III-3 Pretreatment Effect Research - Characterization Studies of Ruhrchemie Catalyst

III-3.1 Experimental

A sample of commercial catalyst synthesized by Ruhrchemie, designated as LP 33/81, with nominal composition of 100 Fe/5 Cu/4.2 K/24 SiO_2 was obtained for this study. The catalyst was calcined in air at 300°C for 5 h prior to any pretreatment.

III-3.1.1 Catalyst Characterization Techniques

Experimental procedures for characterization of the Ruhrchemie catalyst by AA, XRD, BET/PSD, MES, and TEM techniques were similar to those described in Section III-1 of this report. In addition, temperature programmed/isothermal reduction and X-ray photoelectron spectroscopy (XPS) techniques were used to characterize the Ruhrchemie catalyst.

Temperature programmed (TPR) and isothermal reduction studies were performed using both 5% H_2/N_2 and 5% CO/He as reductants. The reactive gas streams were first directed at a constant rate and pressure through the reference compartment of a thermal conductivity detector (TCD) cell via a two-way injection valve, through the catalyst sample, and finally, via a cold trap, through the other compartment of the TCD. Consumption of the CO or H_2 was monitored by a change in the thermal conductivity of the effluent gas stream. A dry ice/acetone bath was used to remove water formed during hydrogen reductions, and a liquid nitrogen bath was used to remove CO_2 formed during the CO reductions. Catalyst sample weights of 10 to 15 milligrams and the reductant flow rates of 12 cc/min were used in all experiments. A temperature ramp of 20°C/min from room temperature to 900°C was used in all temperature-programmed reduction experiments. In isothermal reductions, a ramp of 20°C/min was used until a temperature of 300°C was reached, the latter temperature

then being maintained for either 12 h for H_2, or 8 h for CO reduction.

X-ray photoelectron spectroscopy (XPS) was used to study the surface compositions and oxidation states of iron catalysts following reduction in H_2 and CO. Samples used in the XPS measurements were pressed into thin wafers to fit the copper sample holder and the sample probe of the spectrometer. After either reduction, samples were evacuated for one hour and were transferred without exposure to air, to the antechamber of the glove box attached to the spectrometer. The antechamber was back filled with dry N_2 before transferring the sealed reactor into the main glove-box chamber for sample mounting on the instrument probe. Typical pressure in the XPS analysis chamber during measurement was 10^{-9} Torr. The monochromatic X-ray beam power was maintained at 600 W, and an electron flood gun was used to eliminate sample charging effects. The C1s peak at 284.6 eV, due to adventitious surface carbon, and the O 1s peak at 531.6 eV were used as internal references.

III-3.2   Results and Discussion

III-3.2.1   Atomic Absorption

The amounts of Fe, Cu, and K were determined by Atomic Absorption Spectroscopy using a standard procedure described in Section III-1 of this report. The amount of SiO_2 in the catalyst was estimated indirectly knowing the actual amounts of Fe, Cu, and K and by assuming that the elements were in the form of Fe_2O_3, CuO, and K_2CO_3. The amount of SiO_2 was calculated from the equation:

$$W_{SiO_2} = W_o - W_{Fe}\frac{1}{2}\cdot\frac{Fe_2\cdot O_3}{Fe} - W_{Cu}\frac{CuO}{Cu} - W_K\frac{1}{2}\cdot\frac{K_2CO_3}{K}$$

$$= W_o - 1.43\,W_{Fe} - 1.25\,W_{Cu} - 1.77\,W_K$$

where: W_o is the weight of the sample, and W_i's are the weight of elements

determined by AA.

The composition of the catalyst was found to be 100 Fe/5.6 Cu/5.1 K/31 SiO_2. The catalyst composition was also determined at Sandia National Laboratories as 100 Fe/5 Cu/4 K/27 SiO_2 which is in reasonable agreement with our results, and is closer to the nominal catalyst composition.

III-3.2.2   X-ray Diffraction

<u>As-Prepared and Calcined Catalyst</u>

XRD patterns of the Ruhrchemie catalyst were obtained before and after calcination and are shown in Figure III-3.1. The as-prepared and the calcined catalyst exhibited broad Fe_2O_3 signals indicating that the catalyst was nearly amorphous in nature.

<u>Reduced (Pretreated) Catalyst</u>

The XRD patterns obtained after H_2 reduction are shown in Figure III-3.2. The Ruhrchemie catalyst, after reduction with H_2 at 220°C for 1 h, exhibited weak signals at 2θ=35.4 and 62.5° which correspond to Fe_3O_4 (Figure III-3.2a). Weak XRD signals seen in Figure III-3.2 are due to the presence of silica in the catalyst which is believed to be of amorphous nature. The particle size estimated from the corresponding slow scan using X-ray line broadening technique was 50 Å (Table III-3.1).

The XRD pattern obtained after reduction with H_2 at 280°C for 1 h is shown in Figure III-3.2b. In addition to Fe_3O_4, peaks corresponding to metallic Fe were identified. It should be noted that due to the amorphous silica background only the strongest peaks (maximum intensity) corresponding to Fe_3O_4 or Fe could be clearly observed. The particle size of Fe was estimated to be 80 Å. It can be seen that the particle size increased with an increase in reduction temperature. This increase in the particle size can be attributed to a partial collapse of the iron pore structure on reduction. Sintering of the iron particles is expected to be higher at higher reduction
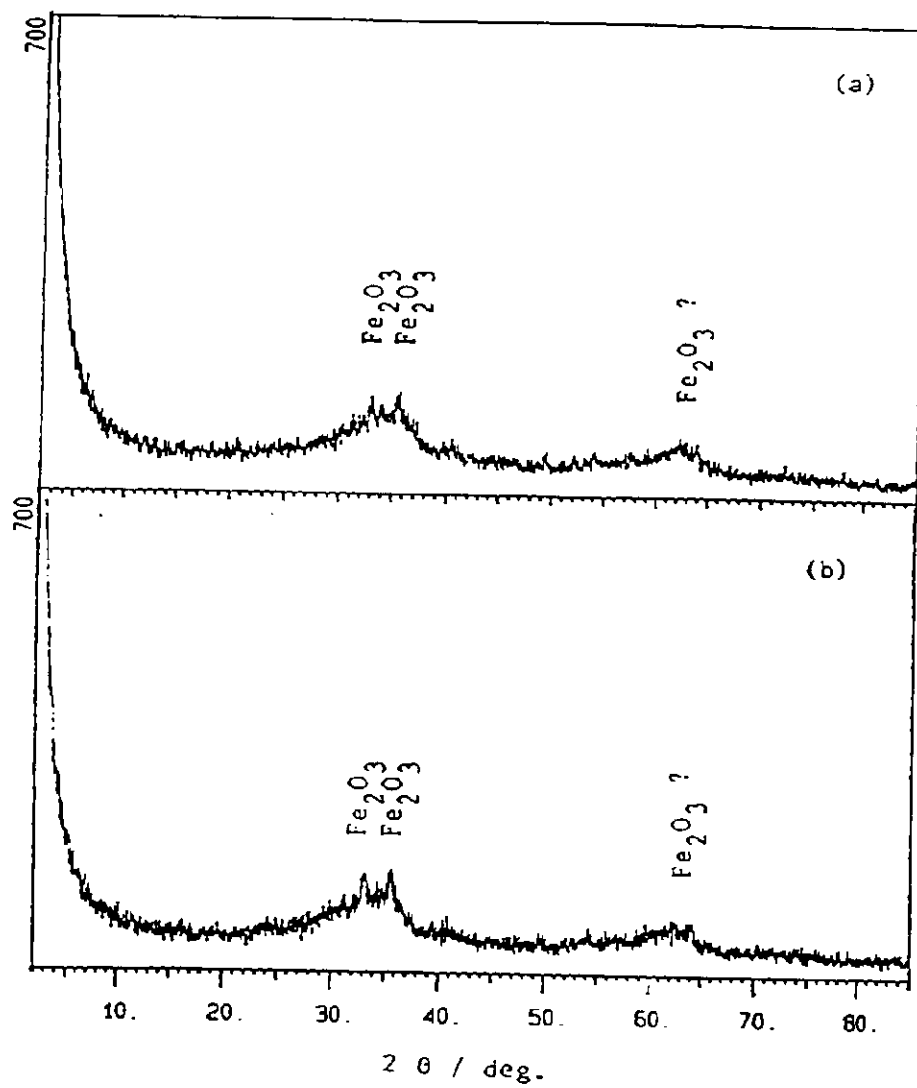
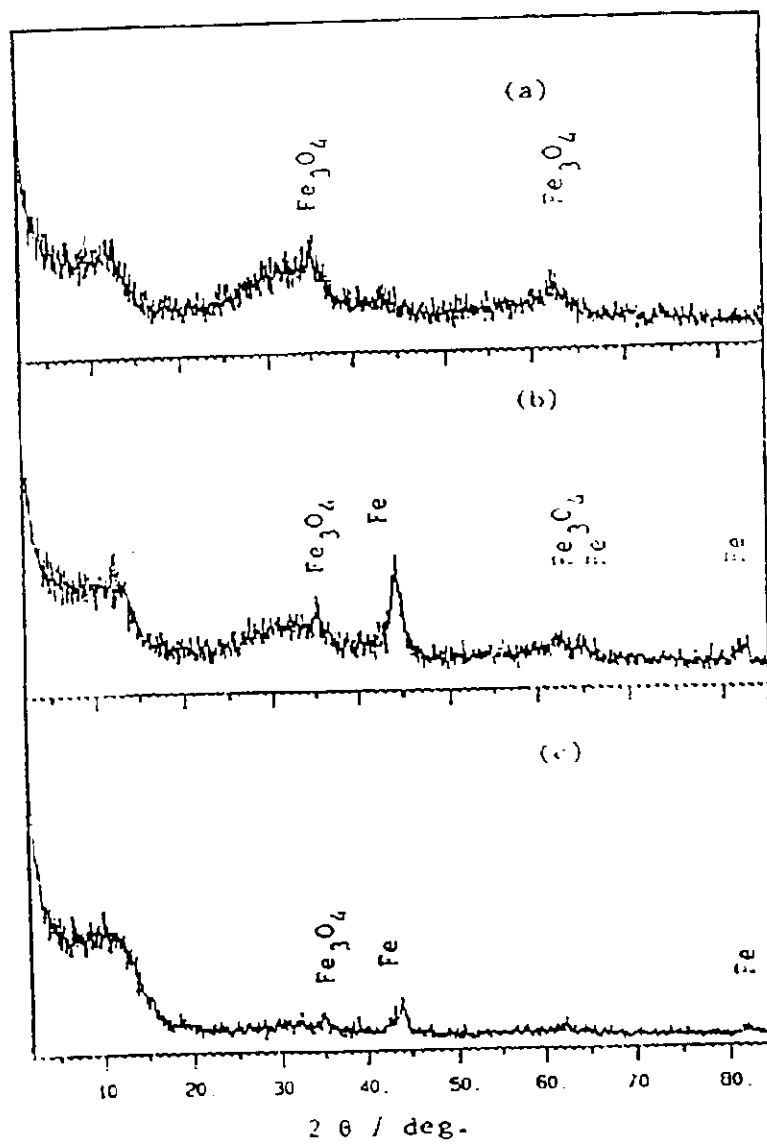Figure III-3.1   XRD patterns of Rurhchemie catalyst: a) as prepared; b) calcined in air at 300°C for 5h.

Figure III-3.2   XRD patterns of Rurhchemie catalyst samples after pretreatment with H_2 at: a) 220°C for 1 h (flow rate = 3550 cc/min); b) 280°C for 1 h (flow rate = 3160 cc/min); c) 280°C for 8 h (flow rate = 125 cc/min).

Table III-3.1   Summary of XRD and TEM Results of Pretreated Ruhrchemie Catalyst Samples.

Run No.	Pretreatment Conditions	Phases Detected by XRD[a]	Average Particle Size Determined by XRD (Å)	Particle Size Range Determined by TEM (Å)
As prepared	None	Fe_2O_3	--	--
Calcined	Air, 300°C, 5 h	Fe_2O_3	--	35
FA-2351	H_2, 220°C, 1h, 3550 cc/min	Fe_3O_4	50	35
FA-2391	H_2, 280°C, 1h, 3160 cc/min	Fe_3O_4, α-Fe	80 (α-Fe)[b]	--
FA-1821	H_2, 280°C, 8h, 125 cc/min	Fe_3O_4, α-Fe	100 (α-Fe)[b]	--
FA-1801	CO, 280°C, 8h, 125 cc/min	Fe_xC[c]	*	--
FA-2511	CO, 280°C, 12h, 125 cc/min	Fe_xC	*	39
FA-2551	H_2/CO=2, 310°C, 6h, 1200 cc/min	Fe_xC	*	--

a: Phases are in decreasing order of relative intensities.
b: Indicates the phase used for particle size determination.
c: Fe_xC denotes iron carbide phase(s).
*:   The particle sizes could not be estimated using XRD because of overlapping signals.

temperatures which was also observed with the unsupported iron catalysts of nominal composition 100 Fe/0.3 Cu/0.8 K (Section III-1).

