

MÖSSBAUER SPECTROSCOPY STUDY OF IRON-BASED CATALYSTS USED IN FISCHER-TROPSCH SYNTHESIS.

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Mössbauer spectroscopy is perhaps the best technique available for quantitative determination of iron phase distributions in complex multiphase samples. It is therefore very well suited to the identification of different phases present in iron catalysts at various stages of genesis in the Fischer-Tropsch (FT) synthesis process. In the present studies, we have carried out Mössbauer characterization of the iron phases present in reduced and used catalysts. A quantitative determination of the phase distribution and its changes with time on steam has enabled us to correlate the iron phases with the FT and WGS activity.

The present studies consists of three parts.

- (A) ROLE OF MAGNETITE IN FISCHER-TROPSCH SYNTHESIS
- (B) STUDY OF CO-PRECIPIATED FISCHER-TROPSCH IRON CATALYSTS
- (C) EFFECT OF PRE-HEAT TREATMENT ON A
FISCHER-TROPSCH IRON-CATALYST

(A) ROLE OF MAGNETITE IN FISCHER-TROPSCH SYNTHESIS

We have carried out Mössbauer characterization of iron catalysts extracted from the Fischer-Tropsch (FT) demonstration run conducted at the Pilot Plant of DOE at the Alternate Fuels Development Unit, LaPorte, Texas during August 1992 with a view to gain insights into the FT and Water-Gas-Shift (WGS) reactions.

Typical composition of the catalyst studied:

K₂O: % 5.1, SiO₂: % 8.3, CuO: % 2.6, Fe₂O₃: % 69.6. LOI: % 14.8

These catalysts drawn at different time-on-stream (TOS) periods up to 450 hours were provided by AIR PRODUCTS AND CHEMICALS, Inc.

Changes in the various FT run conditions like space velocity,(S.V.) pressure,(P) and gas ratio (H_2/CO) made during the run to investigate their effects on the FT conversion process are given in Table I

Table I

FT run conditions for the LaPorte Demonstration Pilot plant [1]

Description	SYNGAS	S.V (SL/h-kgFe)	Pressure (PSIG)	Temp. C	No of Days
Activation	$H_2/CO=0.7$	2000	150	280	1
Baseline (B.L)	$H_2/CO=0.7$	2500	200	265	9
Effect of S.V.	$H_2/CO=0.7$	5000	200	265	3
Effect of P	$H_2/CO=0.7$	5000	400	265	2
Return to B.L.	$H_2/CO=0.7$	2500	200	265	2
Nat. Gas	$H_2/CO=2.0$	2500	200	265	2

Typical Mössbauer spectra of the catalyst used in an autoclave and in the LaPorte plant FT run are shown in Fig.1. The variation of iron phase distribution in the catalysts drawn from the LaPorte plant is show in Fig.2. Variation of the B/A ratio (i.e. ratio of Fe atoms in octahedral sites to tetrahedral sites), usage ratio, CO-conversion rate and space velocity as a function of time on stream are shown in Fig.3.

- * We find significant correlations between the iron-phase distribution, FT and WGS activities.
- * Magnetite is involved in the water gas shift reaction.
- * The ratio of the relative population of Fe atoms at B-sites to that of A-sites in the magnetite phase is correlated to the usage ratio, U defined as the moles of H₂ converted per mole of CO converted in the FT reaction.
- * The B/A ratio is low for a higher WGS reaction activity and high nearing the stoichiometric value of 1.9 for the FT synthesis.
- * A decrease in the B/A ratio indicates an increase in cation deficiencies at the B-sites as Fe₃O₄ is oxidized towards γ-Fe₂O₃. Possibly, the H₂O generated in the WGS reaction oxidizes Fe₃O₄ to γ-Fe₂O₃ leading to a decrease of the B/A ratio.

Rethwisch and Dumesic have shown that magnetite is involved in the WGS process. [2,3]. According to them, the WGS reaction can take place through:

- (a) a "regenerative mechanism" in which only the B-site iron atoms in magnetite are involved and/or
- (b) an "adsorption mechanism".

Our results are consistent with the observation that magnetite is involved in the WGS reaction process. If the regenerative mechanism is operative, the WGS activity can be expected to be proportional to the B-site population. However, our present measurements indicate that the WGS activity and the B-site population are inversely proportional. Therefore the "adsorption" mechanism may be operative in the present case.

