EFFECT OF PARTIAL METAL REDUCTION ON THE CATALYTIC PROPERTY OF Fe/SiO$_2$ IN CO HYDROGENATION

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Abstract — Effect of partial metal reduction on the property of supported iron catalysts has been studied using 9.1 wt% Fe/SiO$_2$ as a model catalyst and CO hydrogenation as a test reaction. The extent of iron reduction does not alter the intrinsic activity of iron nor distribution of the hydrocarbon products with specific carbon numbers, but significantly changes the olefin/paraffin ratio among the products. This kinetic behavior agrees with the result of gas chemisorption that the H$_2$/CO adsorption ratio decreases as the catalyst is reduced poorly. Well-reduced iron catalysts deactivate during the reaction because the carbon species deposited on the surface gradually transform into less-reactive ones as observed in the TPSR experiments.

INTRODUCTION

Iron is difficult to reduce completely, particularly when it is dispersed as fine particles on the catalyst support. Accordingly, most of the iron catalysts are used as partially reduced ones containing the unreduced iron oxides even after reduction at elevated temperatures. A question arises about whether the unreduced iron oxides are catalytically inert or modify the intrinsic activity of the reduced iron. A few previous studies [1-5] suggest that the modification is possible.

An example is given by Dwyer and Somorjai [2] who measured the methanation rate on two kinds of iron foil : one cleaned by ion sputtering of possible impurity elements such as oxygen and sulfur, and the other intentionally exposed to oxygen pressure of 4 Torr at 300°C for 20 minutes. They observed that the oxygen-exposed foil showed the higher methanation rate than the clean one. This may be interpreted as that the surface oxygen modifies the electronic property of the iron foil and eventually changes its catalytic

activity. Another example, although it is not for iron but for cobalt, directly indicates modification of the catalytic property of supported cobalt catalysts due to partial metal reduction [4]. That is, a poorly reduced cobalt catalyst exhibits a higher olefin/paraffin ratio among products in CO hydrogenation than a relatively well-reduced one.

With the above background considerations, we have studied the changes in the kinetic behavior of supported iron catalysts in CO hydrogenation due to different extents of metal reduction. Iron catalyst is a complicated system to study. As is well-known, iron is relatively easily deactivated by the surface carbon deposition in CO hydrogenation [6]. Furthermore, there still remains uncertainty about the nature of the active sites in CO hydrogenation, e.g., reduced iron [7], partially reduced magnetite [8], or carbided iron [9]. All these factors make interpretation of the experimental results sometimes controversial.

In this study, we have changed only the extent of iron reduction by preparing the iron catalyst in one batch and then by reducing it under different conditions. The kinetic behavior of the partially-reduced catalysts has been correlated with the results of gas chemisorption and temperature-programmed surface

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reaction (TPSR).

EXPERIMENTAL

1. Catalyst Preparation and Reduction

The sample catalyst used in this study is Fe/SiO_2 with the nominal metal loading of 9.1 wt%. Silica support is a standard material (JRC-SiO-6) obtained from Japanese Catalysis Society with the reported surface area and pore volume of 85 m^2/g and 1.11 cc/g, respectively. The silica support has been ground into 40/80 mesh and dried in an oven before use. Iron salt, $Fe(NO_3)_3 \cdot 9H_2O$, with the purity of 99.997% has been purchased from Aldrich and used without further purification. The catalyst has been prepared by the incipient wetness method as described by Vannice [10], and dried in an oven at 120°C for 24 hours before storage in a dessicator.

The catalyst has been reduced by heating in dihydrogen stream. The heating scheme is as follows : 1) heat from room temperature to 125°C at 5°C/min, 2) remain at 125°C for 30 minutes, 3) heat again at 5°C /min up to 200°C, 4) heat up to the final reduction temperature at 10°C/min, and 5) remain at the final temperature for specified period. The extent of reduction has been estimated by oxygen titration at 400°C [11]. It is assumed that iron forms Fe_2O_3 after oxidation at 400°C [12].

2. CO Hydrogenation

The rates and the product distribution in CO hydrogenation over the iron catalysts have been measured in a conventional microreactor unit with the reactant stream comprising H_2 and CO at 3 : 1 ratio. The reactant gases are purified by passing them through Molecular Sieve 5A and MnO traps in series. CO has been purified further after flowing through an activated carbon column. The products of the reaction are analyzed by Traco 565 GC equipped with a flame ionization detector. Details of the GC column and the operating conditions are described elsewhere [13].