The XRD pattern obtained after hydrogen reduction at 280°C for 8h and at a flow rate of 125 cc/min showed the presence of Fe_3O_4 and Fe phases (Figure III-3.2 c). It is important to note that despite the time of reduction being higher than in the previous case, the reduction was incomplete. The flow rate, however, was lower than that used in the previous H_2 reduction procedures indicating that flow rate of H_2 plays a role in the catalyst reduction. Similar behavior was also observed for the unsupported iron catalyst (100Fe/0.3Cu/0.8K) as described in Section III-1. There, it has been proposed that water formed during reduction plays an important role in the determination of the iron phases formed. At low H_2 flow rate partial pressure of water is high. At these high partial pressures of water, the complete reduction of Fe_2O_3 is not possible. As stated it the Section III-1, it is not clear whether mass transfer also plays an important role in such a reduction process. Lower flow rates coupled with higher reaction rates may indeed yield relatively low mass transfer rates resulting in the partial reduction of the catalyst. The particle size of Fe, estimated from the XRD slow scan, was 100 Å indicating that the average particle size increased further on reduction under these conditions. This can be explained by the fact that high water partial pressure enhances the rate of sintering of the iron particles resulting in larger crystallites (Anderson, 1984; Bukur et al., 1989a).

When the catalyst was pretreated with CO at 280°C for 8 h and 12 h, peaks corresponding to carbide(s) (designated as Fe_xC) phase(s) were identified. The identification of a particular iron carbide in our samples was rather difficult by XRD, since the most intense peaks corresponding to these carbides are close to each other. However, χ-Fe_5C_2 (Hägg carbide), and ε'-$Fe_{2.2}C$ are the most likely carbides present. Fe_xC designates one or more of these carbides. In addition to the carbide peaks, the catalyst pretreated with CO at 280°C for 8 h exhibited sharp peaks at 2θ = 38, 45,

64.7, and 78°. These were assigned to aluminum which was used in our earlier design of the sample holder. The particle sizes after pretreatment with CO were not estimated due to overlapping signals of the carbides. The XRD pattern for the catalyst sample, pretreated with syngas at 310°C for 6 h, is shown in Figure III-3.3c. It can be seen that even in the presence of H_2 no oxide/metallic Fe could be detected. Iron carbide(s) was the only iron phase detected after pretreatment with syngas. Since the presence of Fe/Fe_3O_4 depends on the relative rates of reduction followed by their carburization (by CO) it seems that the rate of carburization of Fe or Fe_3O_4 is faster than the rate of H_2 reduction. It is interesting to note that all the CO or syngas pretreatment procedures yield carbide(s) regardless of the temperature or flow rate of the reducing gas. This suggests that the carburization of the iron phases is indeed rapid and may not be a strong function of the initial phase of iron. Earlier, it has also been reported that the use of promoters like Cu and K enhances the rate of carburization of iron catalysts (Vogler et al., 1984).

Used Catalysts

XRD patterns of H_2 pretreated catalysts after reaction in a fixed bed reactor were obtained and are illustrated in Figures III-3.4 and III-3.5. The XRD pattern of the used catalyst from run FA-0113 (pretreated with H_2 at 220°C for 1 h) from the top part of the reactor showed the presence of bulk Fe_3O_4 and Fe_xC phases (Figure III-3.4a). The presence of Fe_xC suggests that some carburization occurred under FTS conditions. Recently, Lox et al. (1988) reported a study on characterization of Ruhrchemie catalyst (pretreated with H_2 at 220°C for 3 h) after 200 h of reaction using XRD. Their study has also shown the presence of oxides (other than Fe_2O_3) and a mixture of carbides after 200 h of reaction. The used catalyst from the bottom part of the reactor showed the presence of only Fe_xC phase(s) (Figure III-3.4b). It should be noted that some Fe_3O_4 in the form of fine particles (< 40 Å) may be also present in the sample, but could not be detected by XRD.
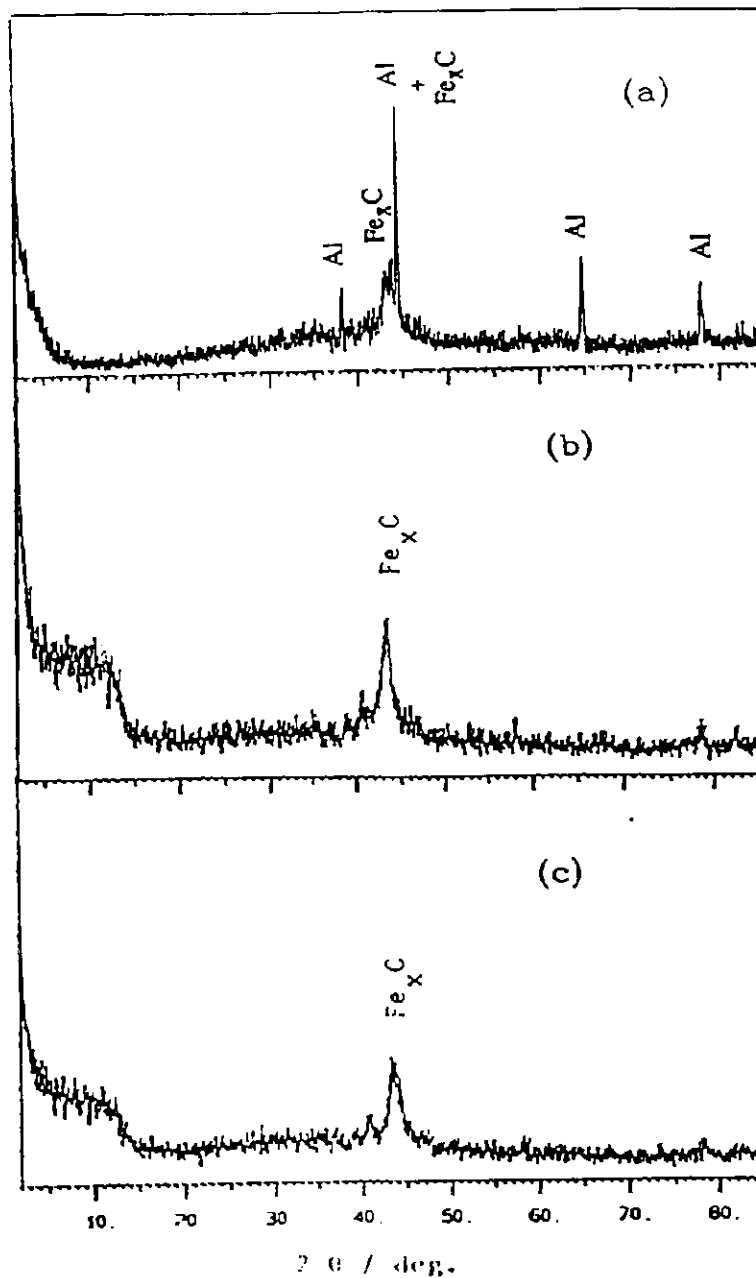
Figure III-3.3   XRD patterns of Rurhchemie catalyst samples after pretreatment with
CO or syngas: a) CO (125 cc/min) at 280 °C for 8h; b) CO
(125 cc/min) at 280 °C for 12h; c) syngas ($H_2/CO=2.0$, 1200 cc/min) at
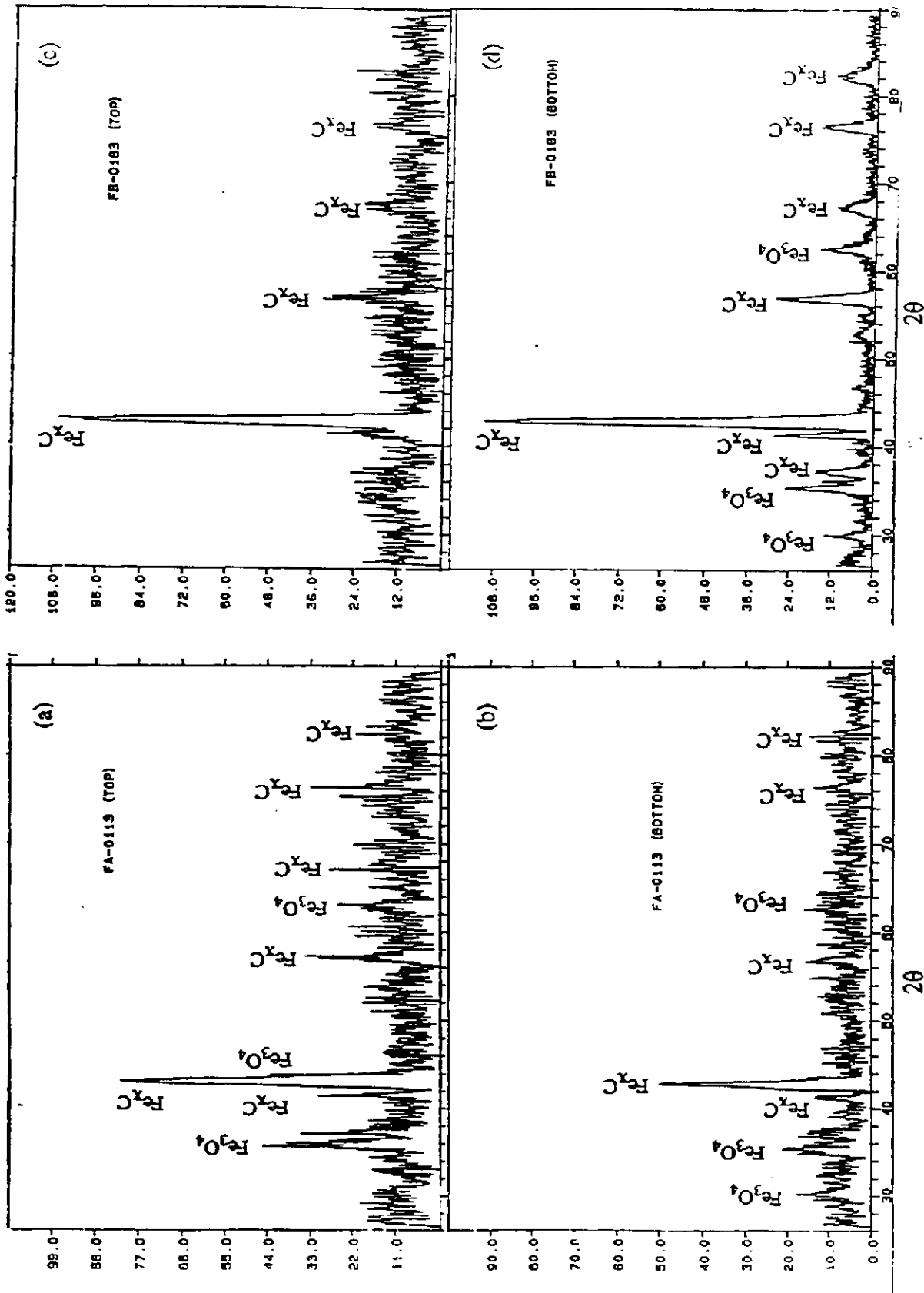310 °C for 6h.

Figure III-3.4   XRD patterns of Ruhrchemie catalyst samples after FT synthesis and pretreatment with H_2: a) FA-0113 (top); b) FB-0113 (bottom); c) FB-0183 (top); d) FB-0183 (bottom) (see Table III-3.2 for the pretreatment conditions used).

The XRD patterns of used catalyst pretreated with H_2 at 280°C for 1h from the top and the bottom parts of the reactor are shown in Figures III-3.4 c and d. Bulk Fe_xC phase(s) were present in both, top and bottom parts of the reactor. However, the catalyst sample from the bottom part of the reactor also showed the presence of Fe_3O_4 phase. Although some Fe_3O_4 was present in the reduced catalyst, the formation of Fe_3O_4 in the used catalyst sample from the bottom part of the reactor due to oxidation of Fe_xC by water formed during FTS cannot be ruled out (Dry,1981; Anderson, 1984).

The XRD patterns of the used catalyst, pretreated with H_2 at 280°C for 8 h, from the top and bottom parts of the reactor are shown in Figures III-3.5a and b. The phases identified are listed in Table III-3.2. It should be noted that only Fe_xC phase(s) could be detected in the used catalyst samples by XRD. However, some bulk Fe_3O_4 was present in the reduced catalyst. It seems that most of the bulk Fe_3O_4, with particle sizes greater than 40 Å, is carburized under FTS conditions.