There is a correlation between the space velocity of syngas and the B/A ratio as shown in Fig.3d and Fig.3a respectively.

THE PRESENT INVESTIGATION LEADS TO THE FOLLOWING CONCLUSIONS:

- (a) Magnetite is involved in the WGS reaction, consistent with the findings of Rethwisch and Dumesic [2,3].
- (b) Apart from the quantity of magnetite present, it is the B/A ratio which may be significant for the WGS reaction.
- (c) Whenever WGS activity is high, the B/A ratio is low, indicating that cation deficient magnetite gives rise to better WGS activity in the present FT run.
- (d) The inverse interdependence of the B/A ratio and WGS activity indicates that the "adsorption" mechanism is probably operative in the WGS reaction.

(B) STUDY OF CO-PRECIPIATED FISCHER-TROPSCH IRON CATALYSTS

It has been shown that the support of a catalyst significantly affects its activity, stability and selectivity during Fischer-Tropsch (FT) synthesis [4]. A support like SiO_2 or Al_2O_3 etc. is used to increase the surface area for metal crystallites in the catalysts.

We have carried out Mössbauer studies of iron catalysts containing various amounts of silica to investigate the effect of silica on the iron phase distribution obtained on reduction and after FT synthesis.

The catalysts studied :

$100\text{Fe}/5\text{Cu}/4.2\text{K}/x\text{SiO}_2$ where $x = 0, 8, 16, 24, 25, 40,$ or 100 .

Reduction of the calcined catalysts in carbon monoxide at 280°C for 12 h at atmospheric pressure led to conversion of the catalysts predominantly to χ -carbide, Fe_3C_2 as given in Table I.

A separate set of CO-reduced catalysts, when subjected to FT run conditions, viz., $\text{H}_2/\text{CO}=1.0$, at 235°C , 15 atm in a fixed bed reactor, were oxidized predominantly to magnetite, Fe_3O_4 , as shown in Table II.

It is observed that the χ -carbide formed on reduction in CO decreases with the silica content as shown in Fig.4. The FT activity of the catalyst, as measured [4] by the conversion of $(\text{CO}+\text{H}_2)$ at 10-50hrs on stream, decreases with the silica content

in a trend similar to that of the χ -carbide variation as shown in Fig.4. Our data show a correlation between the FT activity (at 10-50 hrs on stream) and the χ -carbide content of reduced catalysts (Fig.4). During FT synthesis some of the χ -carbide (Fe_3C_2) gets converted into magnetite as shown in the Table II.

The activities of catalysts with low silica contents ($x=0$ and 8) decrease with time on stream, i.e. as χ -carbide is converted to magnetite. For example, at the end of the tests (140-170 hrs), the (H_2+CO) conversions of the catalysts with $x=0$ and $x=8$ were 47% and 45% , respectively [4]. On the other hand , the activities of the catalysts with high silica contents ($x=40$ and 100), remain essentially constant up to 170 hrs on stream [4].

The above results indicate that χ -carbide is more active for FT synthesis than the iron oxide phases.

During reduction of the catalysts in CO, iron silicate is formed on the surface of Fe/Cu/K/xSiO_2 catalysts. This surface layer of iron silicate decreases diffusion of carbon and formation of χ -carbide. The 100 SiO_2 catalyst contains only 4% χ -carbide, while the catalyst which does not contain any silica contains 87% of χ -carbide and the catalysts with intermediate values of silica give intermediate amounts of χ -carbide.

The ratio of the relative population of Fe atoms at B-sites (octahedral) to that of A-sites (tetrahedral) in the magnetite in different catalysts varied with the content of SiO_2 . The B/A ratio decreased from 1.76 (for $x=0$) to 0.9 (for $x=100$) with increasing SiO_2 content.

The usage ratio, (defined as the moles of H_2 converted per mole of CO converted, - low usage ratio means high water-gas-shift (WGS) activity) increased from 0.72 (for $x=0$) to 1.5 (for $x=100$) with an increase of SiO_2 content [4].

Lund and Dumesic [5] have suggested that the WGS reaction takes place through a regenerative process in which only the B-site iron atoms in magnetite are involved.

Our results indicate that magnetite is involved in the WGS reaction and are consistent with the model given by Lund and Dumesic.

Table I:
Iron phase distribution in the catalysts reduced in
CO at 280°C for 12 h at atmospheric pressure.