3. Chemisorption and Temperature-Programmed Surface Reaction (TPSR)

The amounts of dihydrogen or carbon monoxide adsorbed on the catalysts have been measured in a volumetric gas adsorption unit. Since the adsorption of dihydrogen on iron is an activated process [14], the adsorption amount of dihydrogen has been obtained by measuring the desorption isotherm at room temperature and extrapolating the curve to zero pressure. The amount of CO adsorption has been obtained from the adsorption isotherm at room temperature. TPSR of the surface carbon species deposited on the

catalyst during reaction has been made by heating the catalyst in dihydrogen stream at 10°C/min up to 800°C. The effluent stream is sampled every 30 seconds and analyzed for methane by an on-line GC.

RESULTS AND DISCUSSION

1. Reduction of Iron Catalyst

The 9.1 wt% Fe/SiO_2 catalyst prepared in this study has been reduced in dihydrogen stream at different temperatures and for various reduction periods. Table 1 shows that the extent of reduction is significantly influenced by the final reduction temperature but not by the period of final reduction after ten minutes. This indicates that the reduction proceeds rapidly enough to reach the equilibrium state in about 10 minutes. Since the change in the standard free energy for iron oxide reduction is relatively small [15], the reduced iron coexists with the unreduced iron oxide after reduction. The catalysts have been reduced to different extents, 3, 21, 34, and 63%, by reducing at different temperatures between 320 and 450°C.

2. Rates of CO Hydrogenation

The rates of CO hydrogenation on the iron catalysts change characteristically as shown in Fig. 1 depending on their percentage reduction. As the reaction proceeds, the 63%-reduced catalyst, Fe (63%), monotonically loses its initial high activity but those reduced to less than 34% show an initial increase in the rate followed by a gradual decrease after about 2 hours. After about 4 hours, the rates become almost same regardless of the extents of the catalyst reduction.
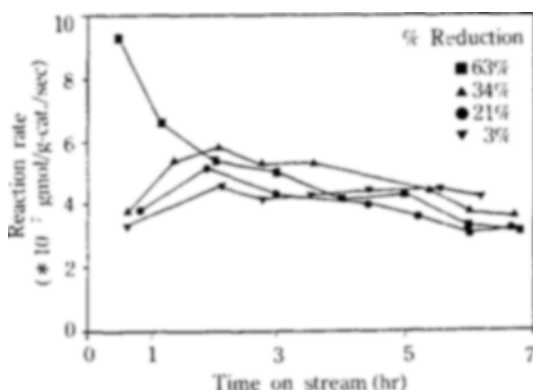
The reason for the monotonic decrease in the rate on Fe (63%) is because the catalyst is deactivated by surface carbon deposition during the reaction, as has been studied previously [6]. Other possible reasons such as sintering, reoxidation of iron, and poisoning by sulfur are ruled out in this case because the reaction temperature has been relatively low and the reactant gases have been thoroughly purified by the traps. The surface carbon deposition has been confirmed by TPSR as will be described later.

The initial rate increase on the relatively poorly-reduced catalysts suggests that the catalysts are reduced further during the reaction. Since the reaction temperature is lower than the final reduction temperature by more than 50°C, it is not likely that the catalysts are reduced further by dihydrogen during the reaction. Instead, they seem to be reduced more by carbon monoxide in the reaction stream. In fact, carbon monoxide is more efficient in reducing iron oxide than dihydrogen. This is supported by a thermodynamic

Table 1. Reduction of 9.1 wt% Fe/SiO₂ catalyst in H₂ stream

Reduction condition*	Percentage reduction (%)	Notation of reduced catalyst
R (320,10)	3	Fe (3%)
R (350,10)	21	Fe (21%)
R (350,60)	20	
R (420,10)	34	Fe (34%)
R (450,10)	63	Fe (63%)
R (450,60)	63	

*R (T, t) designates a catalyst reduced at T°C for t minutes.

Table 2. Product distribution in CO hydrogenation on 9.1 wt% Fe/SiO₂ catalysts of different percentage reduction

Catalyst	Hydrocarbon selectivity (mol%)					Time on stream (hr)
	C_1	C_2	C_3	C_4	C_5	
Fe (63%)	52.8	19.0	19.6	2.7	5.7	0.50
Fe (34%)	51.1	16.6	17.7	7.5	7.3	0.63
Fe (21%)	52.1	17.2	17.5	8.3	4.9	0.77
Fe (3%)	49.9	16.1	18.8	9.5	5.7	0.58
	50.5	18.4	16.8	8.4	5.8	2.08
	50.6	18.7	19.2	7.3	4.3	3.55
	48.6	18.7	20.3	7.9	4.5	4.45
	49.0	19.4	18.9	7.2	5.5	6.87

Fig. 1. Changes in the rate of CO hydrogenation with the reaction time on the 9.1 wt% Fe/SiO₂ catalysts of different metal reduction.

calculation that the change in the standard free energy for the iron oxide reduction by carbon monoxide at 270°C is −3.2 kcal/gmol, while the value is 3.5 kcal/gmol for the reduction by dihydrogen.

