CHARACTERIZATION OF IRON-BASED CATALYSTS FOR DIRECT AND INDIRECT COAL LIQUEFACTION

K.R.P.M. Rao, B. Ganguly, M.M. Taghiei, F.E. Huggins, N. Shah,

J. Zhao and G.P. Huffman

Consortium for Fossil Fuel Liquefaction Science,
Institute of Mining and Minerals Research,
University of Kentucky, Lexington, KY 40506-01

The activity and selectivity of catalytic conversion of coal into liquid products by either direct or indirect liquefaction processes may be better understood if the catalysts used in the processes are well characterized in terms of their phases and particle size distribution. In the case of iron-based catalysts, Mössbauer and EXAFS experimental techniques can provide much valuable information for characterization of the catalysts. We have carried out both Mössbauer and EXAFS characterization of some iron-based catalysts used in direct liquefaction of coal as well as in Fischer-Tropsch (F-T) synthesis. The present presentation gives preliminary results on some of the F-T and DCL catalysts studied.

BASIC PRINCIPLE OF MöSSBAUER SPECTROSCOPY

The basic principle of Mössbauer spectroscopy lies in the observation of nuclear resonance absorption / emission of gamma rays in certain nuclei like Fe, Sn, some rare-earths, etc. embedded in any solid matrix . The above phenomenon enables one to experimentally measure various nuclear transitions. It is well known that the nuclear transitions are in turn governed by the nature of the nucleus and its surroundings. The major three factors which affect the nuclear transition are (1) the charge density at the nucleus which is related to the valency of the atom, (2) the electric field gradient at the nucleus which in turn is dependent on the symmetry at the nucleus and (3) the presence of magnetic field at the nucleus which is in turn related to the magnetic nature of the atom.

An iron atom in any given material has a finger-print in terms of the charge density, electric field gradient and the magnetic field at the nucleus and hence a Mössbauer measurement would enable one to identify the various iron phases present in any given substance. It is also possible to have relative quantitative estimates of the different phases present.

The magnetic moments associated with small particles of the order of a few tens of Angstroms are subjected to changes of their direction and this in turn leads to characteristic 'Relaxation Spectra ' of the particles. In the case of iron particles, study of these relaxation spectra enables one to get valuable information regarding the particle size distribution in the samples.

EXTENDED X-RAY ABSORPTION FINE STRUCTURE STUDIES (EXAFS):-

The EXAFS is now a well established technique to idenentify the nature of the surrounding atoms around a probe atom and to determine the distance of the neighboring shells and their coordination numbers. In the case of iron it is possible to study the radial distribution and the coordination numbers up to three or four shells. The EXAFS measurements supplement the Mössbauer results by providing the additional information noted above. With this in view we have carried out EXAFS measurements on some F-T and DCL catalysts.

We have studied the following samples:

(A) F-T catalysts:-

(1) 100 Fe/5 Cu/4.2 K/8 SiO_2 unused

(2) 100 Fe/5 Cu/4.2 used FBR

(3) 100 Fe/5 Cu/4.2 K/8 SiO_2 used FBR

(4) 100 Fe/5 Cu/4.2 K/16 SiO_2 used FBR

(5) 100 Fe/5 Cu/4.2 K/24 SiO_2 used FBR

(6) 100 Fe/5 Cu/4.2 K/8 SiO_2 slurry (reduced with H_2 at 220 K for 1 hr)

(7) 100 Fe/5 Cu/4.2 K/8 SiO_2 slurry (reduced on stream for 400 hrs)

(8) 100 Fe/5 Cu/4.2 K/24 SiO_2 magnetically separated

(9) 100 Fe/5 Cu/4.2 K/24 SiO_2 soxhlet extraction

(B) IRON BASED DIRECT COAL LIQUEFACTION (DCL) CATALYSTS:

(1) Fe_2O_3 on carbon black

(2) Fe_2O_3/SO_4

(3) Bl. Canyon + Fe_2O_3/SO_4

(4) Wyodak coal + $Fe(CO)_5$

(5) Ill # 6 coal + Fe_2O_3/SO_4

(6) Iron-Carbides

The iron-based catalysts were prepared by Dr.D.B.Bukur of Texas A & M University by continuous co-precipitation of Fe and Cu, followed by incorporation of SiO_2 from the solution, and impregnation of potassium. These catalysts were utilized in the Fischer-Tropsch studies carried out at Texas A & M University. Some of the DCL catalysts studied were supplied by

Dr.Irving Wender of University of Pittsburgh, Dr.Joseph Shabtai of University of Utah, Dr.P.C.Eklund of University of Kentucky and Dr.Malvina Farcasiu of DOE.

We have recorded Mössbauer spectra both at room temperature and for some samples at 12 K using a conventional Mössbauer spectrometer. The spectra were analyzed using a non-linear fitting program developed at CFFLS, University of Kentucky, Lexington.

EXAFS measurements were carried out at the NSLS facility of the Brookhaven Laboratory, Upton, N.Y. and the data were analyzed using the EXAPLT ant EXAFIT programs.

RESULTS :

THE SALIENT FEATURES OF THE ANALYSIS OF THE VARIOUS MöSSBAUER SPECTRA RECORDED ARE AS FOLLOWS:

(1) Unused calcined catalyst was found to consist of fine particles of α-FeOOH of about 62 Å or less in diameter. The Mössbauer spectra of the catalyst at 300 K and 12 K are shown in Fig.1 and Fig.2 respectively. The room temperature spectrum of the catalyst is very similar to the room temperature spectrum of Ruhr-Chemie catalyst supplied by UOP, (Fig. 3.)

(2) All the used catalysts obtained from fixed bed reactors were found to consist of magnetite in the range of 40 -80 %, lesser amounts of carbides and unreacted oxides.

(3) The samples obtained by magnetic extraction showed much more magnetite (Fig. 4) , as compared to the sample obtained by soxhlet extraction (Fig. 5).

(4) The slurry sample (Wax + catalysts) obtained after reduction with hydrogen at 220 C, 100 psig, 7500 (cc/min) for 1 hour contained fine particles of α-FeOOH (about 65 Å or less) The Mössbauer spectra of the catalyst at 300 k and 12 K are shown in the Fig.6 and Fig. 7. As compared to the above catalyst, the slurry sample obtained after 400 hrs. on stream contained essentially magnetite and carbides (Fig.8.)

(5) The support material of SiO_2 incorporated in the catalysts does not seem to exhibit any systematic correlation on the phases that were formed in the used catalysts. Two of the used catalysts from the fixed-bed reactor revealed the presence of siderite ($FeCO_3$) besides magnetite and some carbides. One used catalyst showed as much as 12 % of $FeCO_3$ (Fig. 9). EXAFS measurements on these samples are planned to confirm the presence of the siderite phase in these catalysts.

It is interesting to note that one of the used catalyst from a fixed bed-reactor containing 24 SiO_2 showed the presence of about 10% unreacted surface oxide. Low temperature measurements are underway to confirm this result.

The theoretical relaxation spectrum for Fe_2O_3 on carbon black at 300 K compared with the experimentally determined spectrum indicated the presence of a distribution of particles. The theoretical and experimental spectra are shown in the Fig. 10. These spectra indicated that 15% of the particles have particle sizes greater than about 85 Å and the remaining 85% of the particles have a particle size of less than 85 Å. Further detailed estimates of the particle distributions are in progress.

The Mössbauer spectra of two samples of sulfated iron DCL catalysts Fe_2O_3/SO_4 (sample 1) and Fe_2O_3/SO_4 (sample 2) are shown respectively in the Fig. 11a and Fig. 11b. The spectrum of sample 2 consists of large particles greater than about 100 Å while the spectrum of the sample 1 contains both small particles of less than about 65 Å and large particles of size about 100 Å. The same kind of catalyst may have different particle size distribution depending on how it is prepared.