The XRD patterns of the used catalyst, pretreated with H_2 at 280°C for 24 h, from the top and bottom parts of the reactor are shown in Figures III-3.5 c and d. The phases identified are listed in Table III-3.2. Again, Fe_xC phase was the only phase present in both, the top part and the bottom parts of the reactor.

The used catalysts pretreated with CO at 280°C exhibited only bulk Fe_3O_4 phase (see Figure III-3.6 a). It should be noted that the catalyst after CO pretreatment consisted of Fe_xC phases only. The formation of Fe_3O_4 in the used catalyst can be attributed to the oxidation of the carbide(s) by water formed during FTS (Berry and Smith, 1989; Davis and Tungate, 1991). The used catalyst pretreated with syngas from the top part of the reactor exhibited weak Fe_xC signals (Figure III-3.6 b). However, the main phase in the catalyst from the bottom part of the reactor is Fe_3O_4 (Figure III-3.6c; Table III-3.2). This means that the position of the catalyst in the reactor also has effect on the phases present. Generally, the reaction atmosphere is more oxidizing in the bottom part of the reactor due to the formation of CO_2 and H_2O during FTS (Dry,1981).
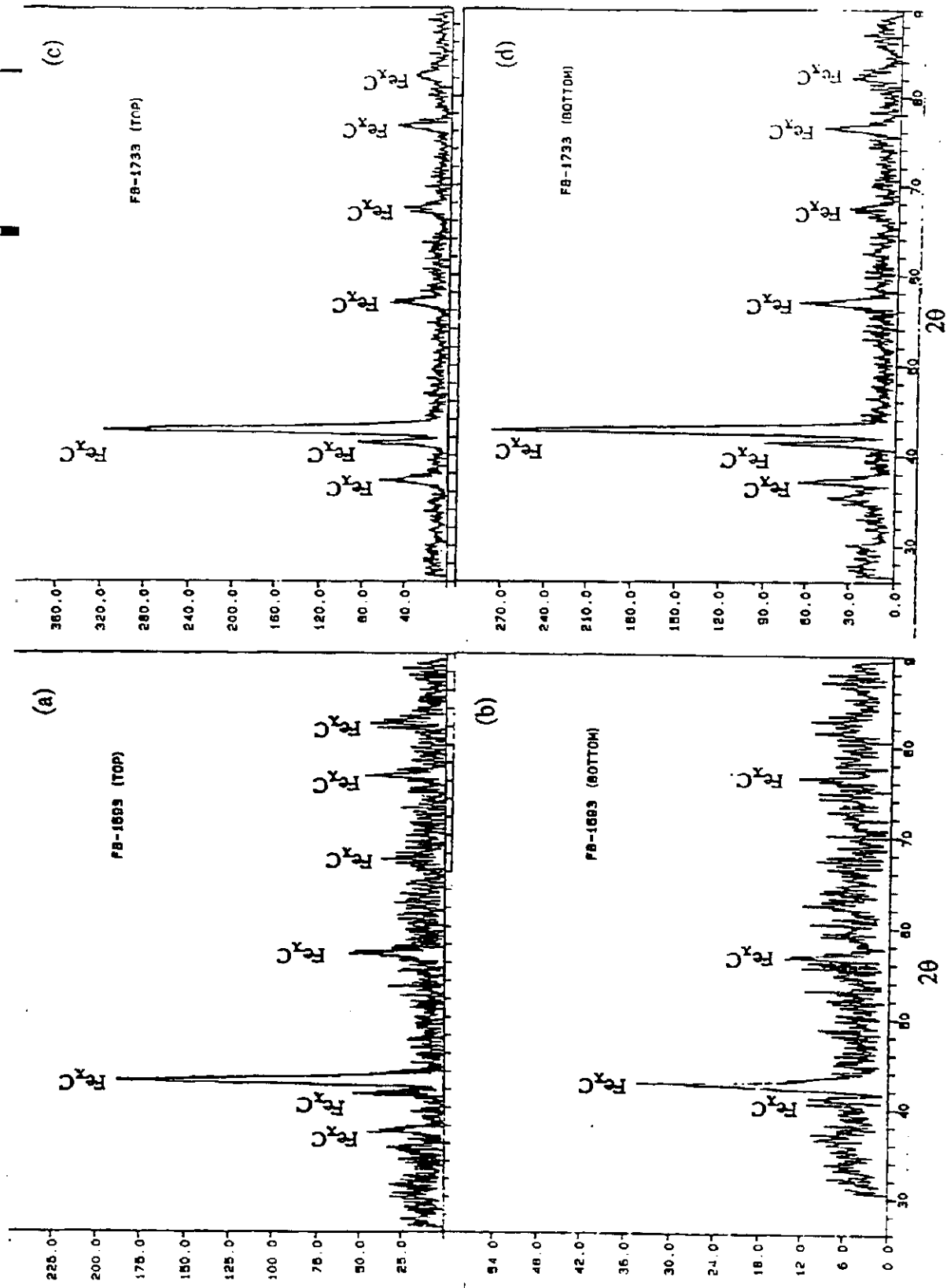
Figure III-3.5 XRD patterns of Rurhchemie catalyst samples after FT synthesis and pretreatment with H_2: a) FB-1593 (top); b) FB-1593 (bottom); c) FB-1733 (top); d) FB-1733 (bottom) (see Table III-3.2 for the pretreatment conditions used).
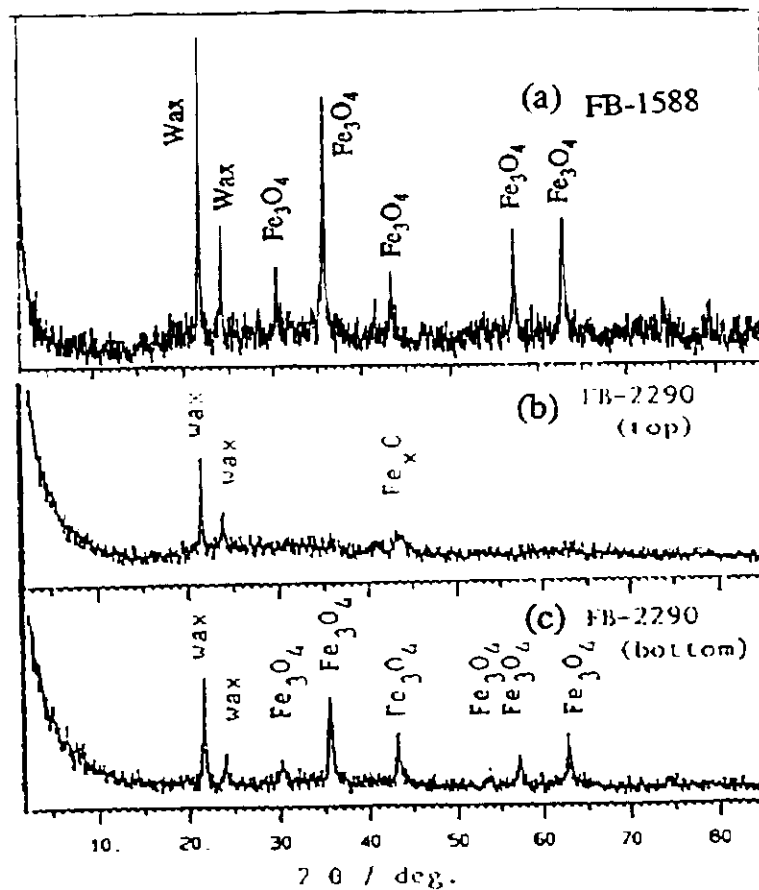
Figure III-3.6   XRD patterns of Rurhchemie catalyst samples after FT synthesis and pretreatment with CO or syngas: a) FB-1588; b) FB-2290 (top); c) FB-2290 (bottom) (see Table III-3.2 for the pretreatment conditions used).

Table III-3.2   Summary of XRD Results of Ruhrchemie Catalyst Samples after FT Synthesis - Fixed Bed Reactor Tests.

Run No.	Pretreatment Conditions; TOS	Phases Detected by XRD[a]	
FA-0113	H_2, 220°C, 1h; 125h	Top:	Fe_xC^b, Fe_3O_4
		Bottom:	Fe_xC, Fe_3O_4
FB-0183	H_2, 280°C, 1h; 100h	Top:	Fe_xC
		Bottom:	Fe_xC, Fe_3O_4
FB-1593	H_2, 280°C, 8h, 154h	Top:	Fe_xC
		Bottom:	Fe_xC
FB-1733	H_2, 280°C, 24h;124h	Top:	Fe_xC
		Bottom:	Fe_xC
FB-1588	CO, 280°C, 12h; 427h	Average:	Fe_3O_4
FB-2290	$H_2/CO=2$, 310°C, 6h; 160h	Top:	Fe_xC
		Bottom:	Fe_3O_4, Fe_xC

a: Phases are in decreasing order of relative intensities.
b: Fe_xC denotes iron carbide phase(s)

III-3.2.3   Mössbauer Effect Spectroscopy

Reduced Catalysts

Although XRD is useful in determining the phases present in the catalyst after pretreatment and after FTS, the relative amounts of these phases cannot be easily quantified. The advantages of MES in determining the nature and the amounts of iron phases in the catalysts are well known (Raupp and Delgass, 1979 a, b). In order to obtain quantitative information on bulk phases present in the reduced and used catalyst after pretreatments with H_2, CO, and syngas Mössbauer effect spectroscopy

(MES) was used. The Mössbauer spectra were obtained and analyzed at the University of Kentucky (The Consortium for Fossil Fuel Liquefaction Science).

Table III-3.3 shows results of MES analysis of the reduced Ruhrchemie catalyst samples. The catalyst, reduced with H_2 at 220°C for 1 h consisted of only the superparamagnetic iron oxide/hydroxide phase. This phase is probably magnetite. The XRD analysis of the used catalyst indicated the presence of Fe_3O_4 with an average particle size of about 50 Å. The positive identification of such small magnetite particles could not be achieved by MES at room temperature. The catalyst reduced with H_2, at 280°C for 1 h contained superparamagnetic iron oxide/hydroxide (87%) and metallic Fe (13%) phases. The major component of the superparamagnetic phase is probably magnetite based on the results from XRD analysis. In the catalyst, reduced with H_2 at 280°C for 8 h, some iron carbide (8%) was also detected in addition to superparamagnetic iron oxide hydroxide (80%), Fe (7%), and Fe_3O_4 (5%) phases (Table III-3.3). The existence of iron carbide phase is attributed to the sample contamination during preparation and/or handling.

The compositions of CO and syngas pretreated catalyst samples, determined by MES, were the same: 54 % of χ-carbide and 46% of superparamagnetic oxide/hydroxide (Table III-3.3). This is in agreement with results obtained with the 100 Fe/0.3 Cu/0.8K catalyst (Section III-1 of this report) where it was found that these two pretreatment procedures yield the same bulk iron phases. The carbide phase was the only phase determined by XRD analysis after these two pretreatments (Table III-3.1). The lack of iron oxide/hydroxide phases by XRD analysis, indicates that crystallites are less than 4 nm in diameter (limit of detection by XRD). Low temperature MES measurements are needed to determine composition of the superparamagnetic phase (probably mostly magnetite - Fe_3O_4, and some unreduced Fe_2O_3).

Table III-3.3   Relative Amounts of Phases Identified by Mössbauer Effect
Spectroscopy in Pretreated Ruhrchemie Catalyst Samples.

Run No.	Pretreatment Conditions	Spm[a] (%)	Magnetite (%)	Fe (%)	χ-Fe$_5$C$_2$ (%)
FA-2351	H$_2$, 220°C, 1h, 3550 cc/min	100	---	---	---
FA-2391	H$_2$, 280°C, 1h, 3160 cc/min	87	---	13	---
FA-1821	H$_2$, 280°C, 8h, 125 cc/min	80	5	7	8
FA-2511	CO, 280°C, 12h, 125 cc/min	46	---	---	54
FA-2551	H$_2$/CO=2, 310°C, 6h, 1200 cc/min	46	---	---	54

a: Spm=superparamagnetic iron oxide/hydroxide.

Used Catalysts

Table III-3.4 summarizes the available results of MES measurements at 300K of some used Ruhrchemie catalyst samples. For the used catalyst, pretreated with CO at 280°C for 12 h, magnetite (68%), superparamagnetic iron oxides (27%) and χ-carbide (5%) were the phases detected. This is in agreement with the XRD results (Table III-3.2). The presence of Fe$_3$O$_4$ in the used catalyst is attributed to the reoxidation of the iron carbide(s) by water.