Although the poorly reduced catalysts gain more active sites due to further reduction during reaction, they experience simultaneously deactivation due to the surface carbon deposition. As a result, the rate on the catalysts goes through a maximum value and then eventually decreases. The two opposite effects on the rate occur more slowly on the poorly-reduced catalysts, as examplified for Fe (3%).

In fact, above explanation about the rate change observed in Fig. 1 is in agreement with the results reported by Reymond et al. [8]. They have observed that the completely-reduced α-Fe catalyst is rapidly deactivated in CO hydrogenation while the unreduced α-Fe₂O₃ catalyst shows a gradual increase in the rate so that the rate on the latter is about 4 times larger than one on the former after 20 hours. Our result in Fig. 1 also shows that the rate is slightly higher on Fe (3%)

than on Fe (63%) after reaction for 6 hours.

The three models that have been described by Niemantsverdriet and van der Kraan [16] for explaining the initial increase in the activity of iron catalysts for Fischer-Tropsch synthesis are not applicable to this case because in this study we have observed the initial rate increase only on the poorly-reduced iron catalysts.

3. Product Distribution in CO Hydrogenation

Although the rate in CO hydrogenation changes characteristically depending on the extent of iron reduction, distribution of the hydrocarbon products with specific carbon numbers remains almost constant as shown in Table 2. The product distribution is also unaffected by the reaction period as exemplified for Fe (3%). The result indicates that the chain propagation step in CO hydrogenation is not affected by the extent of metal reduction nor by the surface carbon deposition. To confirm this view, we have plotted the product distribution data according to the Schulz-Flory-Anderson plot and estimated the chain propagation probability therefrom. The probability values obtained are 0.56, 0.51, 0.57, and 0.58 for Fe (3%), Fe (21%), Fe (34%), and Fe (63%) respectively, which are in support of the above view.

Apart from the above results, distribution of the olefinic and paraffinic hydrocarbons changes significantly with the extent of catalyst reduction as well as with the reaction period. In Table 3, the olefin/paraffin ratios in the products obtained during the initial reaction period are listed for different extents of catalyst reduction. Since the ratio also depends strongly on the conversion [17], we have maintained the conversion almost same in the experiments. As shown in Table 3, the ratio increases as the catalyst is reduced to lower extents. For example, the olefin/paraffin ratios among the C_2 or C_3 hydrocarbons are 4 to 5 times higher on Fe (3%) than on Fe (63%). This trend is

Table 3. Olefin/paraffin ratio in CO hydrogenation on 9.1 wt% Fe/SiO₂ catalysts of different percentage reduction

Catalyst	Time on stream (hr)	Conversion (%)	Olefin/paraffin ratio		
			$C_2=/C_2$	$C_3=/C_3$	$C_4=/C_1$
Fe (63%)	0.50	1.26	0.2	0.7	0.4
Fe (34%)	0.63	0.71	0.5	1.7	5.8
Fe (21%)	0.77	0.70	0.5	1.6	5.1
Fe (3%)	0.58	0.61	1.0	3.6	5.2
Fe (63%)	6.00	0.63	2.2	6.5	6.0
Fe (34%)	6.00	0.70	1.7	5.4	5.7
Fe (21%)	6.00	0.58	2.0	5.9	7.2
Fe (3%)	6.17	0.78	2.6	7.5	8.6
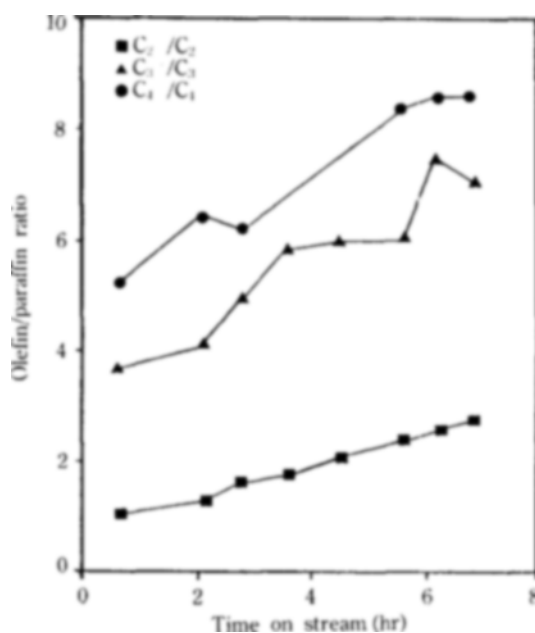
Fig. 2. Increase in the olefin/paraffin ratio among products with the reaction time on 9.1 wt% Fe/SiO₂ reduced to 3%.

