measurement before reaction, and α -Fe₂O₃ produces the active species for F-T reaction by the reduction. F-T reaction works mainly in the presence of carbon monoxide formed by the reversed water-gas-shift reaction or by the decomposition of the methanol. However, in the presence of zeolite, the active sites for F-T reaction are inhibited by the solid-solid interaction with zeolite during the catalytic reaction. This effect was ascertained by the results of the carbon monoxide pulse experiments. The serious deactivation of Fe catalyst for F-T reaction also supports this phenomenon. On the other hand, the methanol formation can be attributed to Fe-promoted ZnFe₂O₄ or the related species. It seems that the influence of zeolite on this methanol synthesis is of minor importance. Therefore, hydrocarbons are produced via methanol over Fe-ZnO/HY. In other Fe-based catalysts such as Fe-Cr₂O₃ and Fe-Al₂O₃, no active species for methanol synthesis was included to result in the extremely poor yields of hydrocarbons over the corresponding composite catalysts. Co-ZnO includes no effective sites for methanol synthesis working with zeolite. The active species for F-T reaction was deactivated completely and, consequently, only carbon monoxide was obtained by the reversed water-gas-shift reaction.

The plausible reaction scheme is illustrated in Fig. 3. Fe-ZnO(4:1) has two kinds of reaction sites, that is, 1) metallic iron or other iron species active for F-T reaction derived from α -Fe₂O₃, and 2) Fe-promoted ZnFe₂O₄ or the related species for methanol synthesis. In the absence of zeolite, the F-T reaction sites exert their activity to produce hydrocarbons with the Schulz-Anderson-Flory distribution, whereas methanol formed is decomposed into carbon monoxide to promote F-T reaction. In the case of the composite catalyst, the F-T reaction sites are deactivated by zeolite while the catalytic activity for methanol synthesis is mostly maintained. Methanol formed which is not decomposed into carbon monoxide reacts over HY to form hydrocarbons with non-Schulz-Anderson-Flory distribution by MTG reaction. As carbon monoxide yielded

from methanol does not take place F-T reaction, the selectivity of carbon monoxide was very high in the case of the composite catalysts.

CONCLUSIONS

Fe-ZnO/HY composite catalyst is an original system which is able to produce olefins with a particular non-Schulz-Anderson-Flory distribution. The Fe-ZnO shows two kinds of catalytic sites, that is, iron species effective for F-T reaction formed from $\alpha\text{-Fe}_2\text{O}_3$, and Fe-promoted ZnFe_2O_4 effective for methanol synthesis. In the absence of zeolite, the F-T reaction sites are very active to produce hydrocarbons with the Schulz-Anderson-Flory distribution. On the other hand, the sites for F-T reaction are deactivated and the sites for methanol synthesis promoted by iron species exhibit the catalytic activity in the case of the composite catalyst. Therefore, hydrocarbons were obtained by MTG reaction with a non-Schulz-Anderson-Flory distribution over Fe-ZnO/HY. The mechanism of the deactivation of the active sites for F-T reaction by zeolite is under investigation.

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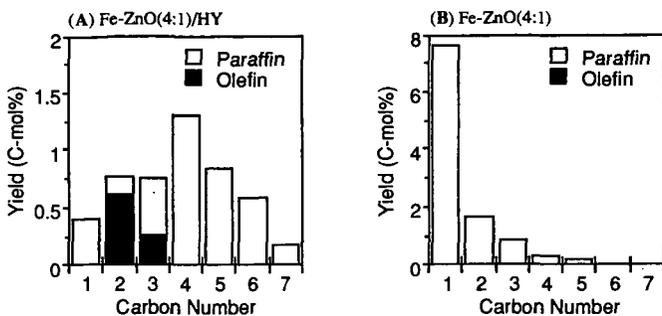


Figure 1. Hydrocarbon Distribution over (A) Fe-ZnO(4:1)/HY and (B) Fe-ZnO(4:1).

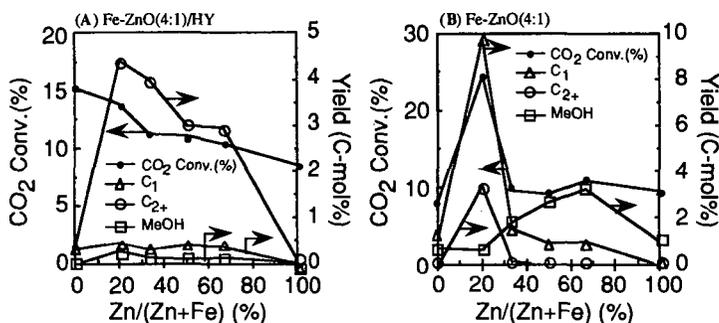


Figure 2. Effect of Zinc Content in (A) Fe-ZnO(4:1)/HY and (B) Fe-ZnO(4:1).

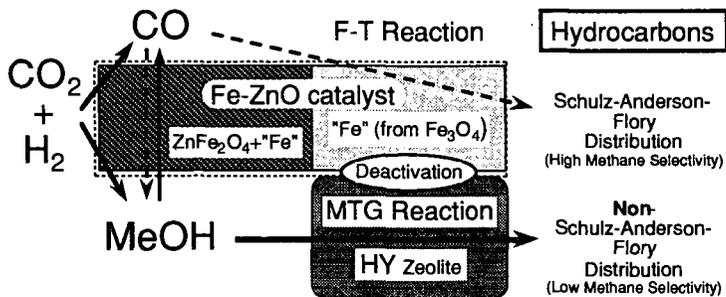


Figure 3. Reaction Scheme of Hydrocarbon Synthesis over Fe-ZnO/HY.