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Studies with a precipitated iron Fischer-Tropsch catalyst reduced by H_2 or CO

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Abstract

A precipitated Fe_2O_3 catalyst precursor was reduced by H_2 or CO and characterized by diffuse reflectance FT-IR with high-pressure syngas adsorption, syngas temperature-programmed desorption (TPD), XRD and BET surface area, and tested for FT synthesis from high-pressure syngas. The results show that on the H_2-reduced sample metallic iron particles are formed and on the CO-reduced sample a mixture of metallic iron and iron carbides are formed. The iron carbides on the CO-reduced sample can be decomposed to metallic iron by H_2 treatment at 300 °C, and the metallic iron on the H_2-reduced sample can be partly converted to iron carbides by CO treatment at 300 °C. Both the metallic iron and iron carbides on the reduced samples have high ability for CO dissociation. The BET surface area of the CO-reduced sample is about five times higher than that of the H_2-reduced sample. The treatment of the CO-reduced sample with H_2 and the treatment of the H_2-reduced sample with CO result in only small changes in the surface areas. During performing high-pressure FT synthesis, amorphous carbon-rich iron carbides and crystalline magnetite are formed, which have relatively weaker ability for CO dissociation than those of metallic iron and iron carbide particles on the freshly reduced samples. CO-reduced sample exhibits remarkably higher catalytic activity for FT synthesis than the H_2-reduced sample. Treatment of the CO-reduced sample with H_2 leads to an obvious decrease in the catalytic activity of the sample, and treatment of the H_2-reduced sample with CO leads to a great increase in the activity. These results clearly indicate that those iron carbides formed during CO reduction of the precipitated Fe_2O_3 sample or CO treatment of the H_2-reduced sample have played an important role in enhancing the catalytic activities of the samples.

Keywords: Iron catalyst; FT-IR; High-pressure syngas adsorption; FT synthesis; Microstructure

1. Introduction

Iron-based catalysts have been used in Fischer-Tropsch synthesis of hydrocarbons from syngas since 1923. A large number of scientific studies have focused on the microstructures, catalyst activity–structure relationships and reaction mechanisms. However, it is still unclear about the composition of the catalytically active phase of iron [1–8]. Part of the confusion stems from the fact that under reaction conditions, iron can exist as a mixture of magnetite (Fe_3O_4), α-Fe or iron carbide phases [1]. Since Dictor and Bell [2] proposed that the active phase for FT synthesis is a mixture of χ- and

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ε-iron carbides and a small amount of α-Fe, more evidence has been found to prove that magnetite is not necessarily the active phase [3,4]. For instance, Huang et al. [3] found by XRD that magnetite is the only crystalline phase when the catalyst has reached its peak activity. However, the magnetite catalyst is inactive when it is initially exposed to syngas. They suggested that a surface phase on the magnetite might be the active phase.

It has been also reported [4,5,9–14] that the reducing pretreatments with H_2, CO or syngas often have significant effects on catalytic activity and selectivity of the iron-based catalysts. For instance, for unsupported iron-based catalyst systems, H_2-reduced samples show obviously lower activities for FT synthesis than the CO- and syngas-reduced samples [9–11]. It has been regarded that reduction of the iron-based sample in hydrogen leads to a metallic state, and CO or syngas reduction leads to metallic state and small amounts of iron carbides. During performing FT synthesis, more iron carbides and iron oxides are formed. However, the effect of the pretreatments for various catalyst systems has not been clearly understood, on which careful investigations may deepen the understanding of the roles of the various iron phases in performing FT synthesis, and might be helpful to prepare industrial catalysts with good activities.

Among the large number of studies devoted to the characterization of iron catalysts, a few deal with investigations of adsorption properties of the surface species [6,15–19]. However, the reports are usually regarding the surface adsorption properties of the oxidized and freshly reduced catalysts. Only a few studies have focused on the interaction of iron-based catalyst and syngas during the reaction at atmospheric pressure [15,16]. Regarding the surface adsorption properties of iron catalyst used for high-pressure FT synthesis, nearly no data can be found in literature.

In the present work, a precipitated Fe_2O_3 catalyst precursor reduced by H_2 or CO and those samples used for FT synthesis were characterized by in situ diffuse reflectance FT-IR spectroscopy with high-pressure syngas adsorption. The results, together with those obtained by syngas temperature-programmed desorption (TPD), XRD and BET surface area measurements, are carefully correlated with the catalytic properties of the samples for high-pressure FT synthesis.

2. Experimental

Precipitated Fe_2O_3 sample used in this study was prepared in the usual batch-wise manner by adding ammonia solution into a solution of $Fe(NO_3)_3{\cdot}9H_2O$. The obtained precipitates were washed with deionized water, followed by drying at 120 °C for 12 h and calcination in air at 350 °C for 2 h. The reduced samples were obtained by calcination of the precipitated Fe_2O_3 samples in a 40 ml/min flow of H_2 or CO/He (20/80) at 300 °C and atmospheric pressure for 6 h. The treated samples were obtained by calcination of the H_2-reduced sample in the CO/He flow or by calcination of the CO-reduced sample in the H_2 flow at 300 °C for 6 h.

The diffuse reflectance FT-IR spectra were recorded with a resolution of 4 cm^{-1} and accumulation of 20 on a Bio-Rad FTS 6000 FT-IR spectrometer supplied with an MCT detector and a diffuse reflectance attachment. The infrared cell with ZnSe windows (Spectra-Tech Inc.) can be used at high pressures and high temperatures. One set of stainless steel gas lines was connected to the cell, which allows in situ reduction, adsorption and FT synthesis. He (>99.999%) used for flushing and thermal desorption of the adsorbed species was further purified by passing it through a deoxy trap. For the high-pressure syngas adsorption and FT synthesis, the pressure was maintained at 1.2 MPa. In all circumstances, the gas flows were maintained at 60 ml/min by mass flow control meters. Approximately 25 mg of oxidized catalyst sample was used for each FT-IR experiment.