in the same direction as one observed on the supported cobalt catalysts [4, 5] that the ethylene/ethane ratio increases as cobalt is reduced poorly.

As the reaction proceeds, the olefin/paraffin ratio changes with the following two features. The ratio increases for all the catalysts, and the effect of metal reduction almost disappears. Increase in the olefin/paraffin ratio with the reaction period is evident as exemplified for Fe (3%) in Fig. 2. The result is not due to further reduction of the Fe (3%) catalyst during reaction because the ratio is always higher than one on the well-reduced Fe (63%) catalyst. Therefore, the

increase must arise from the surface carbon deposition.

It should to be noted, however, that the trend observed in this study is in the opposite direction from one reported by others [9]. Raupp and Delgass [9] have observed that the olefin/paraffin ratio decreases as the iron catalyst is carbided. This agrees with their another observation that the amount of carbon monoxide chemisorption decreases while the dihydrogen chemisorption remains unchanged as the surface is carbided to form Fe₂C. This subject is discussed more in the next section in relation to the reactivity of the surface carbon species. A temporary explanation of the two opposing results is that the surface carbon species deposited during the experiments are different for the two works and therefore the surface has been modified in different manners. In fact. Sancier et al. [18] have reported that the surface carbon species deposited during CO hydrogenation are different depending on the experimental conditions.

The reason for the second feature that the effect of metal reduction disappears with reaction is because the catalysts have been reduced further so that the final extents of reduction are almost the same regardless of the initial values.

4. Gas Chemisorption and Reactivity of Surface Carbon Species

Table 4 shows that the amounts of dihydrogen and carbon monoxide chemisorption decrease as the catalysts are reduced poorly. This is normal because the number of iron atoms exposed to the surface changes in parallel with the extent of catalyst reduction. Table 4 also shows that chemisorption of dihydrogen is suppressed more than that of carbon monoxide and therefore the H₂/CO ratio is lowered on the poorly reduced catalysts. This agrees with the kinetic result that the olefin/paraffin ratio among the hydrocarbon products increases with the poor catalyst reduction.

The observed values of the H₂/CO adsorption ratio between 1.7 and 3.5 are high considering that the stoichiometric number of dihydrogen chemisorption is 0.5 and that of carbon monoxide chemisorption is between 0.5 and 1.0 on most transition metals. But, a similar result has been observed by Rankin and Bartholomew [19] who explained it to be due to small values, less than 0.5, of the stoichiometric number of carbon monoxide chemisorption on iron.

Exposure of the reduced iron to the surface, as calculated from the gas adsorption results, increases when the catalysts are reduced to lower extents. This indicates that the dispersed iron particles are reduced in an egg-shell form, i.e., the reduction proceeds from

Table 4. Amount of chemisorption and % exposure of reduced metal on 9.1 wt% Fe/SiO₂ catalysts

| Catalyst	Amount of chemisorption (μmol/g-cat.)			% Exposure of reduced metal based on chemisorption of		Specific activity ×10⁵ (mol/g-Fe·s)	Turnover frequency* ×10² (s⁻¹)
	H₂	CO	H₂/CO	H₂	CO		
Fe (63%)	21.9	6.3	3.5	2.8	0.8	1.1	4.2
Fe (21%)	14.8	4.7	3.1	5.7	1.8	1.3	2.5
Fe (3%)	0.8	4.6	1.7	19.7	11.2	7.3	4.1

*Calculated based on H₂ chemisorption.

the particle surface to the core. Should the particles be reduced in a black-and-white form, i.e., the reduction simply increases the number of completely reduced particles, the percentage exposure remains unchangd throughout the reduction process. In case of the egg-shell reduction model, the percentage exposure is the highest during the initial reduction period because only the thin surface layer of the particle is reduced. With a further reduction, the thickness of the reduced iron shell increases and therefore the percentage exposure of the reduced iron decreases and eventually becomes almost constant.