Table III-3.4   Relative Amounts of Phases Identified by Mössbauer Effect
Spectroscopy in Ruhrchemie Catalyst Samples after FT Synthesis.

Run No.	Pretreatment Conditions; TOS	Spm[a] (%)	Magnetite (%)	χ-Carbide (%)
FB-1588 (Middle)	CO, 280°C, 12h; 427h	27	68	5
FB-2290 (Top)	H₂/CO=2, 310°C, 6h; 160h	63	--	37
FB-2290 (Bottom)		45	38	17

a: Spm=superparamagnetic iron oxide/hydroxide.

The phases identified by MES for the catalyst, pretreated with syngas, from the top and bottom parts of the reactor are listed in Table III-3.4. The top part consisted of the χ-carbide and the superparamagnetic iron oxide. MES results for the catalyst sample from bottom part of the reactor, show the presence of χ-carbide, magnetite, and superparamagnetic oxides. These results are in agreement with those obtained by XRD analysis.

III-3.2.4   BET Surface Area and Pore Size Distribution

The BET surface area and the pore volume of the as prepared catalyst obtained by N_2 physisorption were 295 m^2/g and 0.58 cc/g, respectively (Table III-3.5). After calcination the BET surface area and the pore volume were found to be 290 m^2/g and 0.62 cc/g, respectively (Table III-3.5). The BET surface area and the pore volume did not change significantly after calcination, indicating that the porous iron network is resistant to high temperatures. This is due to the presence of silica in the catalyst. The

Table III-3.5   Summary of BET Results of Pretreated Ruhrchemie Catalyst Samples.

Run No.	Pretreatment Conditions	Surface Area (m^2/g)	Pore Volume (cc/g)	Pore Diameter[a] $(\mathring{A})$
Ruhrchemie (as prep)	None	295	0.58	79
Ruhrchemie (calcined)	Air, 300°C, 5 h	290	0.62	86
FA-2351	H_2, 220°C, 1h, 3550 cc/min	179	0.46	103
FA-2391	H_2, 280°C, 1h, 3160 cc/min	136	0.42	124
FA-1821	H_2, 280°C, 8h, 125 cc/min	160	0.49	122
FA-1801	CO, 280°C, 8h, 125 cc/min	118	0.34	115
FA-2551	$H_2/CO=2$, 310°C, 6h, 1200 cc/min	99	0.31	125

a: Pore diameter=(4 x Pore volume)/Surface area.

presence of silica is known to maintain the porous iron oxide/hydroxide network (Bukur et al., 1990b; Dry, 1981). Silica enters the pores of the original network of the catalyst thus providing a rigid matrix which helps prevent a complete collapse of the pore structure of the catalyst.

However, after reduction with H_2 at 220°C for 1 h the BET surface area decreased to 179 m^2/g. This is in agreement with results reported by Dry (1981) and Lox et al. (1988), where a similar decrease in the surface area was observed after a reduction with hydrogen. The decrease in the surface area and pore volume can be attributed to a partial collapse of the porous $Fe_2O_3/FeOOH$ network. Hydrogen reduction at 280°C for 1 and 8 hours led to further decrease in surface area to 136 m^2/g and 160 m^2/g respectively. The pore volumes also decreased significantly after H_2 reduction (Table III-3.5). It is important to note that in the absence of silica, after H_2 reduction, the surface areas decrease to about 40 m^2/g (see Section III-1).

The BET surface area decreased from 290 m^2/g to 118 m^2/g and 99 m^2/g after pretreatment with CO and syngas, respectively. The decrease in the BET surface area was higher for the CO or syngas reduced catalysts than for the H_2 reduced catalysts. Similar trends were seen when the pore volumes of the H_2 and the syngas reduced catalysts were compared. This may be due to the formation of carbonaceous deposits (formed only in the presence of CO) causing blocking of the pores of the catalyst, and resulting in lower surface area than with the H_2 reduced catalyst. Several studies have reported on the formation of carbonaceous deposits (probably in the form of graphitic carbon) on the catalyst after FTS (Vogt et al., 1987; Tungate and Davis, 1991). Although the carbonaceous deposits were reported to be present after FTS, it is likely that these deposits may be formed during CO or syngas pretreatment. Our CO reduction studies (Section III-3.2.6) indicate that there is a possibility of formation of such deposits on the pretreated catalyst.

The pore size distribution for the as prepared and the calcined catalyst obtained

by N_2 physisorption is shown in Figure III-3.7. It can be seen that both, the as prepared and the calcined catalyst exhibited a relatively broad pore size distribution (< 15-300Å; 15 Å was the limit of detection) with a maximum at 200 Å. The pore size distribution for the H_2 reduced catalysts is shown in Figure III-3.8. The pore size distribution of the catalyst reduced with H_2 at 220°C exhibited a bimodal distribution; with maxima at 20 Å and 200 Å. The pore size distributions of the catalyst pretreated with H_2 at 280°C for 1 and 8 hours exhibited a maximum at 200 Å. However, pores with diameters < 15 Å were also present (Figures III-3.8 b and c).

The pore size distributions of the CO and the syngas pretreated catalysts are shown in Figure III-3.9. Although the pore size distribution profiles for the H_2, CO, and syngas reduced catalysts seem similar to that of the calcined catalyst, some differences in the average pore diameter obtained from the surface area and the pore volume were observed. It can be seen that the average pore diameter increased slightly on pretreatment with H_2, CO, or syngas (Table III-3.5). Dry (1981) reported that the average pore size increases after H_2 reduction, and after FT synthesis.

III-3.2.5 Transmission Electron Microscopy

Figure III-3.10 shows the TEM micrographs of the calcined sample under two different magnifications. Particles smaller than 100 Å are distinctly visible from these micrographs. It is, however, difficult to identify the iron phases from these micrographs. Silica being amorphous is unlikely to diffract the electron beam in TEM and hence cannot be clearly seen by TEM. Nonetheless, it can be seen that the particle morphology is essentially spherical. A number average particle size was estimated after measuring the sizes of particles from different portions of the sample. This procedure yielded the particle size to be approximately 35 Å and is listed in Table III-3.1.
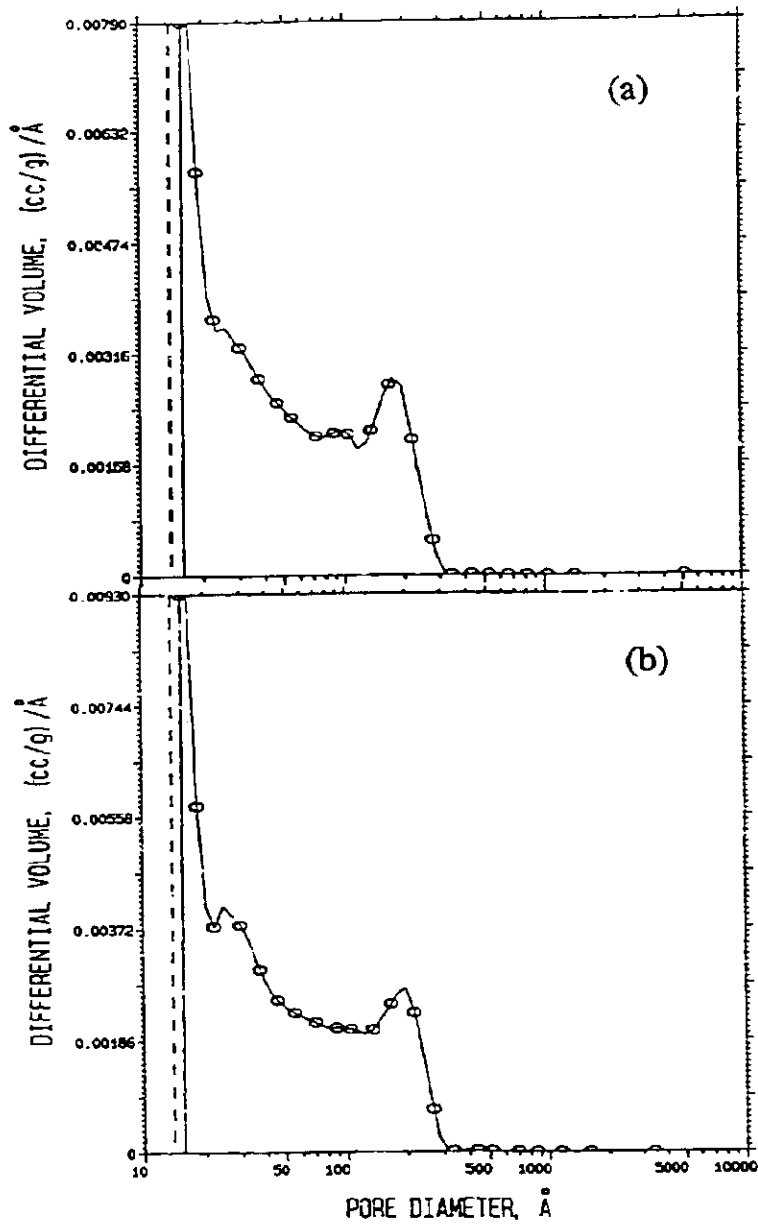
Figure III-3.7   Pore size distribution of Rurhchemie catalyst: a) as prepared;
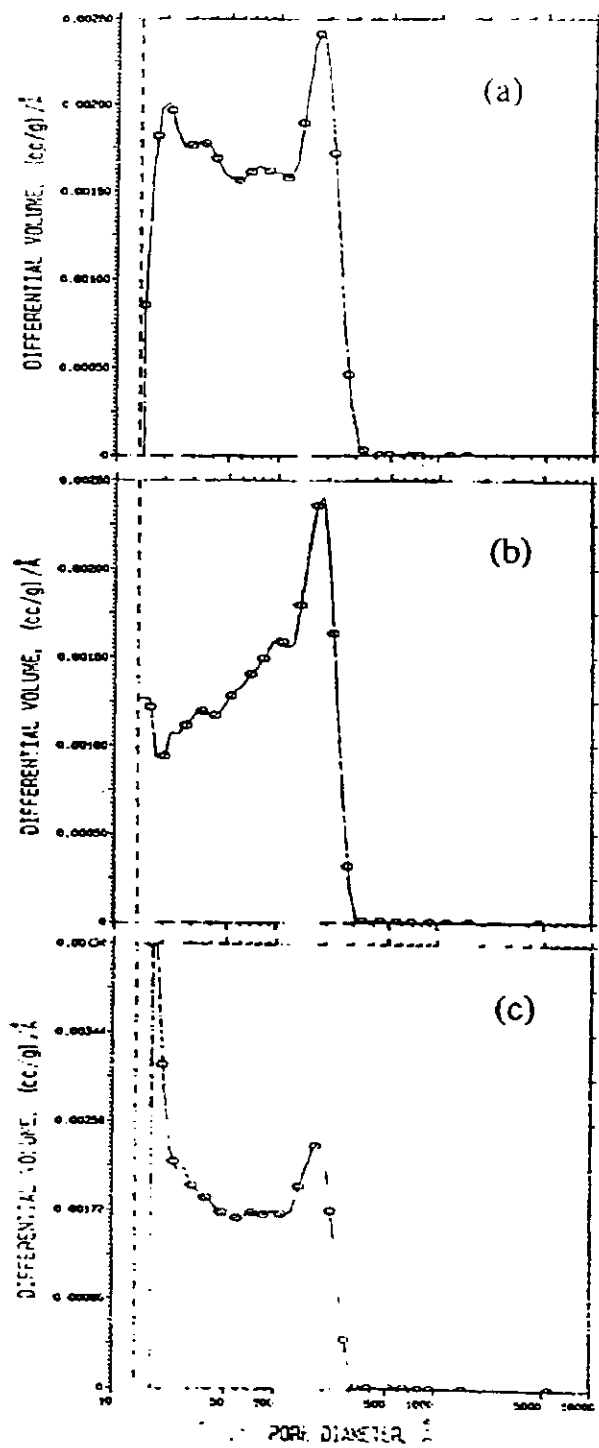b) calcined in air at 300°C for 5h.