TPD with syngas on the H_2-reduced iron sample was carried out by using an on-line gas chromatograph equipped with a thermal conductivity detector (TCD). After 0.3 g of the precipitated iron sample was reduced by H_2 at 300 °C for 6 h, it was employed for syngas adsorption at 1.0 MPa and room temperature for 6 h. Then, the pressure was reduced and the sample was flushed by H_2, the carrier gas for the TCD, for 0.5 h, and the sample was heated in the H_2 flow up to 150 °C at a rate of 10 °C/min.

Powder XRD patterns of the catalyst samples were obtained on a Miniflex diffractometer (Rigaku) using Cu Kα radiation with an Ni filter. Iron phases were determined by comparing the diffraction patterns with those in the standard powder XRD file compiled by the Joint Committee on Powder Diffraction Standards published by the International Center for Diffraction Data. The reduced, treated and used samples were passivated in a stream of 1% O_2/He at room temperature before being transferred from the reactor for XRD measurements.

BET specific surface areas of the oxidized, reduced and treated samples were measured by N_2 physisorption at −196 °C, using a QUANTACHROME MONOSORB surface area analyzer and one-point BET method. Prior to the physisorptions, the samples were outgassed in an N_2 flow at 250 °C for over 0.5 h. The reduced and treated samples were passivated in the stream of 1% O_2/He at room temperature before being transferred from the reactor.

Activities of the reduced and treated catalyst samples for FT synthesis from syngas were measured using a slurry phase reactor with a volume of 100 ml. A volume of 30 ml of n-$C_{16}H_{34}$ was used as the liquid medium. An amount of 0.3 g of oxidized catalyst sample was used for each experiment. The reaction was carried out in a 30 ml/min flow of syngas with H_2/CO/Ar ratios of 62/33/5.0 at 1.0 MPa and 250 °C. Analyses of the gas-phase products were performed every 20 min by an on-line gas chromatograph. The liquid products in the reactor and those collected in an on-line trap at 0 °C were analyzed by an off-line gas chromatograph after the reaction. Anderson–Schultz–Flory (A–S–F) distributions were plotted and the chain growth probability, α, was calculated using the C_{10}–C_{25} data.

3. Results and discussion

3.1. High-pressure syngas adsorption on the reduced iron catalysts

In situ H_2-reduced iron sample was subjected to the adsorption experiment in a syngas flow (H_2/CO = 2, 60 ml/min) at 1.2 MPa and room temperature. Fig. 1(a) shows the spectra recorded after the syngas adsorption was performed for 20 min, referencing to the spectrum recorded at the initial 15 s of the syngas adsorption. From the amplified spectrum attached in Fig. 1, two bands at 2013 and 2033 cm^{-1} are clearly observed. With increasing time, the bands at 2013 and 2033 cm^{-1} slowly increase in intensities. According to the literature [17,19,20], these bands are assigned to linearly adsorbed CO on tops of metallic iron particles. Only very weak bands are observed during the high-pressure syngas adsorption, suggesting that adsorbed CO molecules on the catalyst surface are mainly in dissociated states and not detected by FT-IR [19].

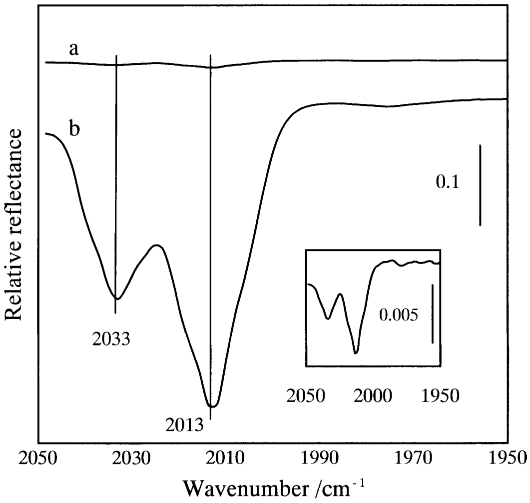

Fig. 1. Infrared spectra recorded from syngas adsorption on H_2-reduced Fe catalyst at 1.2 MPa and room temperature for 20 min (a), and followed by quickly heating the sample in the high-pressure syngas flow up to 100 °C (b).

It has been reported [21–25] that, during dissociative adsorption of probe molecules on metal surface and during desorption of dissociated species from the surface, they may go through the molecularly adsorption states. Therefore, when the dissociated carbon and oxygen atoms on the H_2-reduced sample desorb from the surface, they may recombine to CO molecules and be detected by FT-IR. To observe the recombination of the dissociated carbon and oxygen atoms on the surface, after syngas adsorption for 20 min, the sample was quickly heated in the high-pressure syngas flow. The spectrum recorded after temperature reached 100 °C is shown in Fig. 1(b); the bands at 2013 and 2033 cm^{-1} become very stronger. Thereafter, however, the bands gradually decrease in intensities. After keeping temperature at 100 °C for 1 h, the bands become as weak as those shown in Fig. 1(a) (the data are not shown). By a careful inspection, it is found that raising temperature in the range of about 50–130 °C will lead to obvious increase in the bands, whereas, the intensities of the bands begin to reduce once the temperature is kept constant.

It is also observed that, when the high-pressure syngas adsorption is directly performed at 100 °C, the bands at 2013 and 2033 cm^{-1} are even weaker than those obtained by syngas adsorption at room temperature. These results suggest that the tremendous increase in intensities of the bands by raising temperature might not be due to further adsorption of the gas-phase CO on the catalyst surface but due to recombination of the dissociative CO molecules bound on the catalyst surface at room temperature. The recombined CO molecules were initially adsorbed molecularly on the catalyst surface, followed by gradual desorption in the high-pressure syngas flow.