Precipitated cats.	% χ -Fe ₃ C ₂	% Spm-oxide*	% siderite
100Fe/5Cu/4.2K	87	13	
100Fe/5Cu/4.2K/8 SiO ₂	86	14	
100Fe/5Cu/4.2K/16SiO ₂	47	53	
100Fe/5Cu/4.2K/24SiO ₂	52	48	
100Fe/5Cu/4.2K/40SiO ₂	26	74	
100Fe/5Cu/4.2K/100SiO ₂	4	83	13

*Spm-oxide = superparamagnetic-oxide consisting of particles of about < 100Å

Table II:
Iron phase distribution in catalysts subjected to FT run conditions, viz., H₂/CO=1.0, at 235°C, at atm in a fixed-bed reactor. (These are a separate set of CO reduced catalysts)

Catalysts	%Fe ₃ O ₄	%Spm. oxide	%Fe ₃ C ₂	%other phase
100Fe/5Cu/4.2K	69	6	13	12 siderite
100Fe/5Cu/4.2K/8SiO ₂	60	22	18	
100Fe/5Cu/4.2K/16SiO ₂	87	13		
100Fe/5Cu/4.2K/25SiO ₂	68	27	5	
100Fe/5Cu/4.2K/40SiO ₂	71	23		6 silicate
100Fe/5Cu/4.2K/100SiO ₂	19	78		3 silicate

(C) EFFECT OF PRE-HEAT TREATMENT ON A FISCHER-TROPSCH IRON-CATALYST

Pretreatment of iron catalysts is an important step in the development of an efficient catalyst. It affects dramatically the distribution of iron phases that are formed during the treatment and the changes that occur during FT synthesis. The FT activity and possibly selectivity are related to the iron phases present in the catalyst and changes that take place during synthesis.

The pretreatment is controlled by the type of gas, temperature (T), pressure (P) and gas space velocity (S.V.) used.

In the present investigation, we have carried out a Mossbauer study of a FT iron-catalyst subjected to pretreatment consisting of two periods: a 5.5 hr period of heating from room temperature (RT) to 280°C under He or H₂+CO (H₂/CO=0.7) and a second period of 15.5 hrs of exposure to H₂+CO (H₂/CO=0.7) at 280°C. After the second period, the catalyst was used for FT synthesis at 265°C.

It is to be noted that preheat treatment is to be distinguished from pretreatment and refers to heating the catalyst in a gas atmosphere during ramping of the temperature from the room temperature to the desired temperature for pretreatment.

The catalyst studied was a Ruhrchemie type of catalyst with nominal composition of 100Fe/5Cu/4.2K/24SiO₂.

Details of the two types of preheat, the pretreatment and the FT run conditions are:

Preheat (a) H₂/CO =0.7, S.V.=2.0nL/h-gFe, P=11.5atm., T=RT to 280 C in 5.5hrs

(b) He, P = 11.5 atm., T= RT to 280 C in 5.5 hrs

Pretreatment: H₂/CO=0.7, S.V.=2.0nL/h-gFe, P=11.5atm., T=280°C
for 15hrs

FT run: H₂/CO=0.7, S.V.=2.4nL/h-gFe, P=20.7at m., T=265 C

Samples withdrawn after 3.5 hrs. from the start of the pre-heating are designated as A in each case. Samples were also drawn after 7hrs of pretreatment at 280°C in the case of (CO+H₂) preheated catalyst and after 6hrs of pretreatment at

280°C in the case of helium preheated catalyst. Such two samples are designated as B in each case. The catalyst samples studied were withdrawn from the reactor after different time-on-stream (TOS) periods, viz., 2, 24.5, 49.5, and 96 hrs during FT synthesis. These samples are designated as C,D,E, and F respectively in each case.

The phase distributions determined to be present in the catalysts subjected to the two different treatments are given in Table I and Fig.5.

Table I

Percentage of iron phases in each catalyst

Preheated in (CO+H₂):

Sample	Spm oxide	Fe ₃ O ₄	Fe ₅ C ₂	Fe ₂ 2C	silicate	α-Fe ₂ O ₃
A-3.5 hrs	94					6
B-7.0 hrs	60	10	22			8
C-2 hrs	56	18	26			
D-24.5 hrs	31	14	49		6	
E-49.5 hrs	20	19	48		13	
F-96 hrs	29	7	37		27	

Preheated in helium:

Sample	Spm oxide	Fe ₃ O ₄	Fe ₅ C ₂	Fe ₂ 2C	silicate	α-Fe ₂ O ₃
A-3.5 hrs	89					11
B-6.0 hrs	59	20	6	15		
C-2 hrs	26	12	19	43		
D-24.5 hrs	41	9	11	39		
E-49.5 hrs	31	11	13	45		
F-96 hrs	22	30	10	38		

The iron phases present in the two sets of samples differ. The catalyst preheated in CO+H₂ gave rise to substantial amounts of an iron silicate phase after exposure to syngas (27% after 96hrs). This phase was absent in the catalyst preheated in helium; however, XRD shows that the iron silicate was present after 96hrs.