Two of the Mössbauer spectra of Blind Canyon coal with Fe_2O_3/SO_4 catalysts after 5 minutes and 1 hour liquefaction are shown respectively in the Fig. 12 a and Fig.12 b. The spectrum of the 5 minutes run shows a mixture of magnetite and unreacted Fe_2O_3/SO_4 while that of the 1 hour run shows predominantly the presence of magnetite and relatively small amounts of the unreacted oxide.

The Mössbauer spectrum of the IOM-Ill # 6/Maya coal with Fe_2O_3/SO_4 and IOM-Wyodak/Maya coal with $FeCo_5$ are shown respectively in the Fig. 13 a and Fig.13 b. The IOM of Ill # 6 shows the presence of mostly pyrrhotite while that of Wyodak coal shows the presence of both pyrrhotite and some fine particles of some oxide/hydroxide.

The Mössbauer spectra of Fe carbides made by laser pyrolysis are shown in the Fig. 14. a and Fig.14 b The spectra reveal the presence of Fe-metal, cementite and not so commonly seen phase of iron-carbide, Fe_7C_3.

The size distributions for the various as-dispersed iron DCL catalysts have been determined from the Mössbauer relaxation spectra recorded and the theoretical estimates of the critical volumes of the catalysts at various temperatures. These size distributions are shown in the Fig.15

In-situ iron K-edge EXAFS measurements on sulfated Fe_2O_3 heated with hexahydropyrene up to 400 C were carried out. Both bulk and 30 Å samples of Fe_2O_3 were utilized in the experiments. The EXAFS spectra for the bulk Fe_2O_3 and 30 Å Fe_2O_3 are shown respectively in the Fig.16 and Fig.17. Both the spectra clearly show the growth of pyrrhotite as the temperature is increased.

EXAFS spectra of Ruhr-Chemie sample and that of the soxhlet extraction were recorded and both are seen to be very similar to each other confirming the results of Mössbauer measurements (Fig.18 a and Fig.18 b). In both the cases the ratio of nearest oxygen peak to the nearest iron peak is found to be larger as compared to that found in the case of bulk α-FeOOH as can be expected for fine particles.

Conclusions:-

Mössbauer and EXAFS measurements are very useful in characterizing the catalysts used in the liquefaction of coals. The Mössbauer spectroscopy provides information regarding the different phases present and also the particle size distribution in the catalysts . The EXAFS technique allows one to follow the in-situ chemical reactions, besides identifying and giving the radial distribution of neighboring atoms and their coordination numbers.

Acknowledgements:

Thanks are due to:

-- Dr.D.B.Bukur, Texas A & M University, College Station
-- Dr.Malvina Farcasiu, PETC, DOE, Pittsburgh
-- DR.Irving Wender, University of Pittsburgh, Pittsburgh
-- Dr.P.C.Eklund, University of Kentucky, Lexington
-- Dr.Joseph Shabtai, University of Utah, Utah

for supplying us with the samples.

&

-- DOE, for support of synchrotron facilities at the Brookhaven National Laboratory.

The work is done under the DOE Contract Numbers:

DE-AC22-90PC90039 & DE-FC22-90-PC90029

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Width mm/s	%Fe
∝-FeOOH		0.35	0.59	0.43	62
∝-FeOOH		0.34	1.03	0.46	38

Mössbauer run MK0750 on sample 462 at RT
75a

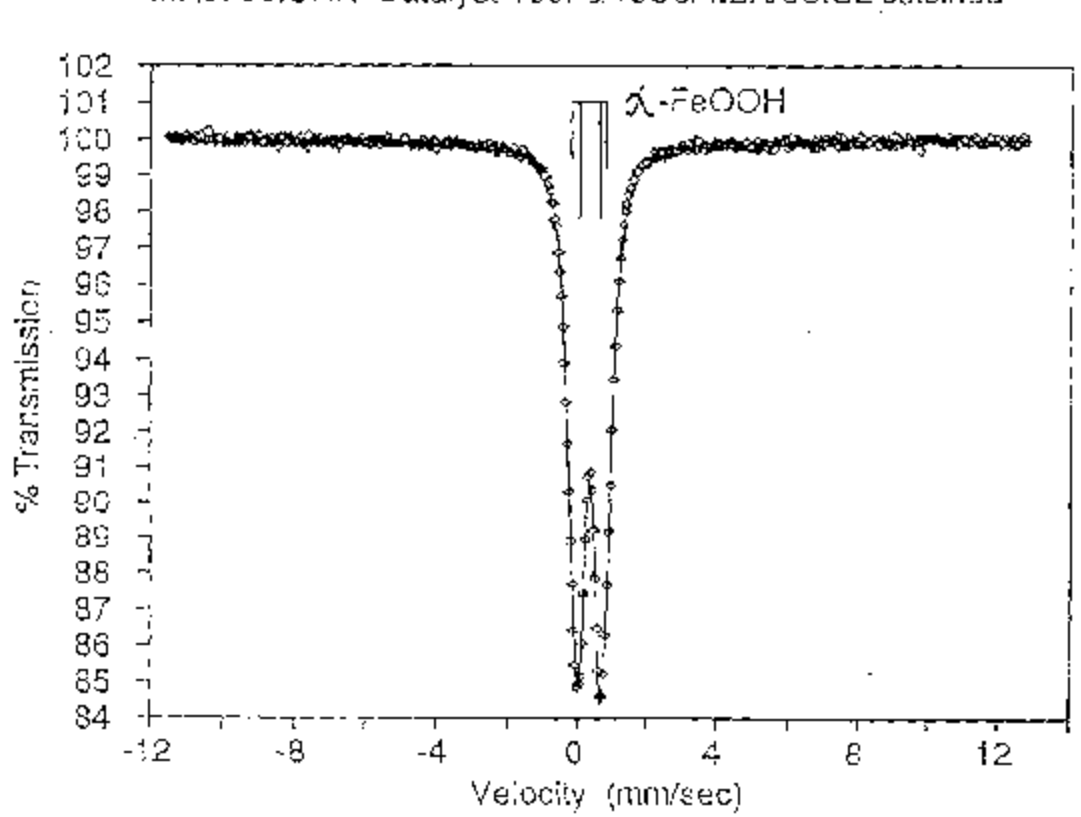


Fig. 1 **Mössbauer spectrum of unused calcined catalyst 100Fe/5Cu/4.2K/8SiO$_2$ at 300 K**

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
α -FeOOH	504	0.49	0.003	0.61	31
α -FeOOH	480	0.48	-0.01	0.79	55
α -FeOOH	441	0.37	-0.06	0.82	13
Spm-Oxide		0.88	1.18	0.27	1