The recombination of dissociated carbon and oxygen atoms was also observed by FT-IR in helium flow. After the high-pressure syngas adsorption at room temperature for 20 min, pressure was reduced and then syngas was replaced with helium at atmosphere pressure. The bands of gaseous CO disappear by simple helium flushing for about 0.5 min. The sample was quickly heated up to 100 °C after helium flushing for 3 min; at this moment no gaseous CO exists in the system. The spectra presented in Fig. 2 are those recorded before and after flashing the sample, referencing to the spectrum recorded after the hydrogen reduction and before the sample was exposed to the syngas. After helium flushing at room temperature, only two weak bands at 2013 and 2033 cm^{-1} are observed. By quickly heating sample to 100 °C in the helium flow, the bands at 2013 and 2033 cm^{-1} become stronger. It is also seen that these bands quickly diminish in the helium flow at 100 °C and disappear completely in about 2 min.

It has rarely been observed by FT-IR for dissociated molecules to go through the molecularly adsorption states during desorption from the surface. This fact may be due to that adsorption experiments are usually performed at low pressures, typically <100 Torr, while desorption of the recombined probe molecules becomes considerably very faster.

To further demonstrate that the remarked increases in intensities of the bands at 2013 and 2033 cm^{-1} by raising temperature up to 100 °C are assigned to recombination of the dissociated carbon and oxygen atoms, syngas TPD was performed by using a gas chromatograph with TCD. The result is shown in Fig. 3. A strong desorption peak centered at 100 °C was observed. Because H_2 was used as carrier gas, TPD results indicate that large amounts of CO molecules have adsorbed on the surface during the

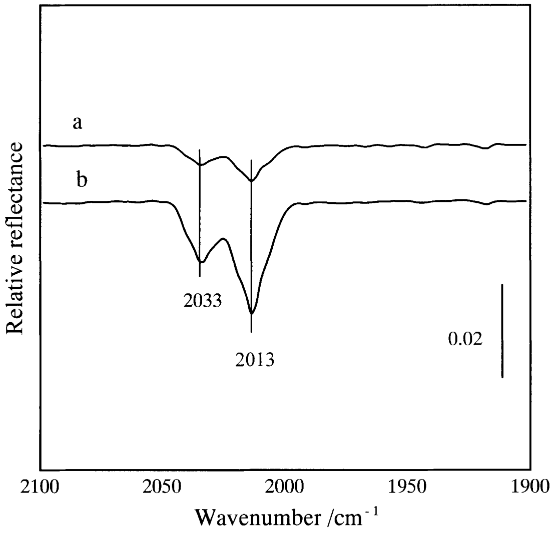

Fig. 2. Infrared spectra recorded from syngas adsorption on H_2-reduced Fe catalyst at 1.2 MPa and room temperature for 20 min, followed by helium flushing at atmosphere pressure for 3 min (a), and then quickly heating the sample in the helium flow up to 100 °C (b).

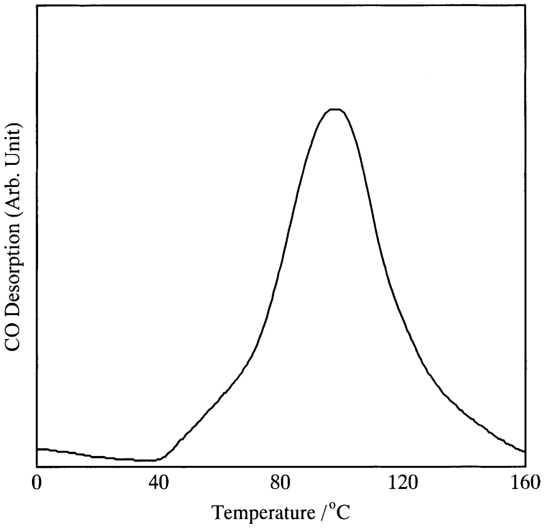

Fig. 3. Syngas TPD curve for H_2-reduced iron sample. After syngas adsorption at 1.0 MPa and room temperature for 6 h, temperature was increased up to 160 °C at a rate of 10 °C/min.

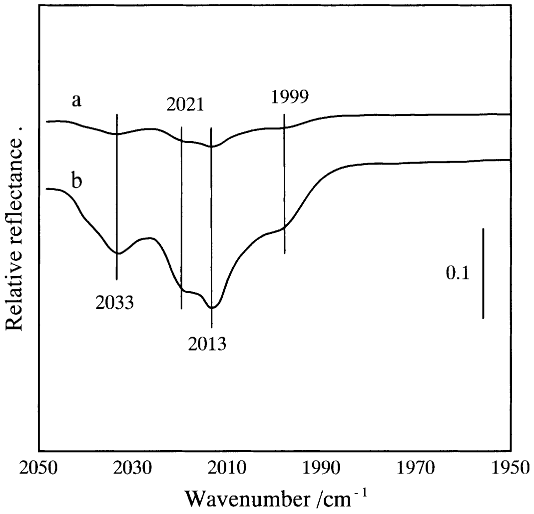

Fig. 4. Infrared spectra recorded from syngas adsorption on syngas-reduced Fe catalyst at 1.2 MPa and room temperature for 20 min (a), and followed by quickly heating the sample in the high-pressure syngas flow up to 100 °C (b).

high-pressure syngas adsorption at room temperature. This result confirms the speculation that, while only weak bands due to CO adsorption are observed by FT-IR, CO molecules adsorbed on the catalyst surface at room temperature are mainly in dissociated states. Furthermore, great increases of the bands at 2013 and 2033 cm^{-1} observed by raising temperature up to 100 °C are definitely due to recombination of the dissociated carbon and oxygen on the surface.