The catalyst preheated in helium gave rise to ε-Fe₂2C after exposure to syngas (38% after 96hrs), while the catalyst preheated in CO+H₂ did not exhibit this phase.

Both catalysts contained magnetite, Fe_3O_4 and $\chi\text{-Fe}_5\text{C}_2$ in significant amounts. The silicate phase in the catalyst treated in $\text{CO}+\text{H}_2$ increased with TOS, while the $\epsilon\text{-Fe}_{2.2}\text{C}$ phase in the catalyst preheated in helium is relatively stable once it is formed.

The fractional amount of $\chi\text{-Fe}_5\text{C}_2$ formed in the catalyst preheated in $\text{CO}+\text{H}_2$ is about twice as much as that formed in the catalyst preheated in helium.

The iron phases formed and their distribution are very sensitive to the preheat conditions that precede pretreatment.

A UCI catalyst of nominal composition $100\text{Fe}/4.3\text{Cu}/8.6\text{K}/7.9\text{SiO}_2$ subjected to pretreatment in $\text{CO}+\text{H}_2$, ($\text{H}_2/\text{CO}=0.7$) at 11.4 atm for 12 hrs at 280°C , when exposed to FT synthesis in $\text{H}_2/\text{CO}=0.7$ at 20.7 atm and 265°C for 500 hrs, gave rise to 72% of $\epsilon\text{-Fe}_{2.2}\text{C}$, 5% of $\chi\text{-Fe}_5\text{C}_2$, 5% of Fe_3O_4 , and 18% of superparamagnetic oxide [6].

The potassium promoted catalyst of composition $65\text{Fe}/0.6\text{Cu}/0.29\text{K}$ when exposed to a gas flow of 1:1 CO/H_2 at 260°C , at 14.6 atm for 24 hrs was converted mainly to $\epsilon\text{-Fe}_{2.2}\text{C}$ and a small amount of Fe_3O_4 . However, after 503 hrs of synthesis, the oxide disappears and the catalyst is 100% $\epsilon\text{-Fe}_{2.2}\text{C}$ phase [7].

Both silica supported and unsupported catalysts, which were pretreated in syngas ($\text{H}_2/\text{CO}=0.7$ or 1.0) when subjected to FT synthesis give rise to the formation of $\epsilon\text{-Fe}_{2.2}\text{C}$ in significant quantities apart from magnetite and smaller amounts of $\chi\text{-Fe}_5\text{C}_2$.

CONCLUSIONS

- * The present measurements indicate that preheating of the catalyst in ($\text{CO}+\text{H}_2$) during heating from room temperature to 280°C prior to pretreatment inhibits the formation of $\epsilon\text{-Fe}_{2.2}\text{C}$ while heating the catalyst in the inert gas He did not prevent formation of the $\epsilon\text{-Fe}_{2.2}\text{C}$.
- * It is observed further that formation of approximately twice the quantity of $\chi\text{-Fe}_5\text{C}_2$ and iron silicate is favored as compared to preheating in helium atmosphere.

RESULTS OF THE PRESENT MÖSSBAUER SPECTROSCOPY STUDIES

- (1) REDUCTION OF IRON FT CATALYSTS IN CO LEADS TO χ -CARBIDE, (Fe_3C_2) FORMATION
- (2) CO-REDUCED CATALYSTS UNDER FT SYNTHESIS FORM MAGNETITE, Fe_3O_4
- (3) ($\text{CO}+\text{H}_2$) REDUCED CATALYSTS UNDER FT SYNTHESIS FORM ϵ -CARBIDE, ($\text{Fe}_{2.2}\text{C}$)
- (4) MAGNETITE, Fe_3O_4 , IS INVOLVED IN THE WATER GAS SHIFT REACTION
- (5) CATION DEFICIENCY OF MAGNETITE INCREASES WATER GAS SHIFT ACTIVITY.
- (6) PRE-HEAT CONDITIONS PRIOR TO PRETREATMENT INFLUENCE THE IRON PHASE DISTRIBUTION
- (7) FT ACTIVITY AND χ -CARBIDE (Fe_3C_2) DECREASE WITH AN INCREASE OF SiO_2 CONTENT.