Figure III-3.8   Pore size distribution of Ruhrchemie catalyst after pretreatment with H₂ at: a) 220°C for 1 h (flow rate = 3550 cc/min); b) 280°C for 1 h (flow rate = 3160 cc/min); c) 280°C for 8 h (flow rate = 125 cc/min).
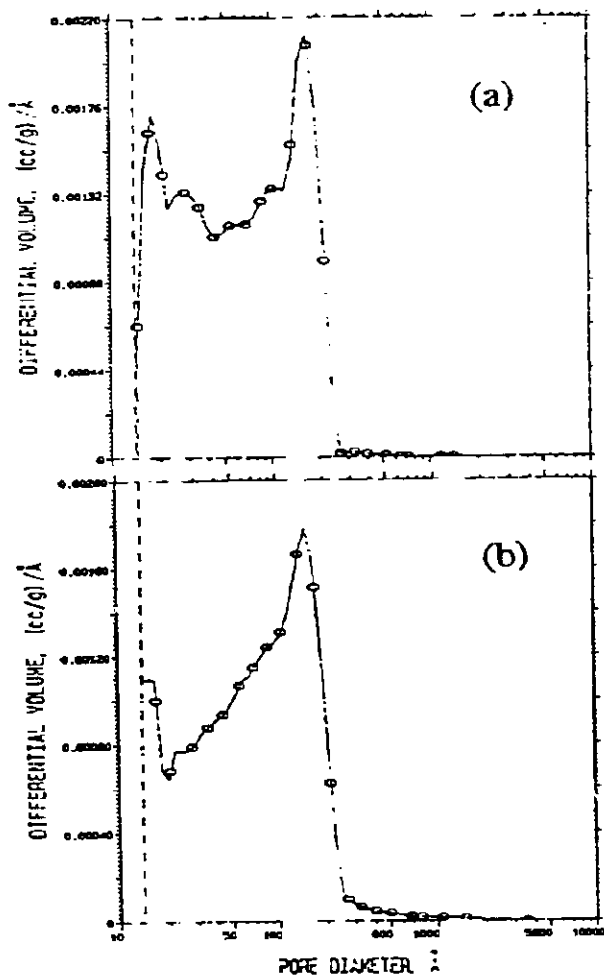
Figure III-3.9   Pore size distribution of Ruhrchemie catalyst after pretreatment with CO or syngas: a) CO (125 cc/min) at 280 °C for 12h; b) syngas ($H_2/CO=2.0$, 1200 cc/min) at 310 °C for 6h.
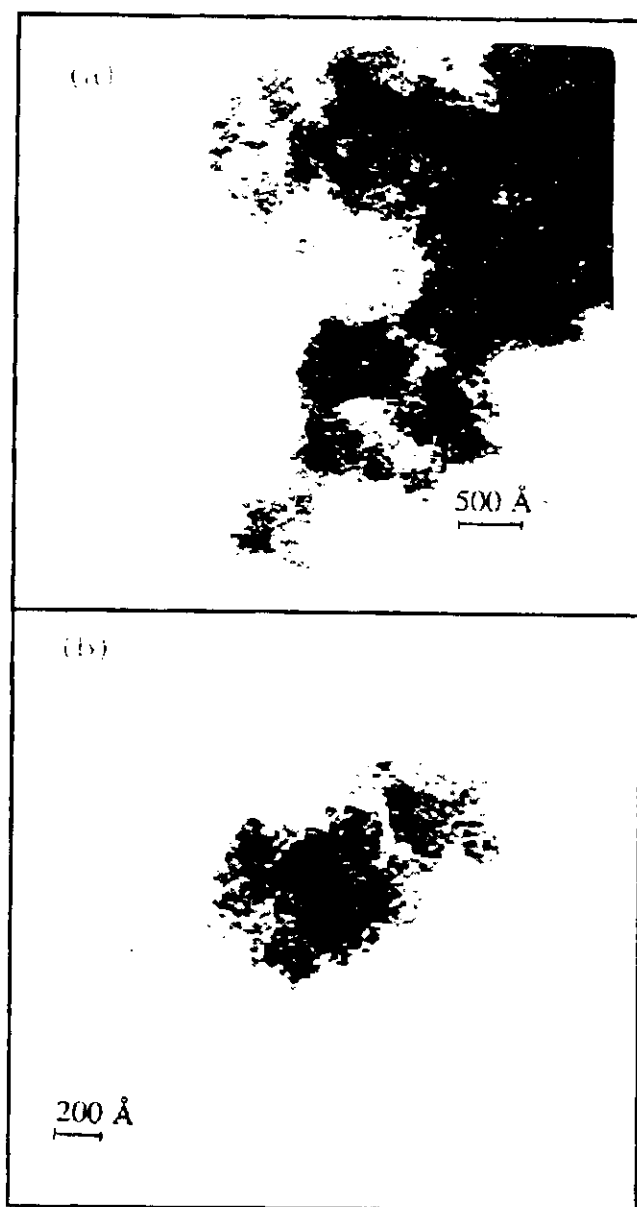
Figure III-3.10   TEM micrographs of calcined Ruhrchemie catalyst at different
magnifications: a) 169,000 X; b) 292,000 X.

The micrographs of the reduced (pretreated) Ruhrchemie catalysts (H_2 at 220°C and CO at 280°C) were also obtained and are illustrated in Figures III-3.11. The particle sizes were obtained by the procedure described above and are listed in Table III-3.1. Slight discrepancy is seen in the particle sizes obtained by XRD and TEM which is well within experimental and sampling errors. The morphology of the catalysts remained spherical even after pretreatment by CO or H_2. The average particle size estimated by TEM after H_2 or CO pretreatment is similar to that of the calcined catalyst.

III-3.2.6 Temperature Programmed Reduction/Isothermal Reduction

The reduction behavior of the Ruhrchemie catalyst was also studied by temperature programmed reduction (TPR) and isothermal reduction. The H_2 TPR profile of the precalcined Ruhrchemie catalyst, determined at a temperature program rate of 20°C/min, is shown in Figure III-3.12. The peak at 340°C is due to the first step of iron reduction ($Fe_2O_3 \rightarrow Fe_3O_4$) while the smaller peak at ~ 300°C arises from the reduction of copper oxide ($CuO \rightarrow Cu$). The broad peak centered at 650°C is due to the reduction of Fe_3O_4 to metallic iron. Thus, it can be seen that the reduction of Fe_3O_4 to Fe is a more difficult step requiring temperatures greater than 600°C for its reduction in temperature programmed mode.

In order to better simulate the reduction conditions followed in FTS, isothermal reduction profiles at 300°C were obtained. Two types of experiments were performed for this purpose. The first involved monitoring the consumption of reductants H_2 and CO using TCD, while the second involved monitoring the formation of products H_2O and CO_2 using mass spectrometry. The former involved use of smaller amounts of catalysts (10-15 mg) and lower flow rates (12 cc/min; also see Section III-3.1.2 for details) whereas in the latter experimental conditions similar to those employed during pretreatment prior to FT synthesis (SV = 3 Nl/g-cat/h; see Section III-1 for details) were used.
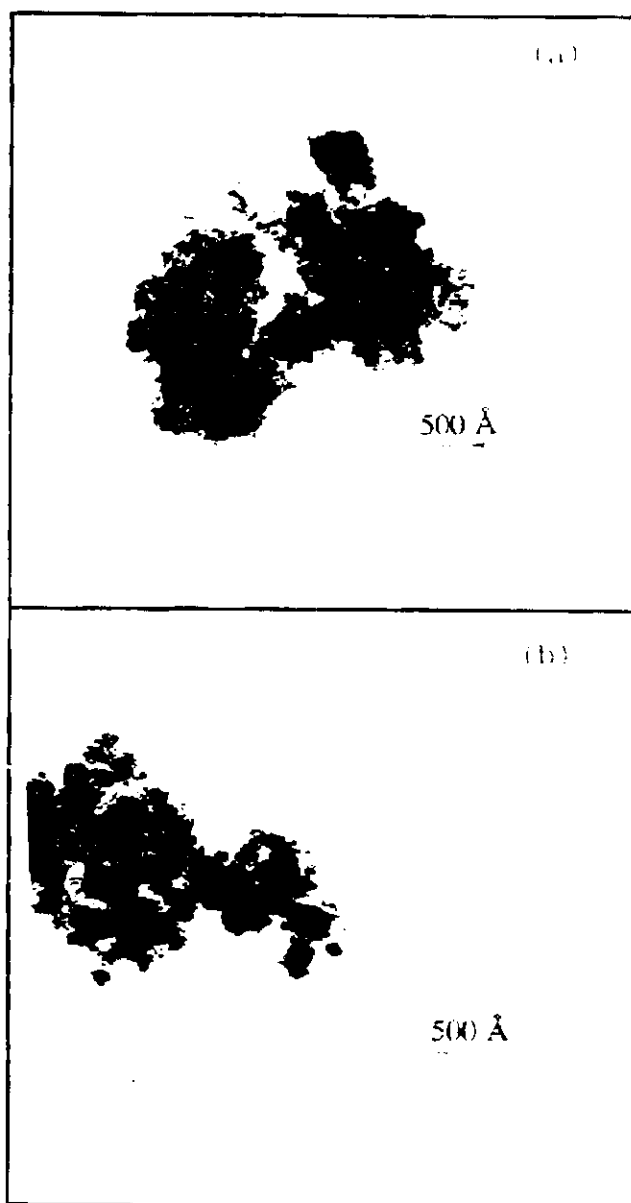
Figure III-3.11 TEM micrographs of Ruhrchemie catalyst samples after pretreatment with H$_2$ or CO: a) H$_2$ at 220°C for 1 h; b) CO at 280°C for 12 h.
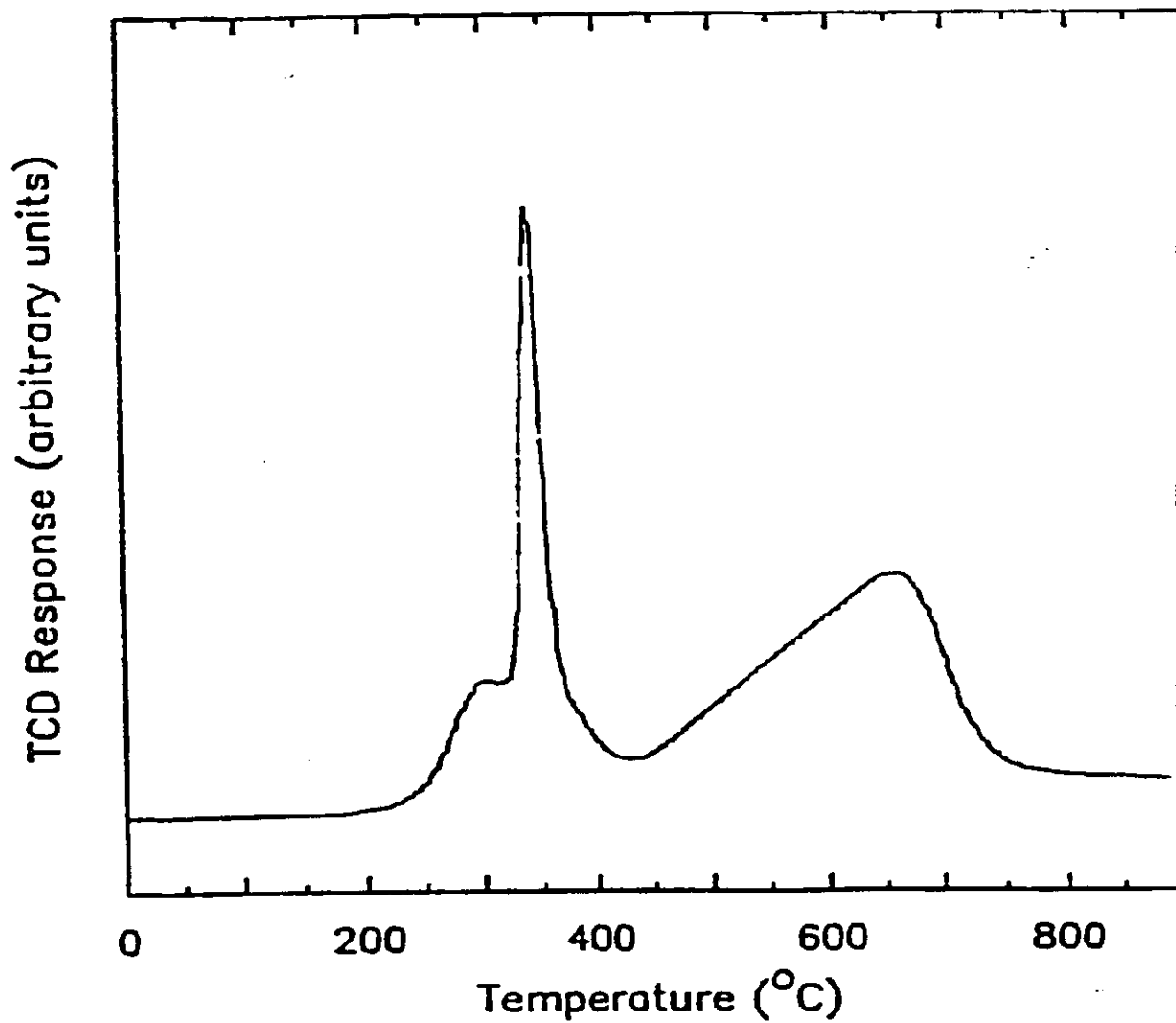
Figure III-3.12   TPR profile in H_2 at 20 °C/min of calcined Ruhrchemie catalyst (16h in air at 300°C).