The experimental procedures used for H_2-reduced sample were also applied to the CO-reduced samples. The results are shown in Fig. 4. On the syngas-reduced sample, high-pressure syngas adsorption at room temperature gives rise to four weak bands at 1999, 2013, 2021 and 2033 cm^{-1}. Compared to the spectra of syngas adsorption on the H_2-reduced sample, two additional bands appear at 1999 and 2021 cm^{-1}. It is also observed that, as shown in Fig. 4(b), quickly heating the sample up to 100 °C in the syngas flow results in a tremendous increase of all the four bands due to CO adsorption. Thereafter, these bands gradually decrease in the syngas flow. Therefore, large quantities of CO molecules are dissociatively adsorbed on the CO-reduced catalyst at room temperature to form dissociated carbon and oxygen, which recombine to CO molecule at 100 °C and then gradually desorb from the surface. The ability of the CO-reduced sample to dissociate CO seems to be weaker than that of the H_2-reduced sample.

The bands at 1999 and 2021 cm^{-1}, which only appear in the spectra of syngas adsorption on the CO-reduced samples, may be assigned to CO adsorption on iron carbide species. One reason for this assignment is that, in XPS spectra, both metallic iron and iron carbides appear at near 707 eV [26], which unambiguously indicates that iron carbides are Fe^0 phases. This fact suggests that CO adsorption on iron carbide phases gives bands with only a small shift in wavenumber from those on metallic iron [15,19]. Another reason is that, as shown later in this paper, syngas adsorption on the samples used for FT synthesis gives rise to strong bands at 1999 and 2021 cm^{-1}. This result strongly supports the above assignment, because during FT synthesis iron carbides are the only Fe^0 species to be formed in large quantities.

With the bands at 1999 and 2021 cm^{-1} being assigned to CO adsorbed on iron carbides, the results of the high-pressure syngas adsorption indicate that on H_2-reduced iron sample only metallic iron species are formed, and that on the CO-reduced sample a mixture of metallic iron and iron carbides are formed.

To investigate the possible transformation between the metallic iron and iron carbide species on the surface, the H_2-reduced sample treated with CO and the CO-reduced sample treated with H_2 at 300 °C for 6 h were subjected to the syngas adsorption as well. The results show that syngas adsorption on the H_2-reduced sample treated with CO gives four weak bands at 1999, 2021, 2013 and 2033 cm^{-1}, and that syngas adsorption on the CO-reduced sample treated with H_2 gives only two weak bands at 2013 and 2033 cm^{-1} (the data are not shown here). These results indicate that the iron carbides on the CO-reduced sample can be transformed to metallic iron by the H_2 treatment, and that the metallic iron particles on the H_2-reduced sample can be partly transformed to iron carbides by the CO treatment.

3.2. Syngas adsorption on the catalysts used for high-pressure FT synthesis

To investigate the changes in microstructure of the reduced iron catalysts during performing FT synthesis, in situ high-pressure syngas adsorption on the used

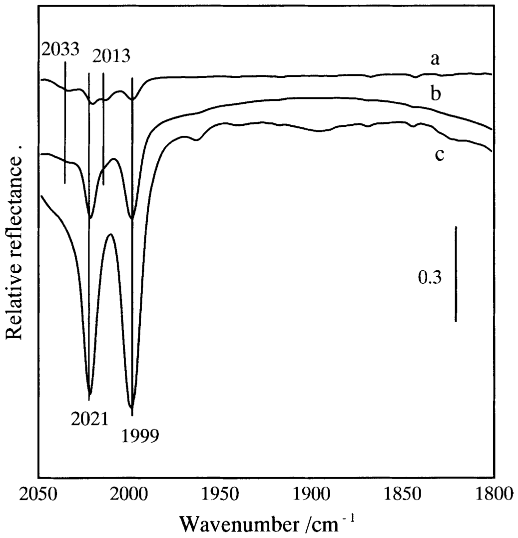

Fig. 5. Infrared spectra recorded from syngas adsorption on H_2-reduced Fe catalyst used for FT synthesis for 15 min (a), 50 min (b), and 3 h (c). The adsorption was performed at 1.2 MPa and room temperature for 20 min.

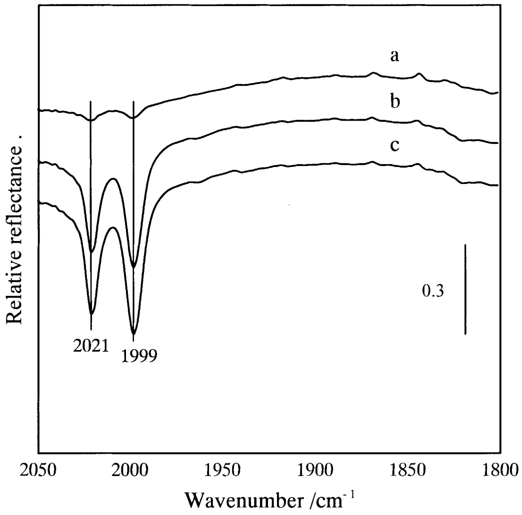

Fig. 6. Infrared spectra recorded from FT synthesis on CO-reduced Fe catalyst used for FT synthesis for 10 min (a), 40 min (b), and 3 h (c). The adsorption was performed at 1.2 MPa and room temperature for 20 min.

samples was carried out as well. After H_2-reduced sample was used for FT synthesis at 1.2 MPa and 250 °C for various times, it was cooled to room temperature in the syngas flow. Fig. 5 show the spectra recorded 20 min after the sample was cooled to room temperature ($<$30 °C), referencing to the same spectrum as used for Fig. 1.