Mössbauer run MK0873 on sample 462 at 12 K

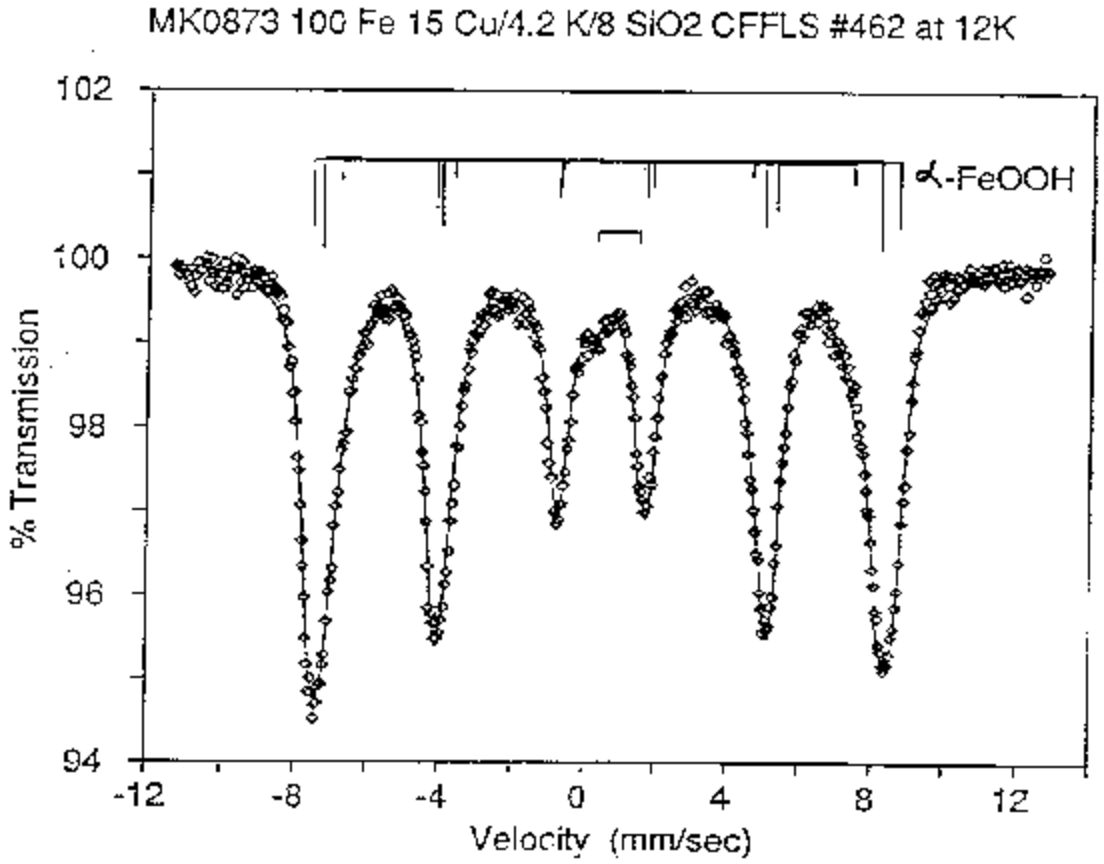


Fig. 2 Mössbauer spectrum of unused calcined catalyst $100Fe/5Cu/4.2K/8SiO_2$ at 12 K

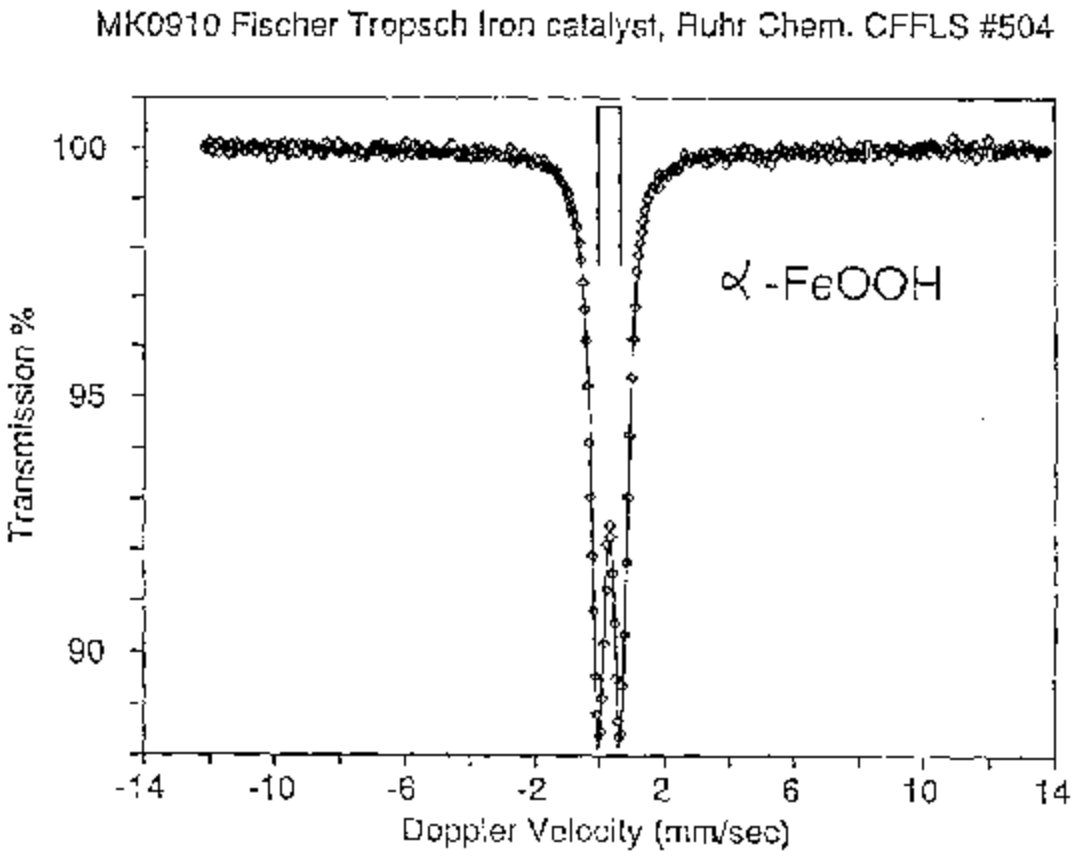


Fig. 3 **Mössbauer spectrum of unused F-T iron Ruhr-Chemie catalyst at 300 K**

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Magnetite-A site	482	0.31	0.00	0.43	25
Magnetite-B site	455	0.65	0.00	0.56	35
Magnetite-sub	422	0.68	0.00	0.54	8
Carbide	201	0.34	0.00	0.81	5
Spm-Oxide		0.37	0.93	0.63	27