The isothermal reduction profile at 300°C of the Ruhrchemie catalyst in H_2 monitored using TCD is shown in Figures III-3.13. The sharp peak in the H_2 isothermal reduction profile (Figure III-3.13) corresponds to the reduction of Fe_2O_3 to Fe_3O_4 and CuO to Cu . The broad peak corresponds to the reduction of Fe_3O_4 to Fe. In the earlier studies it was found that the level of silica influences reduction of Fe_3O_4 to Fe but does not influence the reduction of Fe_2O_3 to Fe_3O_4 and CuO to Cu significantly (Li, 1988, Bukur et al., 1990b). The H_2 isothermal reduction profile indicates that even after reduction at 300°C for over 10 h the reduction to metallic iron is incomplete. This is consistent with the XRD and MES results discussed previously.

Isothermal reduction profile was also obtained by switching from He to H_2 at 280°C and monitoring the composition of the effluents by mass spectrometry as a function of time on stream. The profile obtained for H_2 reduction of the catalyst at 280°C for 8 hours, as seen by the formation of water, is illustrated in Figure III-3.14a. A sharp peak at about 20 minutes of reduction, indicates rapid initial reduction. However, the rate of reduction decreases gradually after about 50 minutes. This is consistent with the H_2 reduction profile shown in Figure III-3.13. As stated earlier, this sharp peak can be attributed to the reduction of Fe_2O_3 to Fe_3O_4 whereas the slow reduction, i.e., after about 50 minutes, can be attributed to the reduction of Fe_3O_4 to metallic Fe. Quantitative information that could be obtained was limited due to lack of proper calibration methods for H_2O observed by mass spectrometry. However, the total amount of water formed during the reduction was collected in a trap and weighed. This amount corresponded to 30% reduction of Fe_2O_3 to Fe. Incomplete reduction of Fe_2O_3 after H_2 reduction under the above conditions was confirmed by XRD results, wherein Fe_3O_4 was detected (Table III-3.1).

The isothermal reduction profile in CO at 300°C obtained by monitoring CO consumption using TCD is shown in Figure III-3.15. A sharp maximum at around 20 minutes can be seen in Figure III-3.15 followed by decrease with time which levels
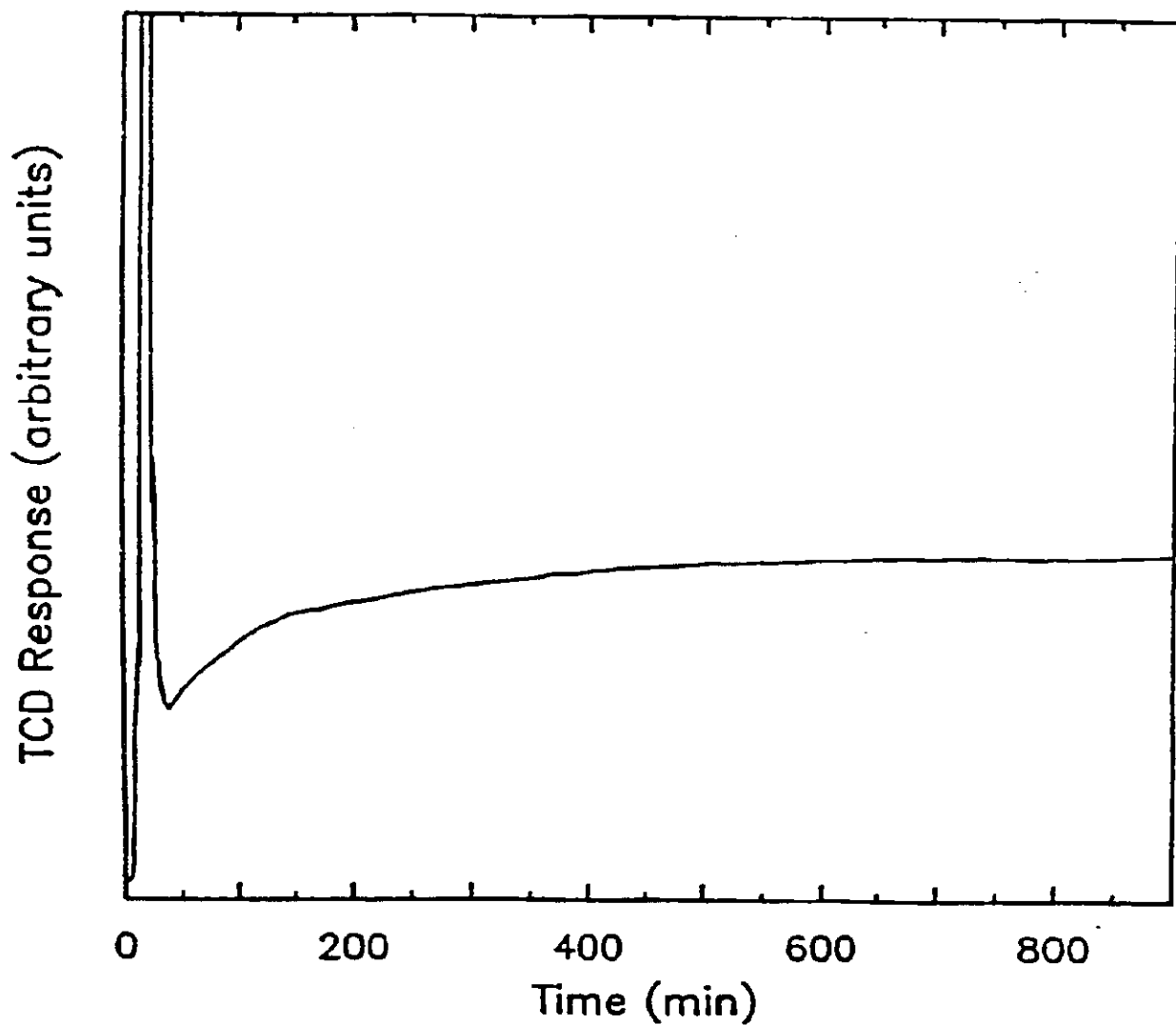
Figure III-3.13   Isothermal reduction profile in H_2 of calcined Ruhrchemie catalyst (16h in air at 300°C).
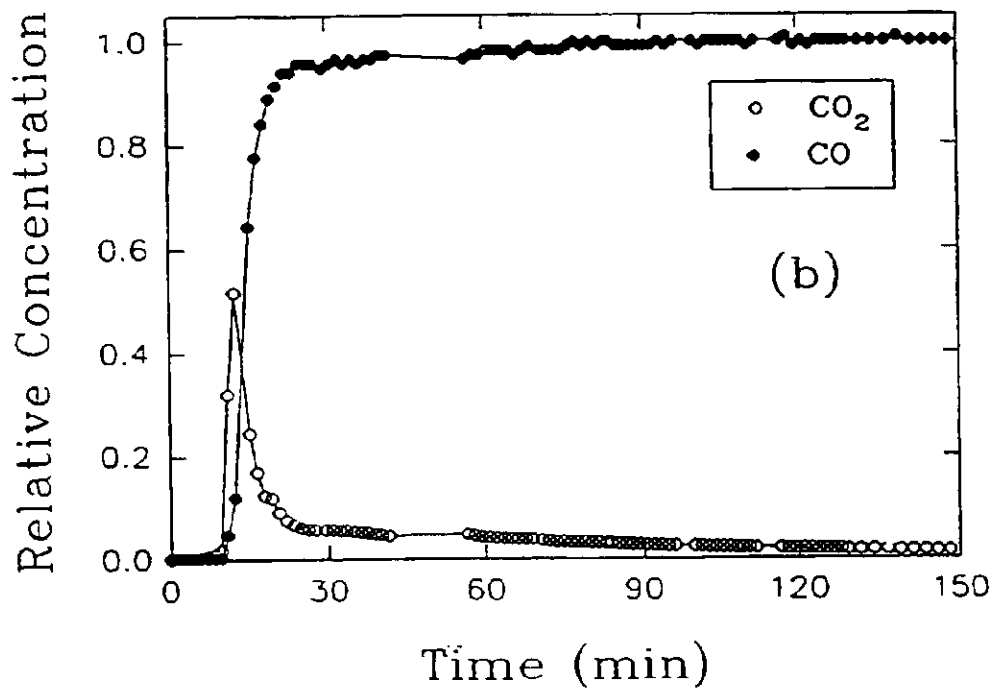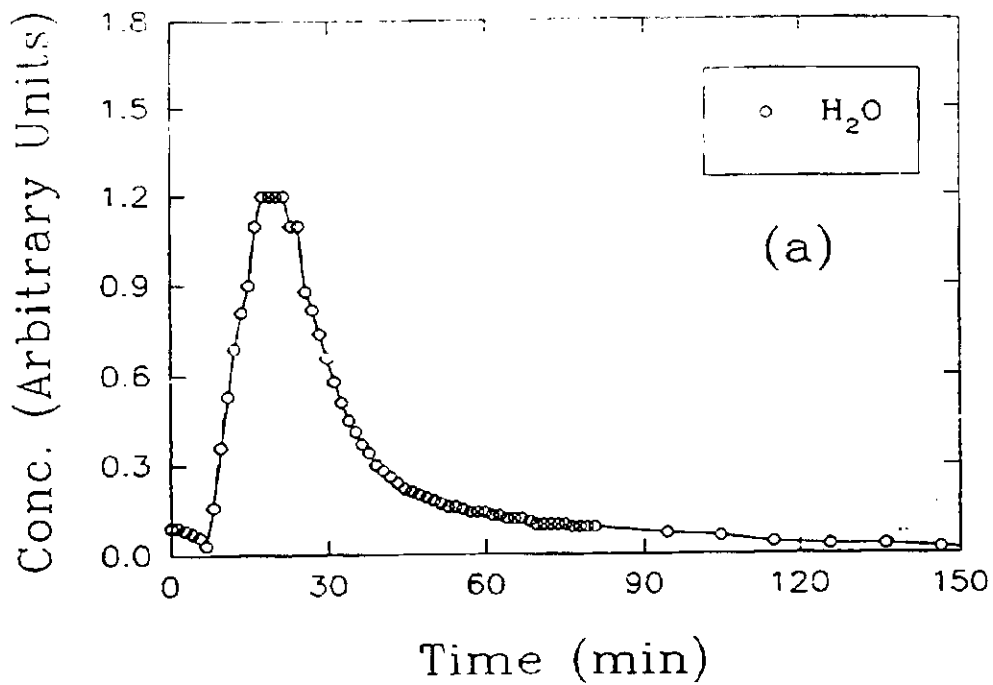
Figure III-3.14   Isothermal reduction profiles of Ruhrchemie catalyst at 280°C as a function of duration of reduction: a) in H_2; b) in CO.
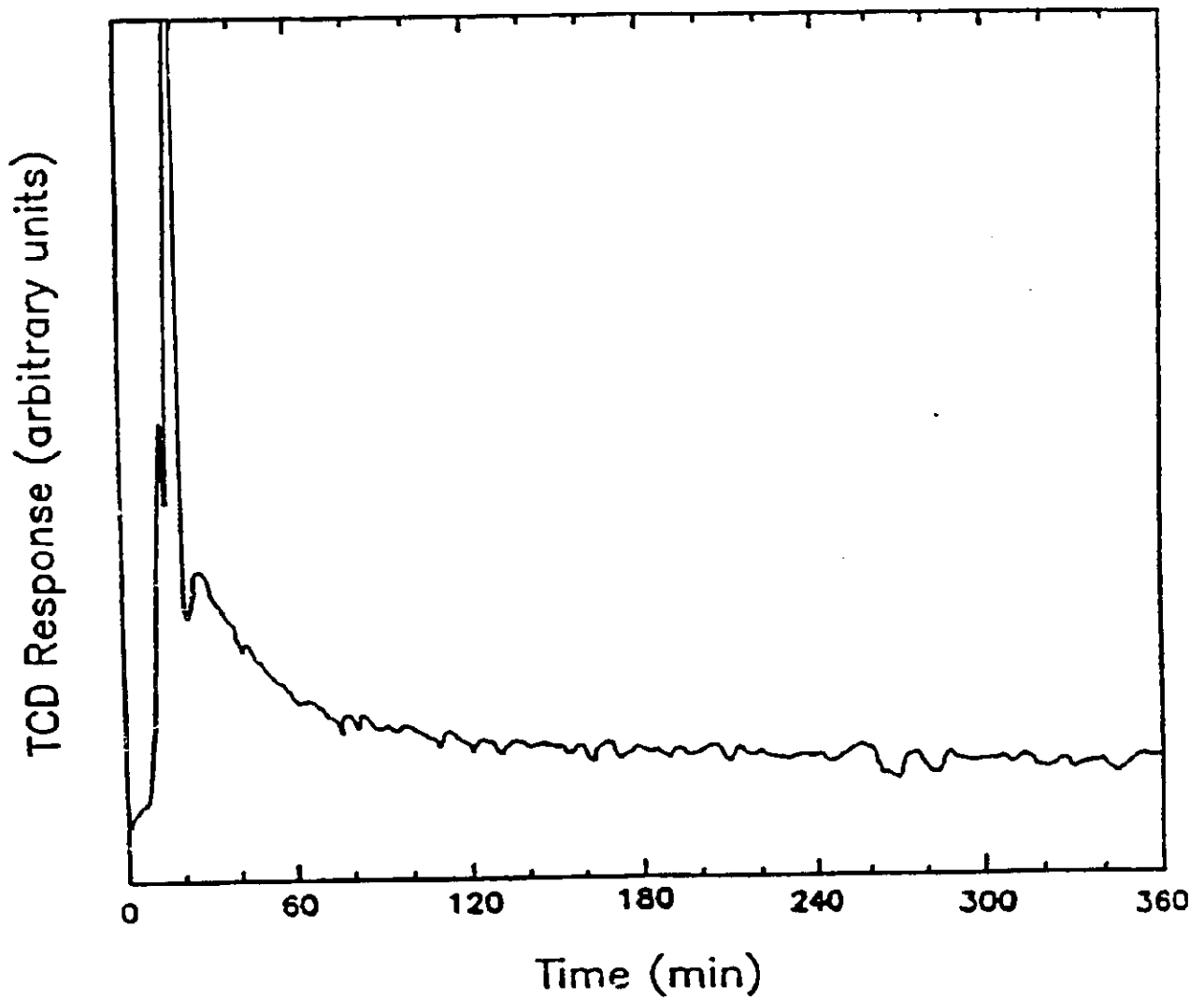
Figure III-3.15   Isothermal reduction profile in CO of calcined Ruhrchemie catalyst (16h in air at 300°C)