On the H_2-reduced sample used for FT synthesis for 15 min, syngas adsorption gives rise to four obvious bands at 2013, 2033, 1999 and 2021 cm^{-1}, as shown in Fig. 5(a), indicating that the metallic iron species on the surface are partly transformed to iron carbides. Fig. 5(b) shows the spectrum of the syngas adsorption on the sample used for FT synthesis for 50 min; the bands at 1999 and 2021 cm^{-1} are growing, and the bands at 2013 and 2033 cm^{-1} become very weaker. Fig. 5(c) shows the spectrum of the syngas adsorption on the sample used for FT synthesis for 3 h, the bands at 1999 and 2021 cm^{-1} become very strong, and the bands at 2013 and 2033 cm^{-1} disappear. These results clearly indicate that, during the H_2-reduced samples were used for FT synthesis, the metallic iron particles on the surface are gradually transformed to iron carbides, which is in agreement with the results reported in literature [2,4,6,7].

After syngas was adsorbed on the used samples for 20 min, the samples were quickly heated up to 100 °C in the high-pressure syngas flow. In this case, the bands at 1999 and 2021 cm^{-1} do not show any increase in intensities. Therefore, the iron carbides formed during the FT synthesis exhibit low ability to dissociate CO. These results suggest that the iron carbides formed on the H_2-reduced sample during performing FT synthesis are carbon-rich ones, while those fine iron carbides formed during the CO reduction are carbon-deficient ones. Fig. 6 shows the spectra of the syngas adsorption on CO-reduced iron sample used for FT synthesis. As shown in Fig. 6(a), syngas adsorption on the sample used for FT synthesis for 10 min gives bands at 1999 and 2021 cm^{-1}, and the bands at 2013 and 2033 cm^{-1} become very weak. Fig. 6(b) shows the spectrum of syngas adsorption on the sample used for FT synthesis for 40 min, the bands at 1999 and 2021 cm^{-1} become much stronger, suggesting quick formation of the iron carbides at the initial 40 min of reaction. Fig. 6(c) shows the spectrum of syngas adsorption on the sample used for FT synthesis for 3 h, the strongest bands at 1999 and 2021 cm^{-1} are observed. However, the formation of iron carbides becomes obviously slow after performing FT synthesis for 40 min.

After syngas adsorption for 20 min, the samples were quickly heated up to 100 °C in the high-pressure syngas flow. By this way, small but noticeable increases in intensities of the bands at 1999 and 2021 cm^{-1} were observed (the data are not shown). Therefore, the iron carbides formed on the CO-reduced samples during performing FT synthesis have relatively higher ability to dissociate CO than those formed on the H_2-reduced sample, indicating that the iron carbides on the CO-reduced sample are relatively carbon-deficient ones than those on the H_2-reduced sample.

It has been reported [27] that, during FT synthesis, several iron carbide phases are formed, but that CO adsorption on the used samples gives bands with same wavenumbers. Therefore, it is difficult to identify the bulk structure of the iron carbides by the syngas adsorption.

3.3. XRD patterns of the reduced, treated and used iron samples

Bulk iron phases of the reduced, treated and used samples were determined by XRD measurements. The results are shown in Fig. 7. The pattern of the H_2-reduced catalyst shows strong peaks at 44.7, 65, 82.3°, which correspond to Fe^0 phase, and weak peaks at 35.4, 56.9, 62.5°, which correspond to Fe_3O_4 phase. The pattern of the CO-reduced catalyst shows weak and broad peaks in the region of 43.2–4.8°, which may be assigned to overlap of the peak of Fe^0 (~44.7°) and the peaks of iron carbide species (43–44°, ε'-$Fe_{2.2}C$ and/or χ-Fe_5C_2 phases). Therefore, a mixture of metallic iron and magnetite are present on the H_2-reduced sample, and a mixture of metallic iron and iron carbides in amorphous states are formed on freshly CO-reduced sample. The result from XRD measurement about the CO-reduced sample is the same as that from the high-pressure syngas adsorption. However, the result from XRD measurement about the H_2-reduced sample is different from that by the high-pressure syngas adsorption, which suggests that a complete reduction of the iron species on the surface of the H_2-reduced sample but only a partial reduction of the iron species in the bulk.

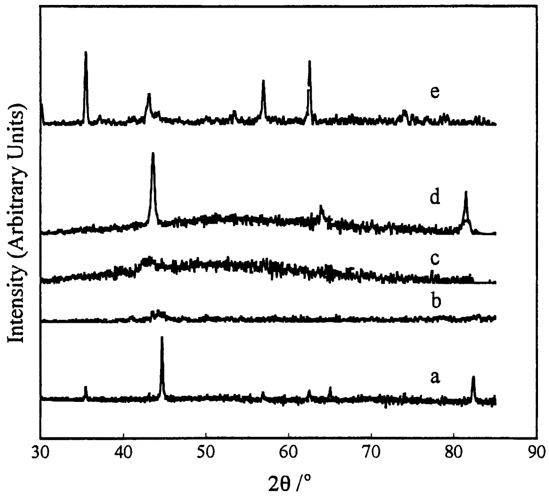

Fig. 7. XRD patterns of the iron catalyst: after reduction with H_2 at 300 °C for 6 h (a); after reduction with CO at 300 °C for 6 h (b); H_2-reduced sample treated with CO at 300 °C for 6 h (c); CO-reduced sample treated with H_2 at 300 °C for 6 h (d); after use of the H_2-reduced sample for high-pressure FT synthesis with fixed bed reactor at 1.0 MPa and 250 °C for 6 h (e).