Mössbauer run MK0877 on sample 501 at 300 K

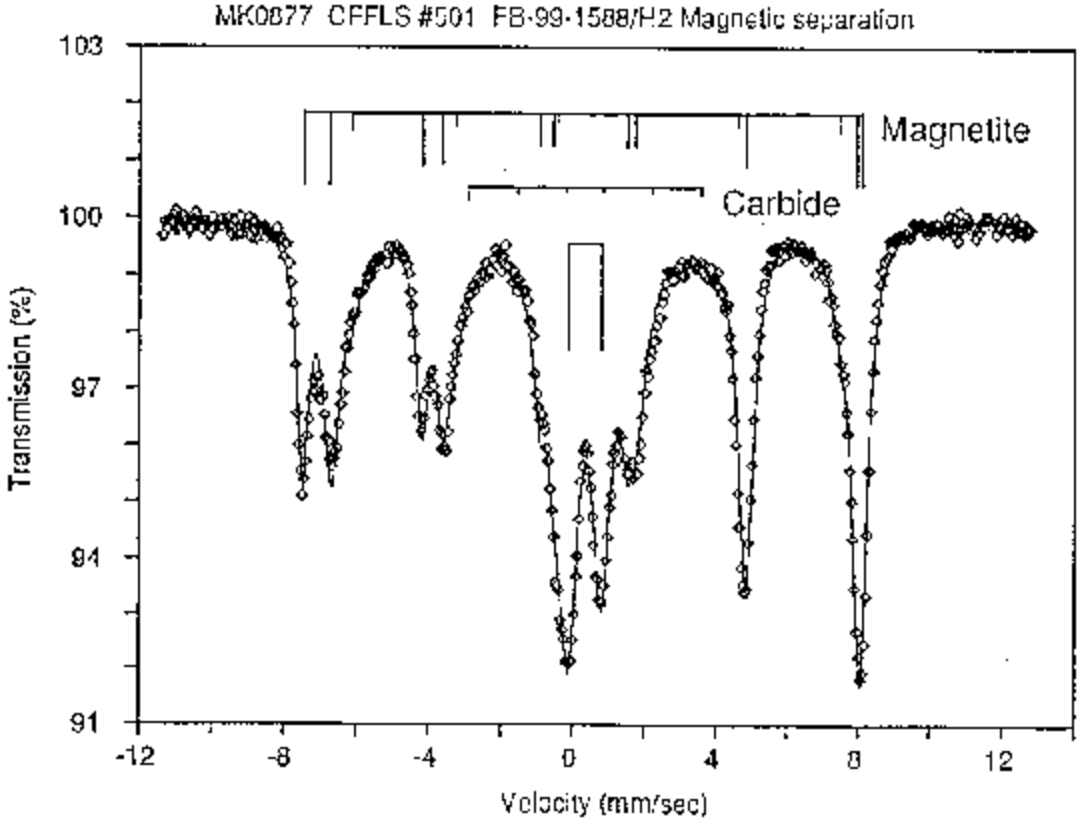


Fig. 4 **Mössbauer spectrum of a magnetically separated catalyst: 100Fe/5Cu/4.2K/25SiO_2 at 300 K**

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm-Oxide		0.37	0.71	0.56	86
Magnetite	481	0.26	0.00	0.63	5
Magnetite	461	0.73	0.00	0.63	3
Carbide	177	0.24	0.00	0.63	5

Mössbauer run MK0884 on sample 502 at 300 K

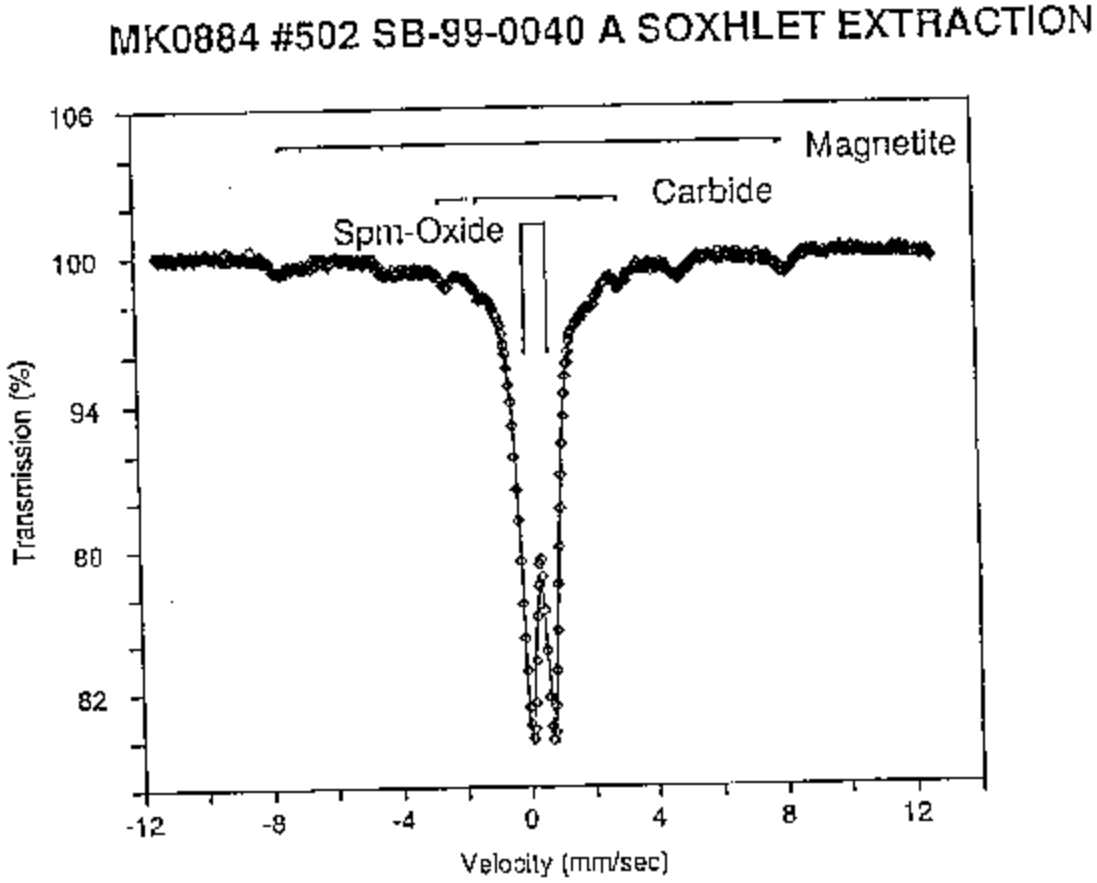


Fig. 5 Mössbauer spectrum of a catalyst: 100Fe/5Cu/4.2K/25SiO_2 obtained by soxhlet extraction.

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Magnetite A-site	474	0.34	0.00	0.41	5
Magnetite B-site	430	0.71	0.00	1.24	18
α-FeOOH		0.35	0.82	0.62	77

Mössbauer run MK0753 on sample 463 at RT

Spm-superparamagnetic

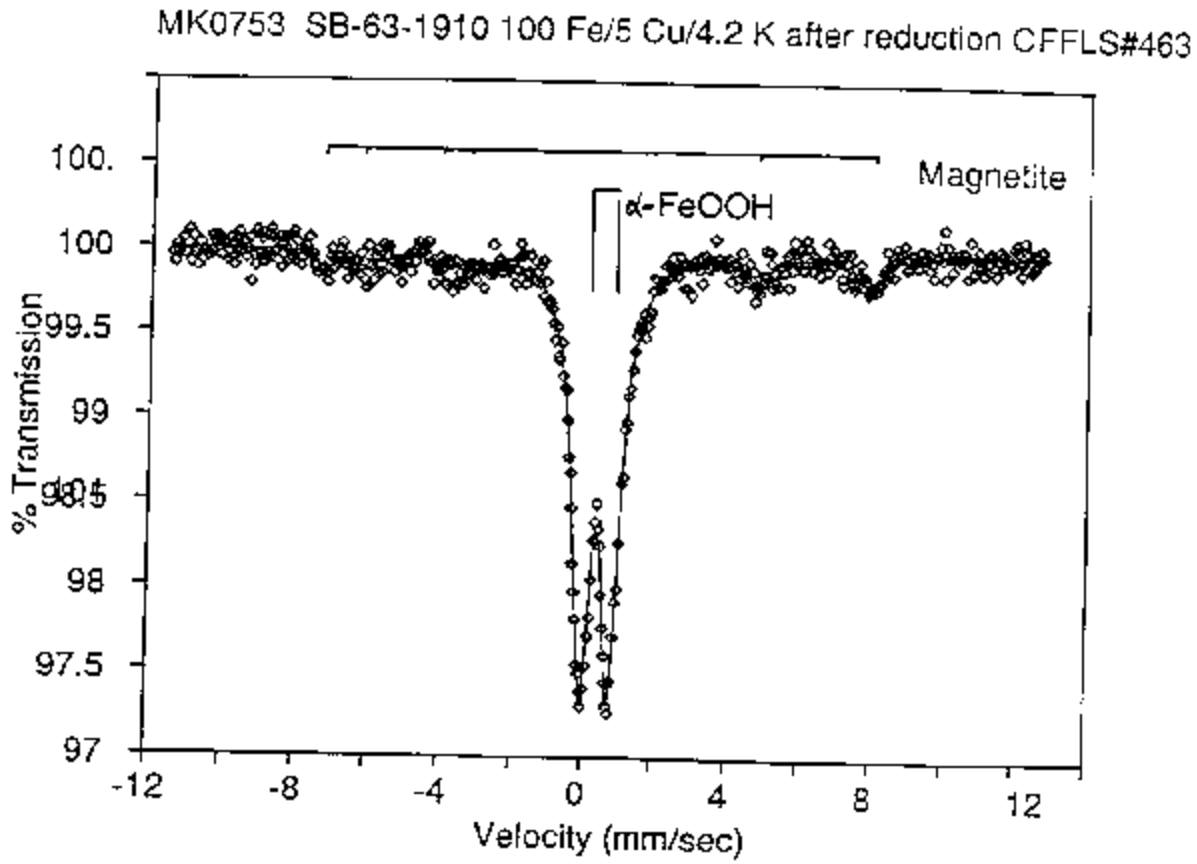


Fig. 6 **Mössbauer spectrum of a catalyst: 100Fe/5Cu/4.2K/8SiO$_2$, a slurry sample after reduction with hydrogen at 220 C, 100 psig, 7500 (cc/min) for 1 h-2.2 g. The spectrum was recorded at 300 K.**