after around 300 minutes. The sharp peak corresponds to the reduction of Fe_2O_3 to Fe_3O_4. A small shoulder visible on the left side of these peaks results from reduction of the copper promoter, which subsequently facilitates the onset and increases the rate of iron reduction (Bukur et al., 1989b). The portion of profile which shows decrease with time corresponds to subsequent reduction of Fe_3O_4 to metallic Fe.

Isothermal reduction, using CO as the reductant, at 280°C for 8h was also carried out by switching from He to CO at 280°C and monitoring the composition of the effluent gas by mass spectrometry as a function of time on stream. Figure III-3.14b shows the relative concentration profiles of reductant CO and product CO_2 (formed during reduction) up to 150 minutes. It can be seen that the CO_2 formation profile is very similar to the CO consumption profile shown in Figure III-3.15. An initial sharp peak is followed by a gradual decrease after about 30 minutes of reduction (Figure III-3.14b). As stated earlier, the sharp peak corresponds to the reduction of Fe_2O_3 to Fe_3O_4, whereas further CO_2 is formed due to the reduction of Fe_3O_4 to Fe and subsequent carbiding. Small amount of CO_2 was seen even after 8 hours of reduction.

The concentrations of CO and CO_2 were also obtained by gas chromatography at 20 minute intervals. Although data could not be acquired as rapidly with a gas chromatograph as with an on-line mass spectrometer, the CO_2 profile so obtained is in qualitative agreement with the profile seen in Figure III-3.14b. Some CO_2 was also detected in the effluent gas by gas chromatography after 8 hours of reduction.

The amount of CO_2 formed during reduction up to about 8 hours was obtained from the CO_2 concentration profile shown in Figure III-3.14b. For this purpose, the data obtained by mass spectrometry was converted into absolute molar flow rate of CO_2 after proper calibration of the mass spectrometer using several known concentration values obtained by gas chromatography and the total flow effluent flow rate. Integration of the CO_2 molar flow rate profile yielded the total amount of CO_2 formed during 8 hours of reduction as 27.5 mmol/g of catalyst. It should be noted that the total

amount of CO_2 that can be accounted for assuming complete reduction of the catalyst is 15.7 mmol/g. Whereas, the total amount of CO_2 that can be formed assuming complete carbiding of the catalyst (to $Fe_{2.2}C$) is 3.5 mmol/g. This means that the total amount of CO_2 formed exceeds the amount of CO_2 that can be accounted for by both reduction as well as carburization. The excess CO_2 is presumably due to the formation of carbonaceous deposits on the catalyst.

III-3.2.7   X-ray Photoelectron Spectroscopy

The programmed/isothermal reduction studies described above reveal overall bulk-phase reduction behaviors of the iron catalysts. In order to obtain additional information about the extent of iron reduction and the catalyst composition in the near surface region, where adsorption and catalysis occur, XPS spectra were obtained after reduction with CO and H_2. Figure III-3.16 shows the XPS spectra in the Fe 2p region after calcination and after CO and H_2 reductions. It has been shown that the Fe $2p_{3/2}$ peak at 711.2 eV with a characteristic satellite peak at 719.5 eV corresponds to Fe^{3+}; peak at 709.7 eV with a characteristic satellite at ~715 eV corresponds to Fe^{2+} species, whereas the one at 706.0 eV corresponds to metallic Fe (Kuivila et al., 1988). The spectrum for Fe_3O_4 is essentially a weighted average of Fe^{2+} and Fe^{3+} spectra, with binding energy of 710.8 eV (Kuivila et al., 1988). Figure III-3.16 a shows a peak at 710.5 eV with a shake-up satellite peak at 719 eV. The binding energy of 710.5 eV indicates the presence of Fe_3O_4 whereas the satellite peak at 719 eV confirms the presence of some Fe_2O_3. Reduction in CO for 16h at 300°C (Figure III-3.16 b) yields peaks at approximately 707.0 and 710.5 eV. Recently, Kuivila et al. (1988) reported that it was possible to distinguish metallic Fe from iron carbides using a rigorous fitting technique resulting in binding energies of 707.0 eV and 707.3 eV for metallic Fe and carbidic Fe respectively. Such a rigorous procedure was not applied in this case. Thus, it is not possible to distinguish between the nature of various reduced iron
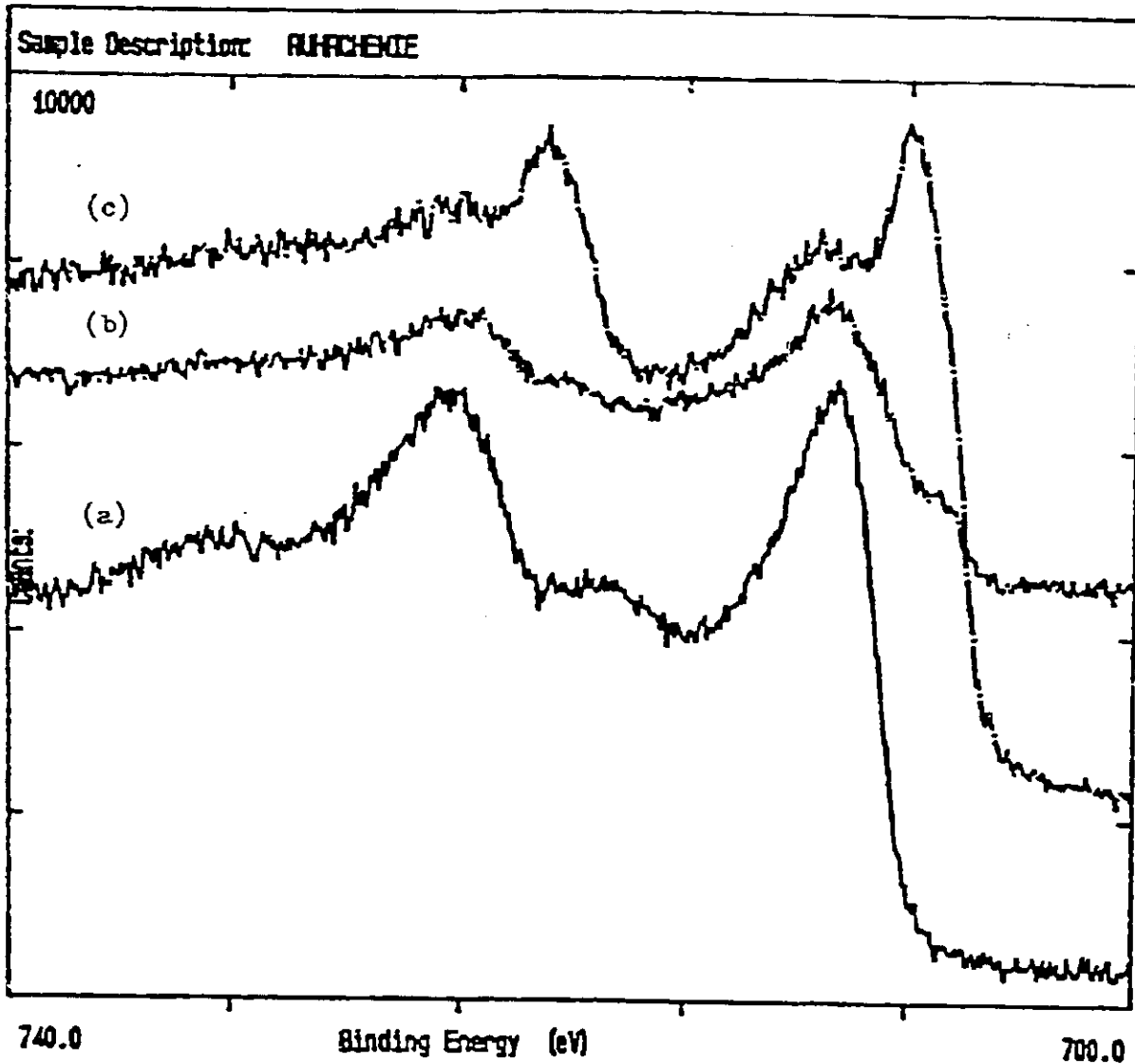
Figure III-3.16 XPS spectra of Ruhrchemie catalyst samples in Fe 2p region:
a) following calcination for 16 h at 300°C; b) following exposure of (a)
to CO at 300°C; c) following exposure of (a) to H_2 at 300°C.

species that exist after CO reduction. Nonetheless, the presence of a peak at 710.5 eV indicates that most of the surface iron remained in the form of unreduced Fe^{3+}/Fe^{2+} species. By contrast, reduction in H_2 under the same conditions resulted in much greater percentage of reduced iron, as shown by the sharp peak at 707-708 eV (Figure III-3.16 c) which is characteristic of metallic Fe.

Figure III-3.17 shows XPS spectra after calcination and after CO and H_2 reductions in the K 2p and C 1s regions. A peak at C 1s binding energy of 284.6 eV corresponds to "graphitic" or "surface carbon", whereas the one at 283.2 eV corresponds to carbidic carbon (Kuivila et al., 1988). After calcination a small peak at ~ 284 eV is observed (Figure III-3.17 a) which is due to residual surface carbon. However, after pretreatment with CO at 300°C, the large peak at ~ 284 eV was observed (Figure III-3.17b). It is not clear whether the peak is due to the presence of surface carbon or carbidic carbon. XRD and MES measurements after CO pretreatment at 280°C have indicated the presence of bulk carbide species. However, the presence of surface carbon species cannot be completely ruled out. As expected, after H_2 reduction the peak corresponding to carbon is absent (see Figure III-3.17 c). In all cases, a small K 2p peak at a binding energy of 293 eV was observed indicating that the concentration of surface potassium is low.