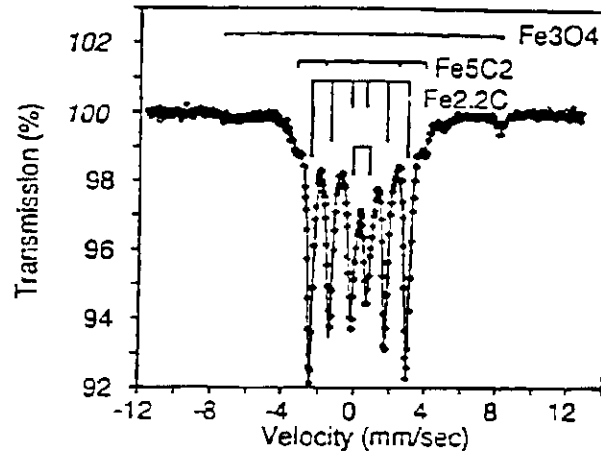
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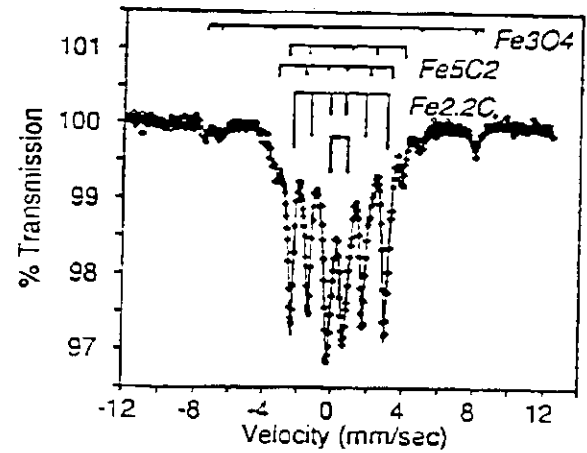
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(a) Mossbauer spectrum of a used UCI catalyst in an autoclave for 500 h



(b) Mossbauer spectrum of a used catalyst in LaPorte F-T run for 450 h

Fig.1 Comparison of Mossbauer spectra of a used catalyst in
(a) an autoclave F-T run (b) LaPorte F-T run