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Width mm/s	%Fe
∝-FeOOH	504	0.47	-0.05	0.79	59*
∝-FeOOH	477	0.32	0.07	0.79	23*
∝-FeOOH	452	0.58	-0.19	0.79	12*
Spm-Oxide/Hydroxide		0.16	0.97	0.61	6

Mössbauer run MK0759 on sample 463 at 12 K
*∝-FeOOH includes 23 % of Fe as magnetite (see RT spectrum UK0006)

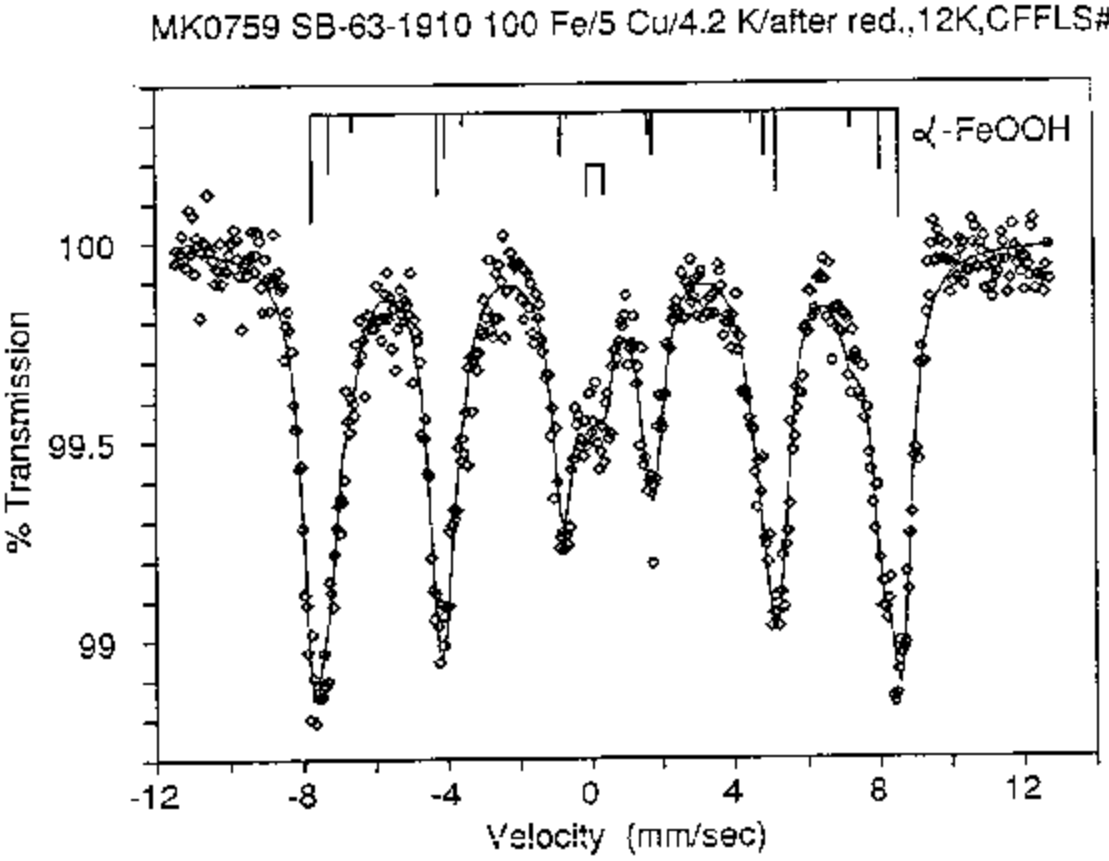


Fig. 7 **Mössbauer spectrum of a catalyst: 100Fe/5Cu/4.2K/8SiO$_2$ a slurry sample after reduction with hydrogen at 220 C, 100 psig, 7500 (cc/min) for 1 h-2.2 g. The spectrum was recorded at 12 K.**

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Magnetite A-site	480	0.29	0.00	0.41	16
Magnetite B-site	453	0.64	0.00	0.62	27
Magnetite-sub.	409	0.72	0.00	1.03	12
ε'-Carbide	170	0.24	0.03	0.48	28
Spm-Oxides		0.36	0.79	0.79	16