Figure III-3.18 shows XPS spectra after calcination and after CO and H_2 reductions in the O 1s regions. The O 1s binding energy for all iron oxides is 530.3 eV. Thus it is not very useful for discriminating between compounds. Nonetheless, the characteristic peak observed for the iron oxides at 530.3 eV decreases in intensity after CO reduction (see Figures III-3.18 a and b) indicating that CO is responsible for at least partial reduction of the oxides. After H_2 reduction, however, a peak at ~ 532 eV is observed (Figure III-3.18 c) which is characteristic of the adsorbed OH group. This means that H_2 reduction is near complete which is consistent with the appearance of the metallic Fe peak in the Fe 2p region. The absorbed OH groups may originate from
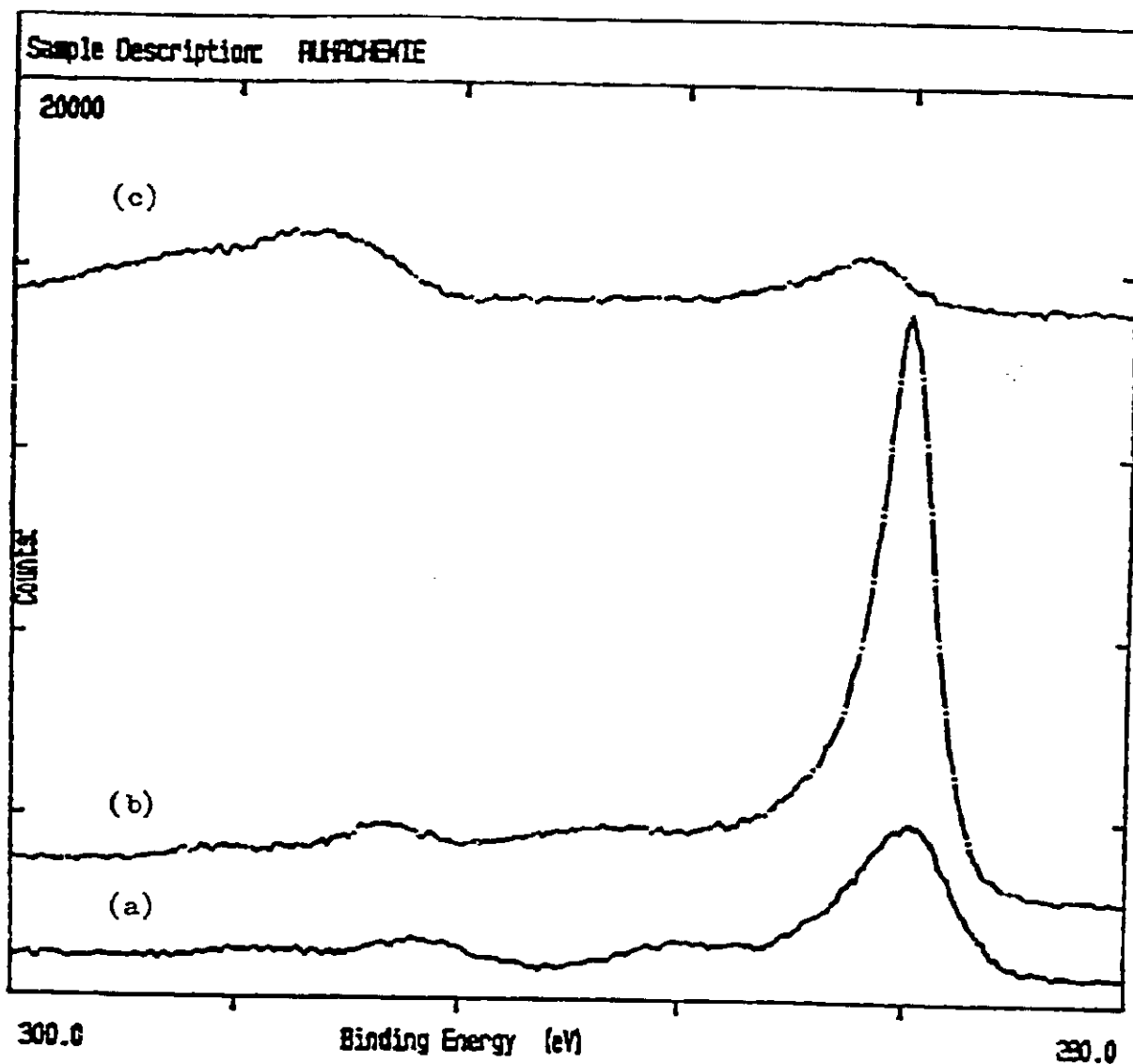
Figure III-3.17   XPS spectra of Ruhrchemie catalyst samples in C 1s and K 2p region: a) following calcination for 16 h at 300°C; b) following exposure of (a) to CO at 300°C; c) following exposure of (a) to H_2 at 300°C.
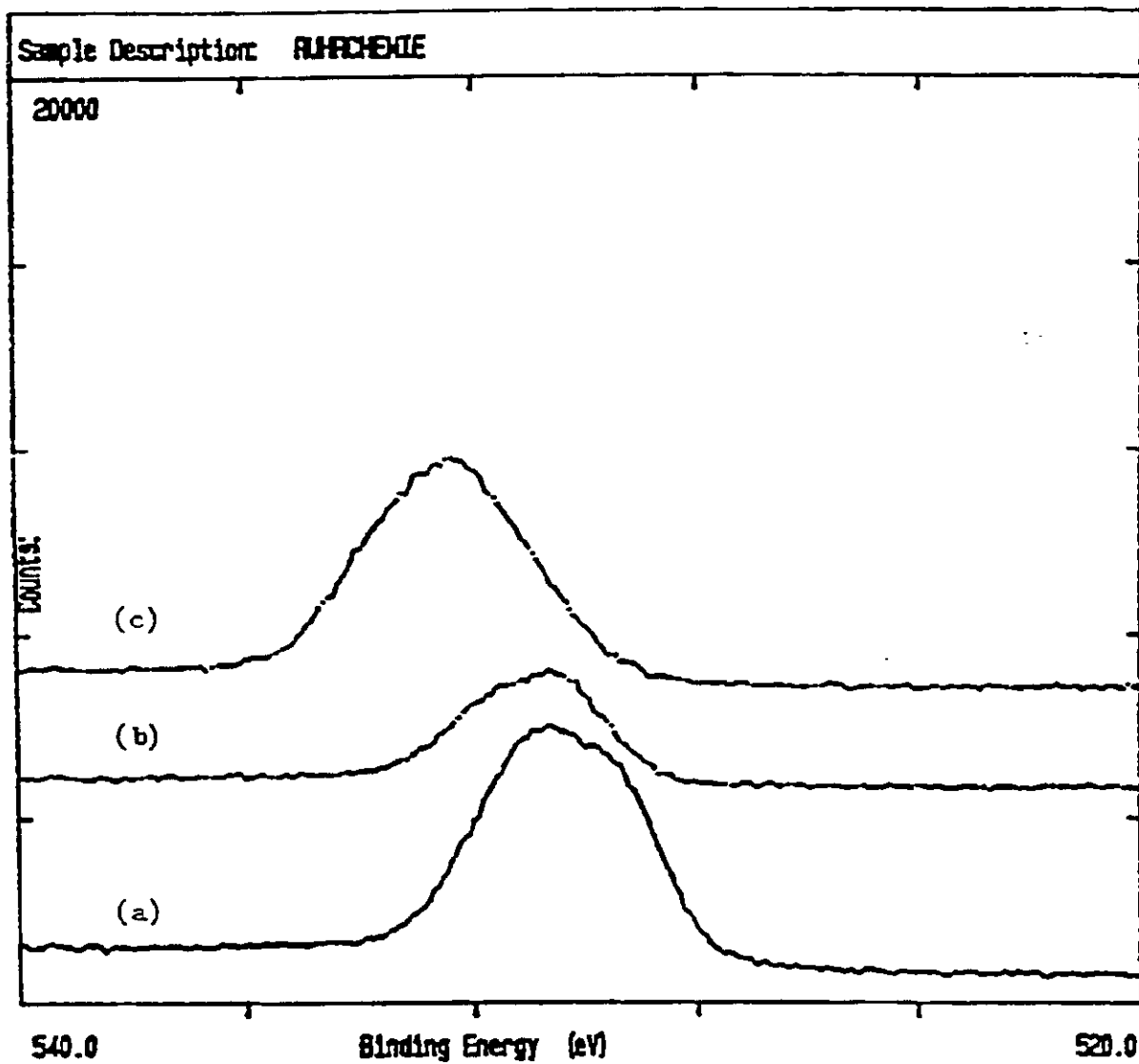
Figure III-3.18   XPS spectra of Ruhrchemie catalyst samples in O 1s region:
a) following calcination for 16 h at 300°C; b) following exposure of (a)
to CO at 300°C; c) following exposure of (a) to H$_2$ at 300°C.

the water formed during reduction of the iron oxides.

III-3.3 Summary

A precipitated iron catalyst with nominal composition 100 Fe/5 Cu/4.2 K/25 SiO$_2$, prepared by Ruhrchemie, was characterized before and after five different pretreatments, as well as after the Fischer-Tropsch synthesis, following these pretreatment procedures, in a fixed bed reactor at 250°C, 1.48 MPa (200 psig), 2 Nl/g-cat/h, H$_2$/CO = 0.67 for 100 - 426 hours.

The as-received catalyst had the BET surface area of 295 m^2/g and the pore volume of 0.58 cm^3/g, both of which remained unchanged (within experimental errors) after calcination in air at 300°C for 5 hours. After different pretreatments with H$_2$, CO or syngas both the BET surface area and the pore volume of the catalyst decreased, while the average pore diameter increased. The surface area of the pretreated catalysts ranged from 100 to 180 m^2/g, whereas the pore volume varied from 0.31 to 0.49 cm^3/g. The decrease in the surface area and the pore volume is attributed to a partial collapse of the porous iron oxide/hydroxide network, which is stabilized by the presence of silica. In the absence of silica the surface areas of pretreated precipitated iron catalysts are between 10 and 40 m^2/g (Bukur et al., 1989b, also see Section III-1 of this report).The pore size distribution of as-received and pretreated catalyst was rather broad with a maximum at about 20 nm, which shifted slightly to higher values after H$_2$ or CO pretreatments. The catalyst, before and after pretreatments, also had micropores less than 1.5 nm (the lower limit of detection) in diameter.

Transmission electron micrographs of calcined sample and samples after pretreatments with either H$_2$ at 220°C or CO at 280°C reveal that particles are small and spherical (~ 3.5 nm). An increase in particle size was observed after H$_2$ reductions by X-ray line broadening method. The particle size increased with reduction temperature (e.g. 5 nm after H$_2$ reduction at 220°C, and 10 nm after

reduction at 280°C for 8 hours). The particle size of Hagg carbide, formed during CO or syngas pretreatments, was not determined due to low intensity of the peaks and /or their close proximity.

The extent of bulk iron reduction following H_2 and CO pretreatments was studied by isothermal and temperature programmed reduction. The isothermal and temperature programmed reduction profiles indicate that the reduction occurs in two steps: Facile reduction of Fe_2O_3 to Fe_3O_4, followed by slow reduction of Fe_3O_4 to either metallic iron (H_2 reduction) or an iron carbide (CO pretreatment). The first step is completed in about 15-30 minutes, whereas the second step is not complete even after 8-10 hours (isothermal reductions with H_2 and CO at 280°C and 300°C). The amount of CO_2 released during the CO pretreatment at 280°C was greater than the stoichiometric amount needed for complete oxygen removal and complete carburization of iron in the catalyst. It is assumed that this is due to formation of carbonaceous deposits by Boudouard reaction.

The catalyst composition in the near surface region, where adsorption and catalysis occur, after H_2 and CO pretreatments was studied by X-ray photoelectron spectroscopy (XPS). Results indicate that H_2 reduction leads to a greater degree of iron reduction than that obtained after the CO pretreatment. However, in both cases a significant fraction of the surface iron remained in the form of unreduced Fe^{3+}/Fe^{2+} species. After the CO pretreatment we were not able to positively identify the nature of the surface iron species due to close proximity of binding energies of metallic iron (707.0 eV) and surface carbide (707.3 eV).

X-ray diffraction (XRD) and Mössbauer effect spectroscopy (MES) were used to identify bulk iron phases in pretreated and used (after FT synthesis) catalyst samples. After H_2 reductions the bulk iron is in the form of either Fe_3O_4 (magnetite) - reduction at 220°C, or a mixture of Fe_3O_4 and α-Fe (reductions at 280°C). During FT synthesis the iron carbides (χ- Fe_5C_2 or ε' - $Fe_{2.2}C$) are formed by carburization of α-Fe and/or

Fe3O4. The used catalysts contain iron carbides and magnetite.

After CO or syngas pretreatments, the χ- carbide and superparamagnetic oxides are the only phases present. The latter is probably in the form of small magnetite particles, which needs to be confirmed by MES measurements at low temperatures. During FT synthesis this carbide is partially converted to Fe3O4. Iron carbide content is higher in samples from the top part of the reactor (reducing atmosphere), whereas Fe3O4 and superparamagnetic oxides are the dominant iron phases in samples from the bottom part (more oxidizing atmosphere).

III-3.4   References

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