XRD pattern of the H_2-reduced sample treated with CO at 300 °C shows weak peaks due to the overlap of metallic iron and magnetite. This result clearly indicates the formation of the crystalline iron and magnetite particles on the H_2-reduced sample onto amorphous metallic iron and iron carbides during the CO treatment. XRD pattern of the CO-reduced sample treated with H_2 shows the obvious peaks at 43.8, 65 and 82° indicating the formation of crystalline iron. However, the positions of these peaks show slight but obvious shifts from those corresponding peaks in the pattern of the H_2-reduced sample, which suggests that small amounts of carbon species remained in the bulk of the crystalline iron to form some very carbon-deficient iron carbides such as $C_{0.08}Fe_{1.88}$. These observations indicate that the CO treatment of the H_2-reduced sample and the H_2 treatment of the CO-reduced sample result in obvious changes in microstructure of the samples. These results are consistent with those obtained from the high-pressure syngas adsorption.

XRD patterns of the H_2- and CO-reduced samples used for high-pressure FT synthesis with fixed bed reactor are similar. So only the pattern of the H_2-reduced sample used for FT synthesis is shown. Strong peaks at 35.4, 43.1 56.9, 62.5 and 89.2° are clearly observed; all these peaks correspond to Fe_3O_4 phase.

Table 1
BET surface areas of the various iron samples

Sample	Reduction conditions	Surface area ($m^2\,g^{-1}$)
Oxidized	–	38
Reduced	CO, 300 °C	37
	H_2, 300 °C	7
Treated	CO, 300 °C; H_2, 300 °C	33
	H_2, 300 °C; CO, 300 °C	11

XRD patterns of the used samples include strong peaks due to Fe_3O_4 phase, which suggests that the oxidized iron species formed during FT synthesis are easily crystallized and that the iron carbides are present in amorphous states. The peak of Fe_3O_4 centered at 43.1° in the XRD patterns of the used samples may overlap the small peaks of the iron carbides.

3.4. BET surface areas of the catalyst samples

BET surface areas of the oxidized, reduced and treated catalyst samples are shown in Table 1. The surface areas of the CO- and H_2-reduced catalysts are 37 and 7 $m^2\,g^{-1}$, respectively. Compared to the surface area of the oxidized catalyst precursor (38 $m^2\,g^{-1}$), it is seen that the surface area of the CO-reduced sample is similar to that of the oxidized catalyst precursor, but that the surface area of the H_2-reduced sample is very low. The surface area of the CO-reduced sample is about five times as high as that of the H_2-reduced sample.

After the H_2-reduced sample was treated with CO at 300 °C, its surface area increases to 11 $m^2\,g^{-1}$. On the other hand, after the CO-reduced sample was treated with H_2, its surface area shows a slight decrease from 37 to 33 $m^2\,g^{-1}$.

H_2-reduced iron sample shows a lower surface area than that of the oxidized catalyst precursor, which suggests significant sintering of the iron species during the H_2 reduction. The existence of magnetite phase on the H_2-reduced sample may be due to that, at the initial time of H_2 reduction, the oxidized iron species on the surface were quickly reduced and sintered, meanwhile effectively inhibits reduction of the internal iron species. In our work, it is found that, during performing H_2 reduction, if the temperature is slowly increased up to 300 °C in the H_2 flow (0.2 °C/min), the reduced sample contains only metallic iron species. It has been reported that, when iron sample was reduced by H_2 at 280 °C, a mixture of metallic iron and magnetite were formed; however, when the sample was reduced at a lower temperature of 240 °C, only metallic iron was formed. This may be due to that, during H_2 reduction at 240 °C, the sintering of the metallic iron becomes slow, so that the internal iron species are completely reduced. During the CO reduction, sintering of the iron species does not occur.

XRD results show that, during the H_2-reduced sample was treated with CO, crystalline iron and magnetite species were transformed to iron carbides. This result clearly indicates that carbon species have entered into the bulk of the sintered iron, which may result in the significant increase in surface area of the sample. The results from the high-pressure syngas adsorption and XRD measurements show that, during the H_2 treatment of the CO-reduced sample, amorphous iron carbides were transformed to crystalline iron. However, the BET surface area of the sample shows only a small decrease compared with that of the CO-reduced sample. This result indicates that during the H_2 treatment, the iron species on the surface are not sintered.

3.5. Activities of the reduced iron samples for FT synthesis

After the oxidized iron samples were in-situ reduced in H_2 or CO flows at atmospheric pressure and 300 °C for 6 h, they were employed for FT synthesis in 30 ml/min syngas (H_2/CO/Ar = 33/63/4) at 1.0 MPa, 250 °C with a slurry phase reactor. The changes of CO conversion with reaction time over the H_2- and CO-reduced samples are shown in Fig. 8. Table 2 shows the distributions of the gaseous products when the reaction was performed for 7 h.

On the H_2-reduced sample, CO conversion increases at the initial time of reaction and reaches the maximum of 25% after reaction for over 2 h. Thereafter, CO conversion decreases slowly to 23% after reaction for 11 h. On the CO-reduced sample, CO conversion increases sharply at the initial 4 h of reaction and reaches its maximum of 69% after reaction for about 7 h. Then, however, CO conversion

Table 2
Activity data of the various iron samples after reaction for 7 h

Reduction conditions	CO conversion (CO%)	Yields of CO_2 and HC (CO%)				α
		CO_2	C_1	C_2	C_3–C_5	
H_2, 300 °C	24.1	4.2	2.9	1.9	7.4	0.87
CO, 300 °C	68.9	13.9	6.6	5.6	21.5	0.85
H_2, 300 °C; CO, 300 °C	46.9	8.6	4.1	3.6	16.7	0.85
CO, 300 °C; H_2, 300 °C	32.3	7.5	3.8	2.6	9.7	0.86

decreases markedly with time and becomes 40% after reaction for 11 h.