Mössbauer run MK0754 on sample 464 at RT
Spm-Superparamagnetic

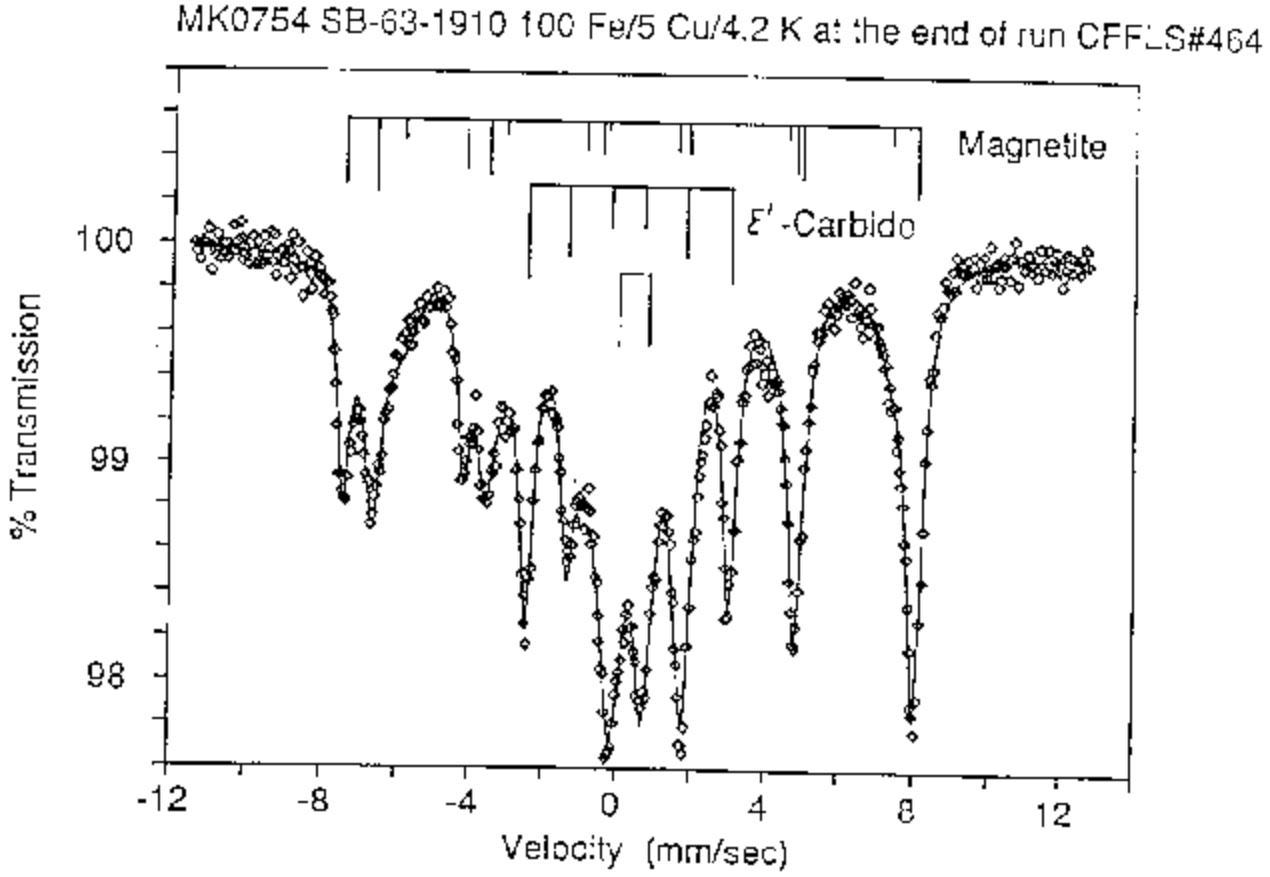


Fig. 8 **Mössbauer spectrum of used calcined catalyst: 100Fe/5Cu/4.2K/ at the end of the run.**

	Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Component 1	Magnetite A-site	490	0.29	0.00	0.32	25
Component 2	Magnetite B-site	459	0.68	0.00	0.37	44
Component 3	X-carbide	222	0.31	-0.04	0.45	7
Component 4	X-carbide	181	0.21	0.00	0.41	6
Component 5	FeCO3 (siderite)		1.23	1.77	0.32	12
Component 6	Spin Oxide		0.37	0.86	0.72	5

Mössbauer run MK0805 on sample 486 at RT. Spm - superparamagnetic

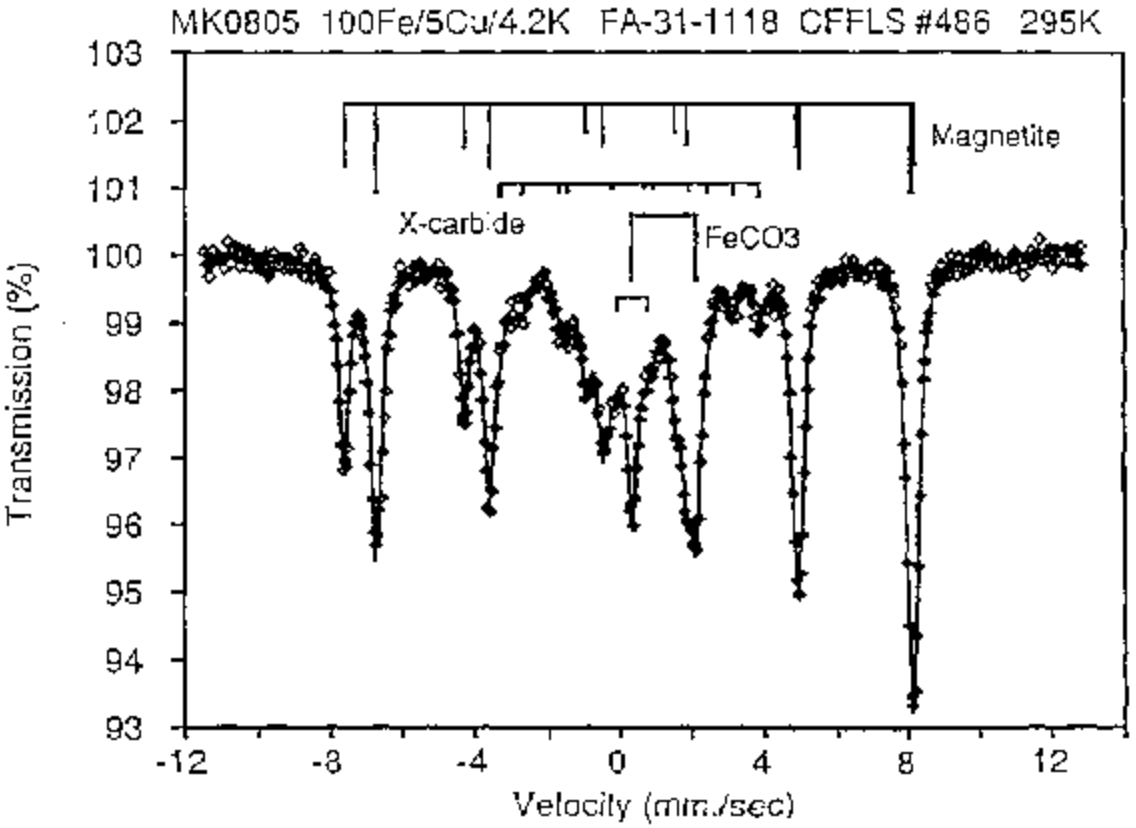
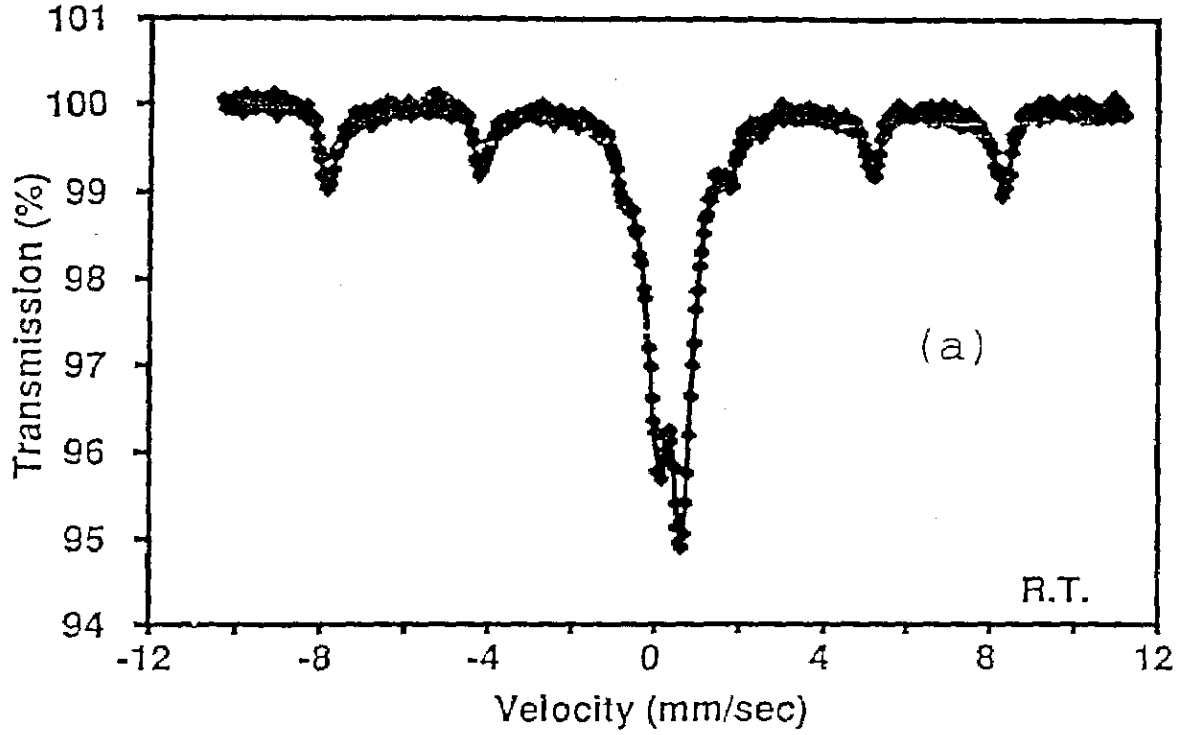