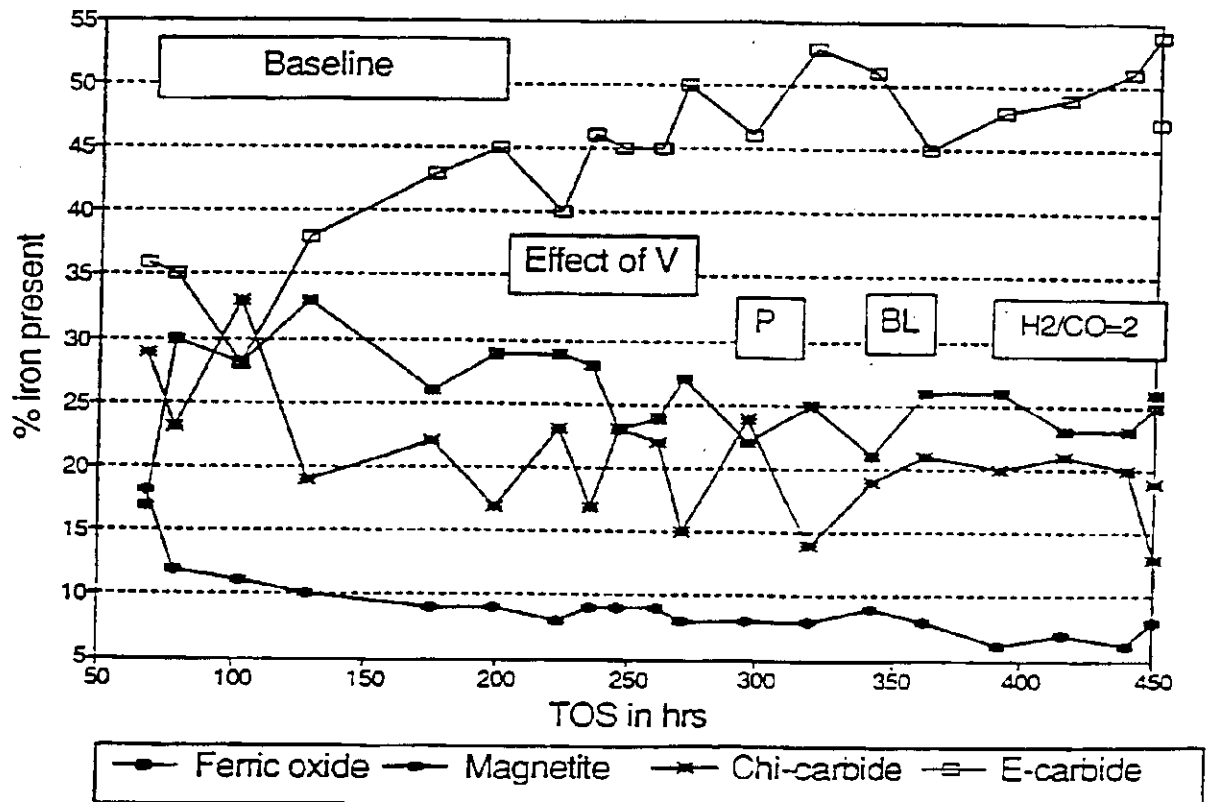


Fig. 2 Variation of iron phases in the catalysts with TOS

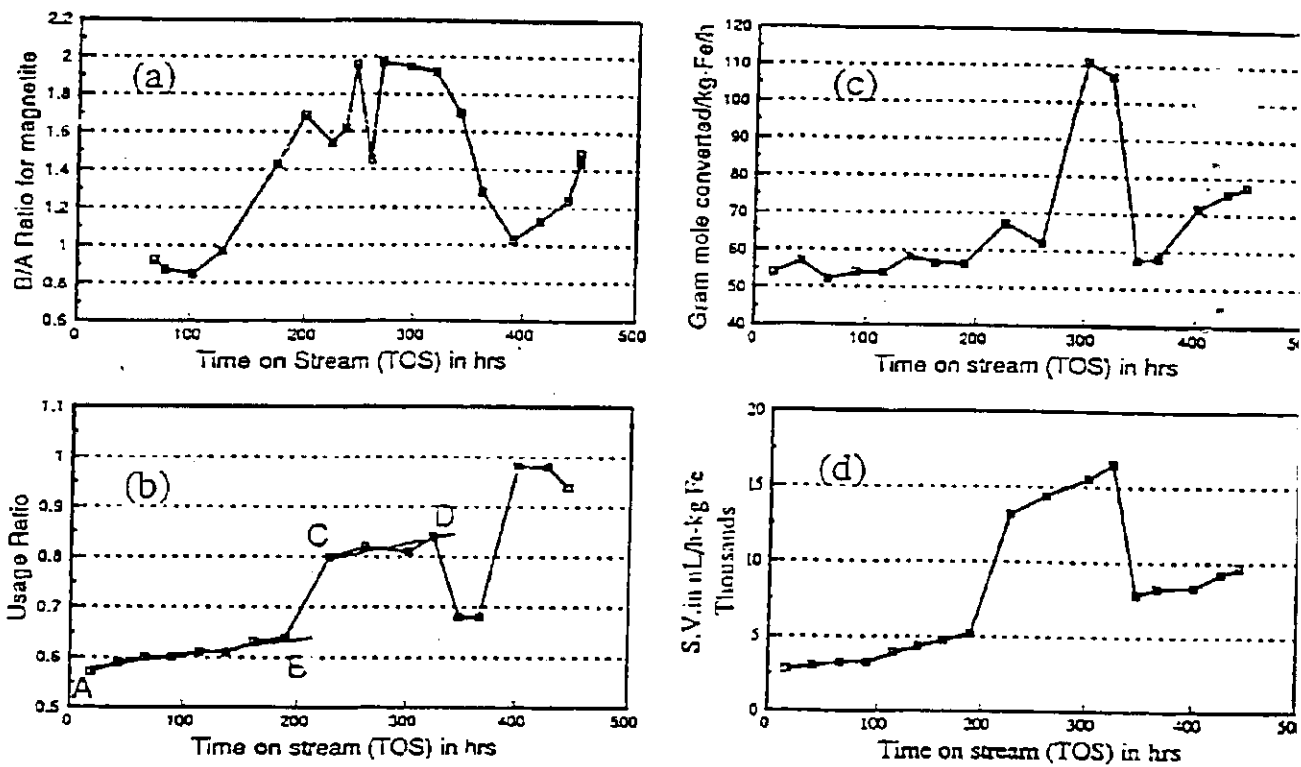


Fig.3 Variation of (a) B/A ratio, (b) usage ratio, (c) CO conversion rate, and (d) space velocity as a function of time on stream