In comparison with the low but stable catalytic activity for FT synthesis of the H_2-reduced sample, the catalytic activity of the CO-reduced sample is much high but unstable. Similar activity results have been reported for various unsupported iron-based catalyst systems [9–11], suggesting that there are similar pretreatment effects for these various unsupported iron-based catalysts.

Both the CO-reduced sample treated with H_2 and the H_2-reduced sample treated with CO were tested for the high-pressure FT synthesis under the same reaction conditions. Activity data of the treated samples are shown in Fig. 9. Over the CO-reduced sample treated with H_2, CO conversion reaches a maximum of 35% after reaction for 2 h. Thereafter, CO conversion slowly decreases. After reaction for 15 h, CO conversion is still 33%. On the other hand, over the H_2-reduced sample treated with CO, CO conversion increases at the initial 5 h of reaction and reaches its maximum value of 47%. Then, CO conversion significantly reduces and becomes <40% after reaction for 15 h. Therefore, H_2 treatment of the CO-reduced iron sample results in a significant decrease in catalytic activity of the sample for FT synthesis. Conversely, CO treatment of the H_2-reduced sample results in a great increase in its activity for FT synthesis.

As shown in Table 2, distributions of the reaction products from FT synthesis show little changes between all the four samples, suggesting similar microstructure of the active sites over these samples. Therefore, the changes in catalytic activity among

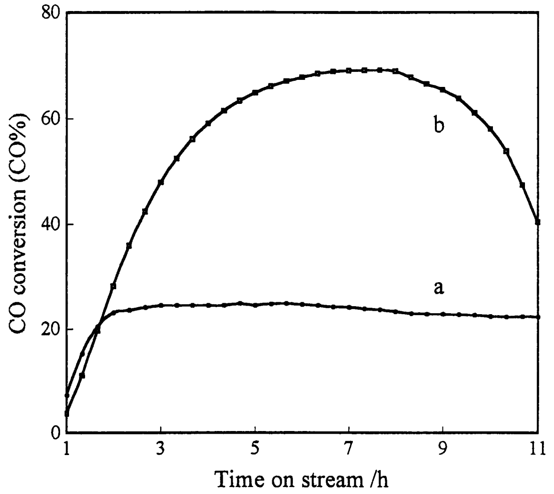

Fig. 8. Changes in CO conversion with time on stream on the (a) H_2 and (b) CO reduced samples. Reaction conditions: 1.0 MPa, 250 °C, $W/F = 3.7\ g\,h^{-1}\,mol^{-1}$.

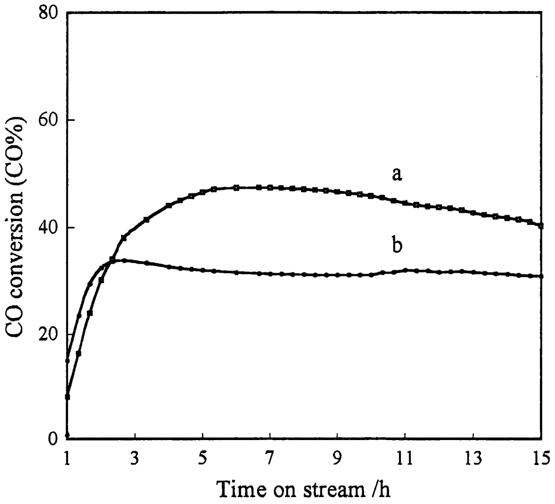

Fig. 9. Changes in CO conversion with time on stream on the CO-reduced sample treated with H_2 (b) and on the H_2-reduced sample treated with CO (a). Reaction conditions: 1.0 MPa, 250 °C, $W/F = 3.7\ g\,h^{-1}\,mol^{-1}$.

these samples are mainly due to the differences in the number of the activity sites over the samples.

It is meaningful to elucidate the reason for the CO-reduced iron sample to show higher activity for FT synthesis than the H_2-reduced sample. Some researchers suggested it might be due to that H_2-reduced samples have lower ability for CO dissociation, because of sulfur migration from bulk of the catalyst on to the surface during the H_2 reduction [9]. Our results from high-pressure syngas adsorption indicate that the H_2-reduced iron sample shows high ability to dissociate CO as well, which suggests that sulfur migration is not the main reason for low activities of the H_2-reduced samples.

It has also been suggested that the sintering of the iron species occurring during the H_2 reduction might be responsible for the low catalytic activity of the H_2-reduced samples [9]. In this work, however, it is found that the CO-reduced sample treated with H_2, which has only a slightly lower surface area than the freshly CO-reduced sample, shows significantly lower catalytic activity for FT synthesis than the CO-reduced sample. The H_2-reduced sample treated with CO still shows a small surface area, but its catalytic activity is significantly higher than that of the CO-reduced sample treated with H_2. These results clearly indicate that, the samples with small surface area but containing the fine iron carbides show significantly higher catalytic activity for FT synthesis than the samples with high surface area but containing only metallic iron species. Therefore, the fine iron carbides formed during the CO reduction of the precipitated catalyst precursor or during the CO treatment of the H_2-reduced sample have played a very important role in enhancing the catalytic activity of the samples.

The results from the high-pressure syngas adsorption and XRD measurements indicate that, during performing FT synthesis, the metallic iron and the fine iron carbides on the freshly reduced samples are gradually transformed to crystalline Fe_3O_4 and carbon-rich iron carbides. The catalytic activities of the samples may be mainly determined by the microstructure of the iron carbides formed during FT synthesis. Iron carbides formed during FT synthesis on the H_2-reduced sample are obviously carbon-rich ones, and those formed on the CO-reduced sample are relatively carbon-deficient ones. During FT synthesis on the H_2-reduced sample, it takes about 2 h for sample to reach its peak activity. Conversely, during FT synthesis on the CO-reduced sample, it takes about 7 h for the sample to reach its peak activity. Therefore, the formation of carbon-rich iron carbides on the H_2-reduced sample may have, to some extent, inhibited the transformation of the internal iron species into active sites. Deactivation of the CO-reduced sample after reaction for 10 h may be correlated with the relatively higher ability for CO dissociation of the newly-formed iron carbides on the surface, which might result in the formation of more inactive carbon species on the surface.