Fig. 9 **Mössbauer spectrum of used catalyst: 100Fe/5Cu/4.2K revealing the presence of siderite, $FeCO_3$**



Simulated spectrum of Fe2O3 on Carbon black

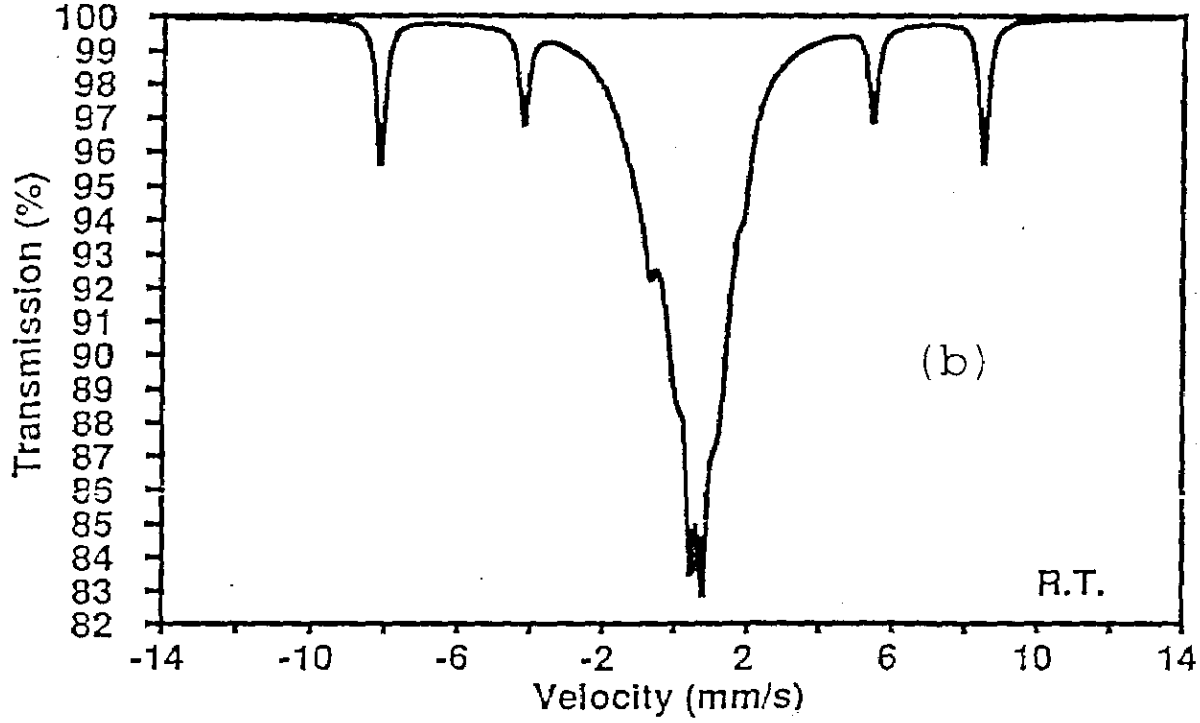
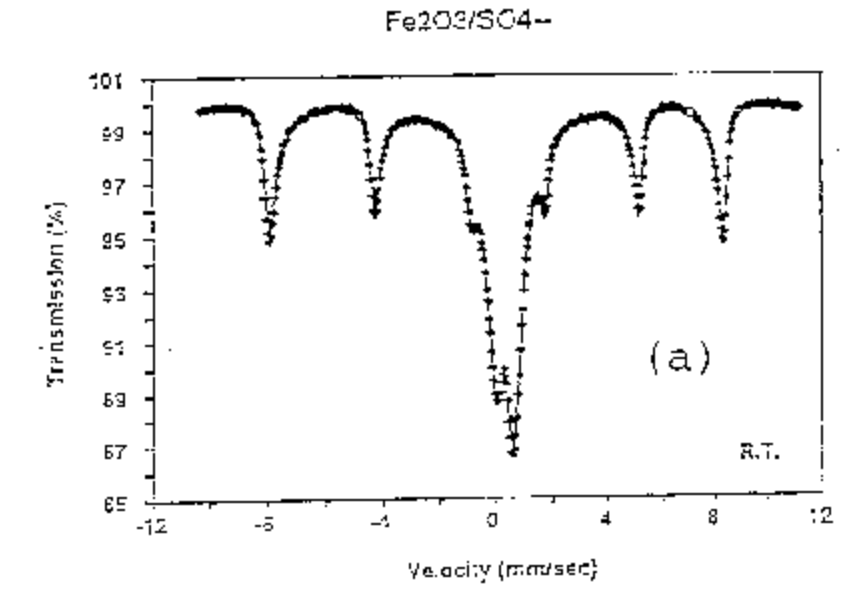


Fig. 10(a) Mössbauer spectrum of Fe_2O_3 on carbon black at 300 K
(b) Theoretically simulated relaxation spectrum



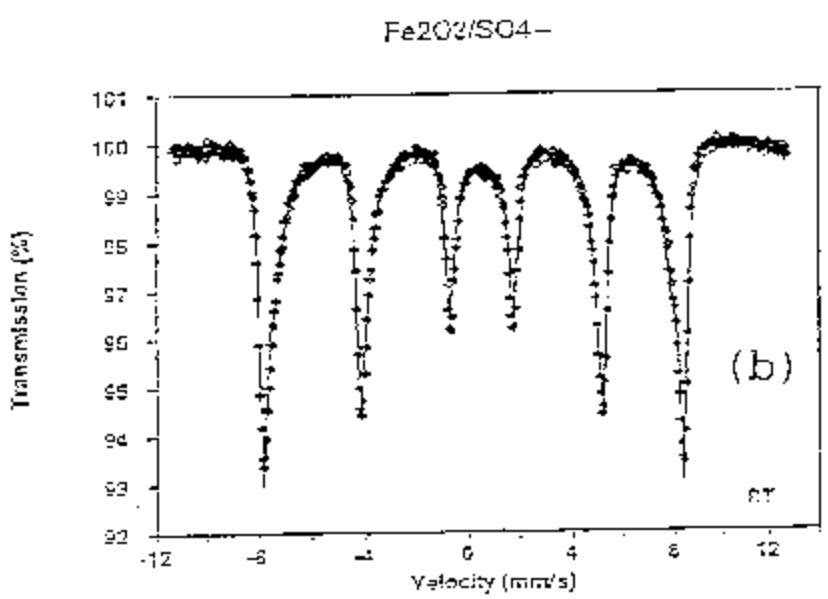
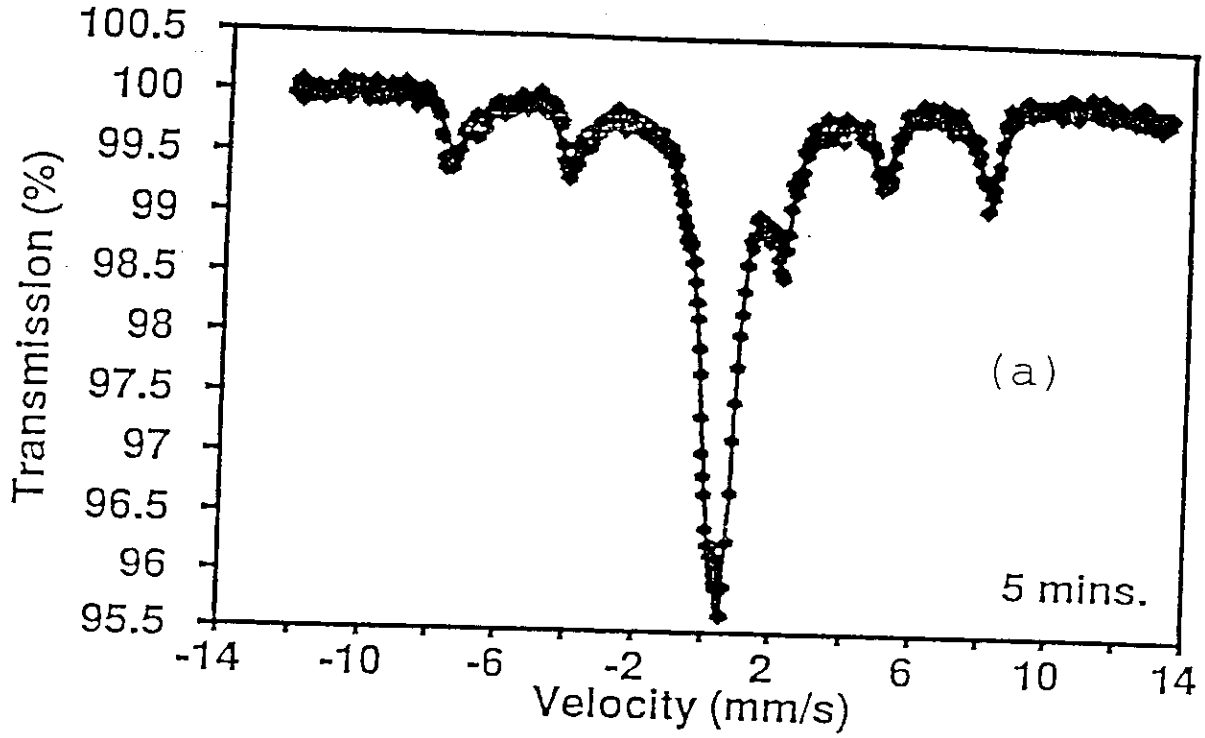