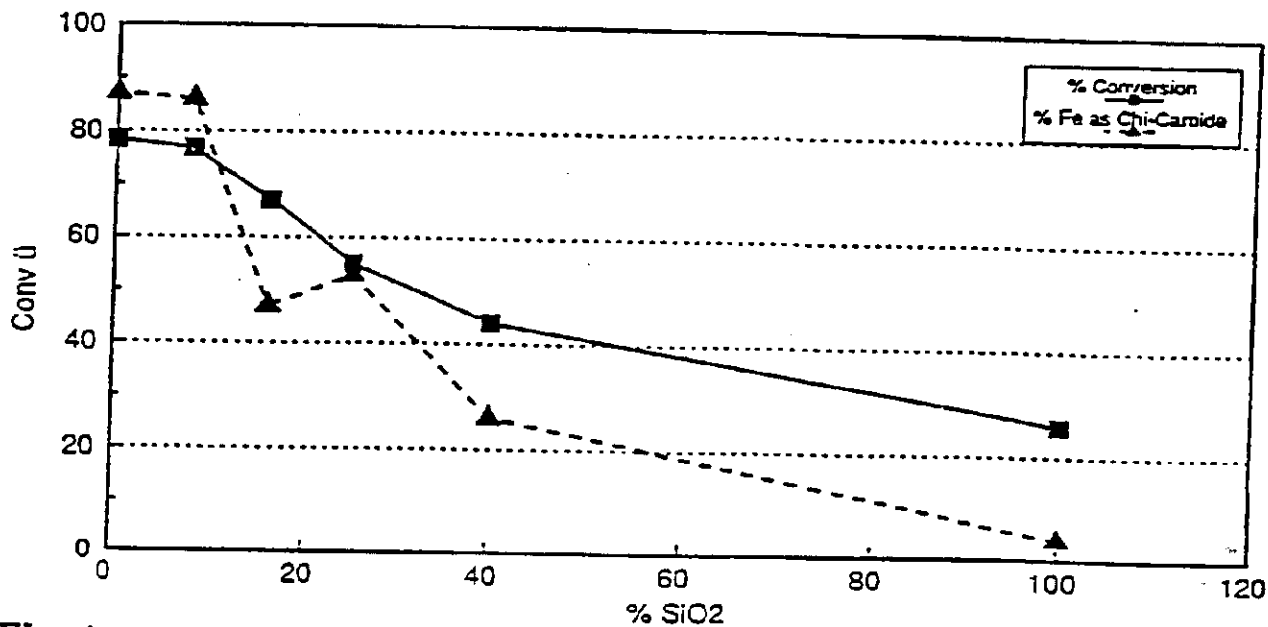


Fig. 4 Variation of (a) Chi-carbide formed on reduction and (b) (CO+H₂) converted at 10-50hrs of TOS with silica content