If the catalytic property of the reduced iron surface is modified by its interaction with the unreduced iron oxide, it is expected that changes in the kinetic behavior of the catalyst are most significant when the catalyst is reduced very poorly. In fact, such a result is observed on Fe (3%), i.e., the largest olefin/paraffin ratio.

Although the rate of CO hydrogenation expressed per weight of the reduced iron increases with the poor catalyst reduction, the rate remains almost constant when it is expressed per the surface-exposed iron atom, i.e., in turnover frequency (TOF). Accordingly, we may conclude that for the iron catalyst the partial metal reduction does not alter its intrinsic activity in CO hydrogenation but changes the olefin/paraffin ratio among the products.

To study the properties of the carbon species deposited on the catalyst surface during reaction, we have performed the TPSR experiments on the catalysts of different metal reduction after using them in CO hydrogenation at 270C for 30 minutes or for 5 hours. Methane produced in the reaction has been monitored versus the linearly increasing temperature.

Fig. 3 (a) shows that, after reaction for 30 minutes, Fe (63%) is covered with a relatively large amount of the carbon species that react with dihydrogen near 300 and 340C, while Fe (3%) is covered with a less amount of carbon reacting at 300 and 400C [Fig. 3 (b)]. It is therefore apparent that the carbon species deposited on Fe (63%) are more reactive than those on Fe (3%). When Fe (63%) is used in CO hydrogena-
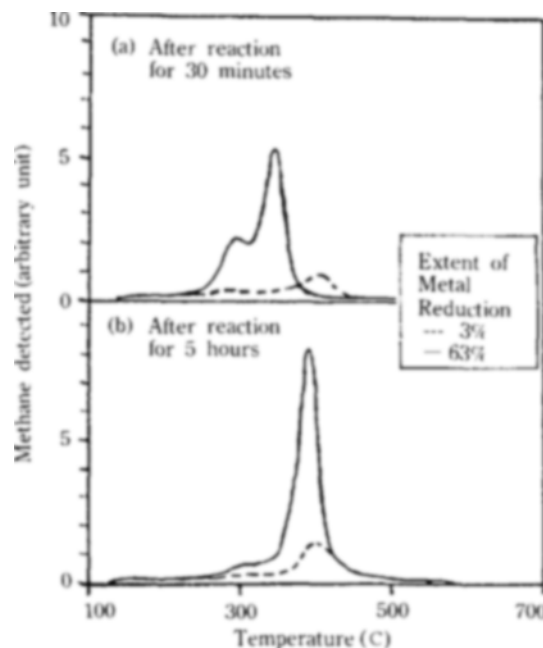
Fig. 3. Temperature-programmed surface reaction(TPSR) of the carbon species deposited on the 9.1 wt% Fe/SiO₂ catalysts reduced to different extents after reaction in CO hydrogenation.

tion for 5 hours, however, the temperatures of methane production shift to 300 and 400C, the same temperatures as observed on Fe (3%) for all the reaction period. The result suggests that the carbon species initially deposited on Fe (63%) transform into less reactive ones after reaction for 5 hours. In fact, this explains the rapid decrease in the reaction rate on Fe (63%) shown in Fig. 1, i.e., the catalyst surface is covered with less-reactive carbon species during reaction.

It should be noted that the temperatures of methane production in TPSR do not necessarily indicate the reaction temperature in CO hydrogenation. Instead, they represent the relative activity of the surface carbon species for hydrogenation. More studies are necessary about the nature of the carbon species deposited on

the iron surface.

CONCLUSION

In this study, we have investigated the property of the partially reduced iron catalysts and have obtained the following conclusions.

1. The rate of CO hydrogenation on the well-reduced iron catalyst decreases monotonically with time due to the surface carbon deposition. But, the rate on the poorly-reduced catalysts goes through a maximum because the catalysts are reduced further and simultaneously deactivated during the reaction.

2. The extent of iron reduction does not alter the intrinsic reaction rate nor the distribution of hydrocarbon products with specific carbon numbers but changes significantly the olefin/paraffin ratio among the products.

3. The change in the olefin/paraffin ratio agrees with the chemisorption result that the H_2/CO adsorption ratio decreases as the catalyst is reduced poorly.

As a whole, the extent of iron reduction modifies the property of the iron catalysts in a characteristic manner as described above and therefore should be considered as one of the important parameters in catalyst preparation.

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