4. Conclusions

Precipitated iron catalyst precursor was reduced by H_2 or CO at 300 °C for 6 h, respectively. On the H_2-reduced sample metallic iron particles are formed and on the CO-reduced sample a mixture of metallic iron and iron carbides are formed. The iron carbides on the CO-reduced sample can be decomposed to metallic iron by H_2 treatment at 300 °C, and the metallic iron on the H_2-reduced sample can be partly converted to iron carbides by CO treatment at 300 °C. Both the metallic iron and iron carbides on the reduced samples have high ability to dissociate CO. During the H_2 reduction, the iron species are significantly sintered; but during the CO reduction the sintering does not occur. As a result, the BET surface area of the CO-reduced sample is about five times as high as that of the H_2-reduced sample. Treatment of the CO-reduced sample with H_2 and treatment of the H_2-reduced sample with CO result in only small changes in the surface areas. During performing high-pressure FT synthesis over the reduced samples, amorphous carbon-rich iron carbides and crystalline magnetite are formed. CO-reduced sample exhibits remarkably higher catalytic activity for FT synthesis than the H_2-reduced sample. Treatment of the CO-reduced sample with H_2 leads to an obvious decrease in the activity of the sample, and treatment of the H_2-reduced sample with CO lead to a great increase in the activity. These results clearly indicate that the fine iron carbides formed during CO reduction of the iron catalyst precursor or CO treatment of the H_2-reduced sample have played an important role in enhancing the catalytic activities of the samples.

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References

[1] G. LeCaer, J.M. Dubois, M. Pijolat, V. Perrichon, P. Bussiere, J. Phys. Chem. 86 (1982) 4799.

[2] R.A. Dictor, A.T. Bell, J. Catal. 97 (1986) 121.

[3] C.S. Huang, L. Xu, B.H. Davis, Fuel Sci. Technol. Int. 11 (1993) 639.

[4] M.D. Shroff, D.S. Kalakkad, A.G. Sault, A.K. Datye, J. Catal. 156 (1995) 185.

[5] D.S. Kalakkad, M.D. Shroff, S.D. Kohler, N.B. Jackson, A.K. Datye, Appl. Catal. A 133 (1995) 335.

[6] J.W. Niemantsverdriet, A.M. van der Kraan, W.L. van Dijk, H.S. van der Kraan, J. Phys. Chem. 84 (1980) 3363.

[7] A. Loaiza-Gil, B. Fontal, F. Rueda, J. Mendiadua, R. Casanova, Appl. Catal. A 177 (1999) 193.

[8] G. Ravichandran, D. Das, D.K. Chakrabarty, J. Chem. Soc. Trans. 90 (13) (1994) 1993.

[9] D.B. Bukur, M. Koranne, X. Lang, K.R.P.M. Rao, G.P. Huffman, Appl. Catal. A 126 (1995) 85.

[10] D.B. Bukur, X. Lang, J.A. Rossin, W.H. Zimmerman, M.P. Rosynek, E.B. Yeh, C. Li, Ind. Eng. Chem. Res. 28 (1989) 1130.

[11] B.H. Davis, F.L. Tungate, G.J. in Stigel, R. D. Strivastava (Eds.), in: Proceedings of the Indirect Liguefaction Contractors' Review Meeting , Pittsburgh Energy Technology Center, US Department of Energy, Pittsburgh, 1991, p. 58.

[12] D.B. Bukur, L. Nowicki, K. Manne, X. Lang, J. Catal. 155 (1995) 366.

[13] D.B. Burkur, X. Lang, Y. Ding, Appl. Catal. A 186 (1999) 255.

[14] R.J. O'Brien, L. Xu, R.L. Spicer, B.H. Davis, Energy Fuels 10 (1996) 921.

[15] E. Boellaard, A.M. van der Kraan, J.W. Geus, Appl. Catal. A 147 (1996) 229.

[16] A.F.H. Wielers, A.J.H.M. Kock, C.E.C.A. Hop, J.W. Geus, A.M. van der Kraan, J. Catal. 117 (1989) 1.

[17] E. Guglielminotti, J. Phys. Chem. 98 (1994) 4884.

[18] E. Guglielminotti, F. Boccuzzi, F. Oinna, G. Strukul, J. Catal. 167 (1997) 153.

[19] M. Jiang, N. Koizumi, M. Yamada, J. Phys. Chem. 104 (2000) 7636.

[20] U. Seip, M.C. Tsai, K. Christmann, J. Küppers, G. Ertl, Surf. Sci. 139 (1984) 29.

[21] R. Imbihl, J.E. Demuth, Surf. Sci. 173 (1986) 395.

[22] D.W. Moon, S.L. Bernasek, D.J. Dwyer, J.L. Gland, J. Am. Chem. Soc. 107 (1985) 4363.

[23] D.W. Moon, D.J. Dwyer, S.L. Bernasek, Surf. Sci. 163 (1985) 215.

[24] J. Benziger, R.J. Madix, Surf. Sci. 94 (1980) 119.

[25] W. Erley, J. Vacuum, Sci. Technol. 18 (1981) 472.

[26] C.S. Kuivila, J.B. Butt, P.C. Stair, Appl. Surf. Sci. 32 (1988) 99.

[27] S.A. Eliason, C.H. Bartholomew, Appl. Catal. A 186 (1999) 229.