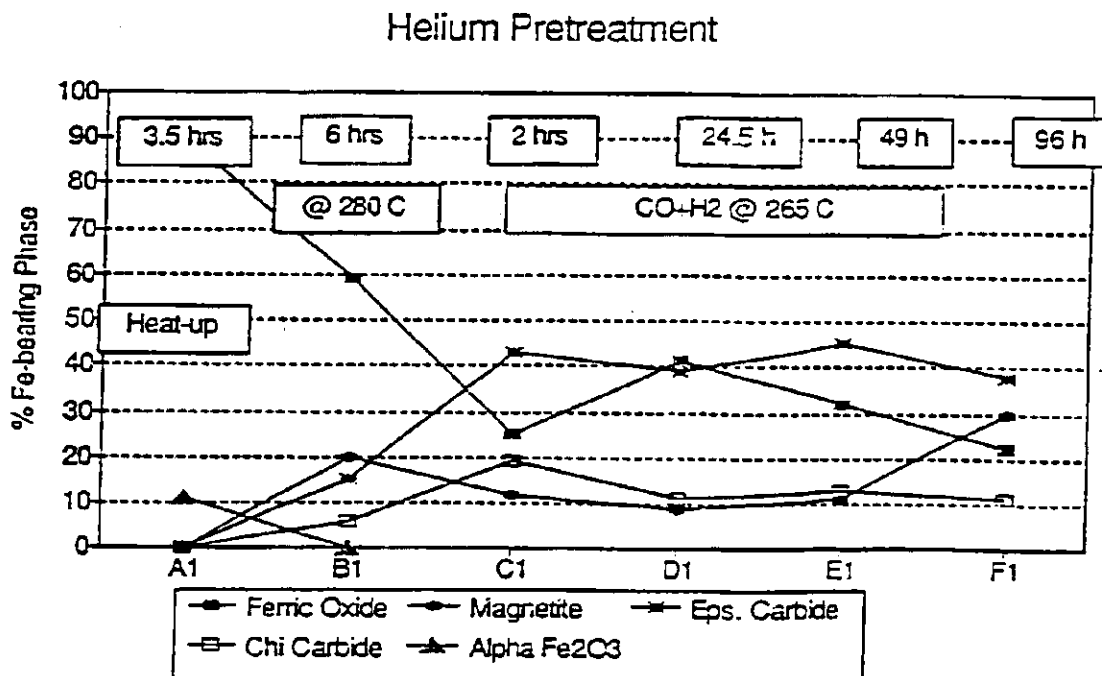
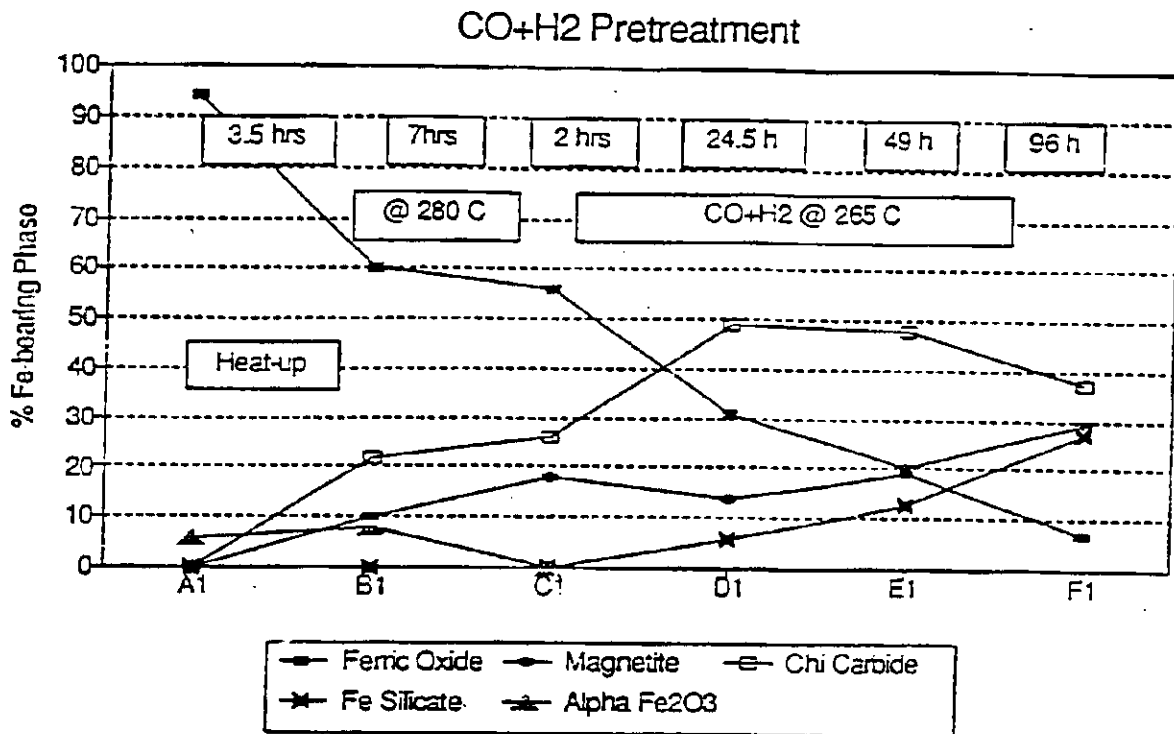


Fig. 5 Iron phase distribution in different catalysts and its variation with TOS