Fig. 11(a) Mössbauer spectrum of Fe_2O_3/SO_4 : sample 1
(b) Mössbauer spectrum of Fe_2O_3/SO_4 : sample 2



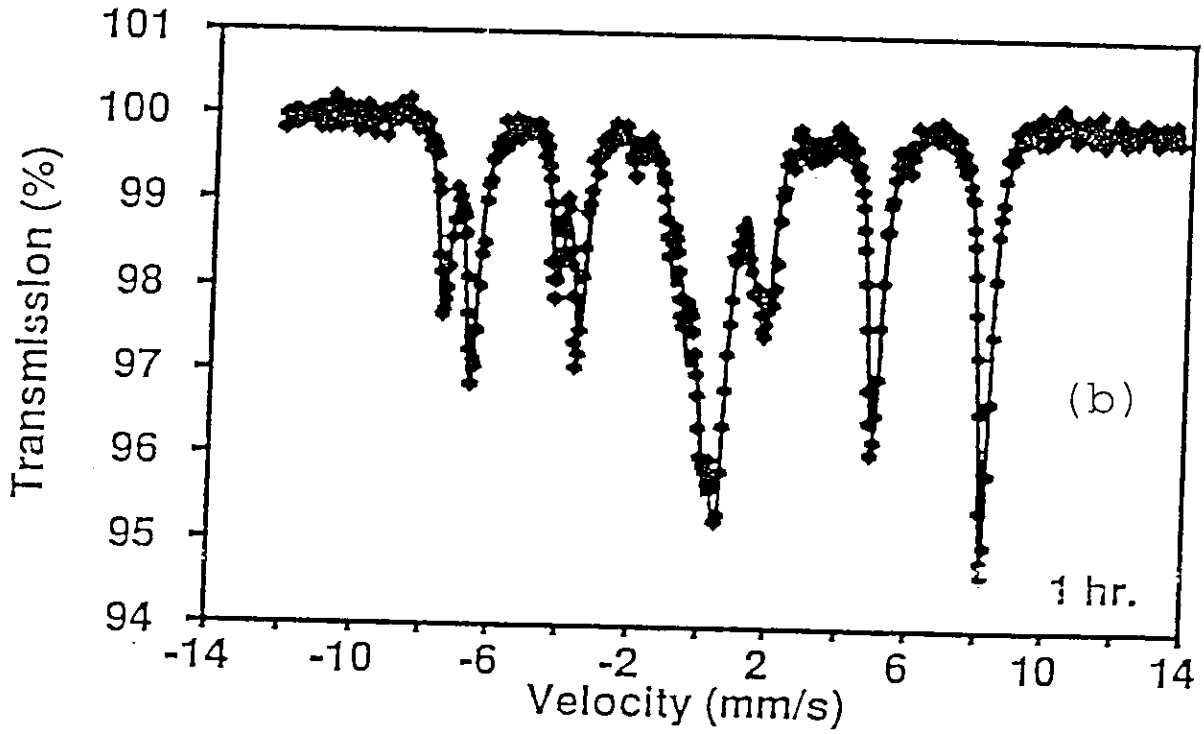
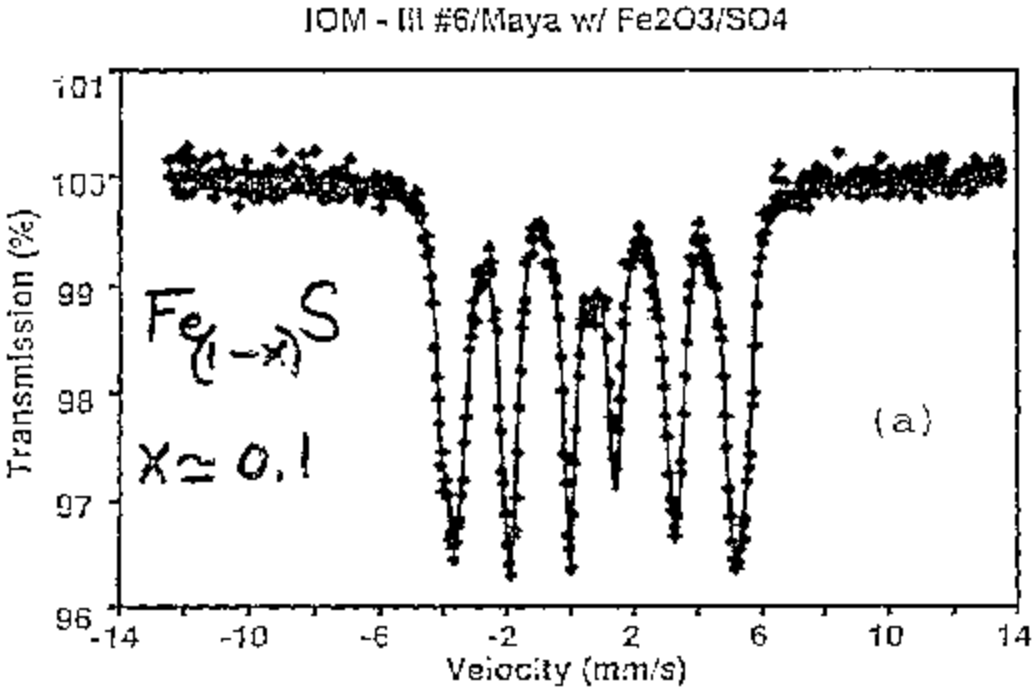


Fig. 12(a) Mössbauer spectrum of Blind canyon coal mixed with Fe_2O_3/SO_4 - after 5 mins. of liquefaction run

(b) Mössbauer spectrum of Blind canyon coal mixed with Fe_2O_3/SO_4 - after 1 hour of liquefaction run



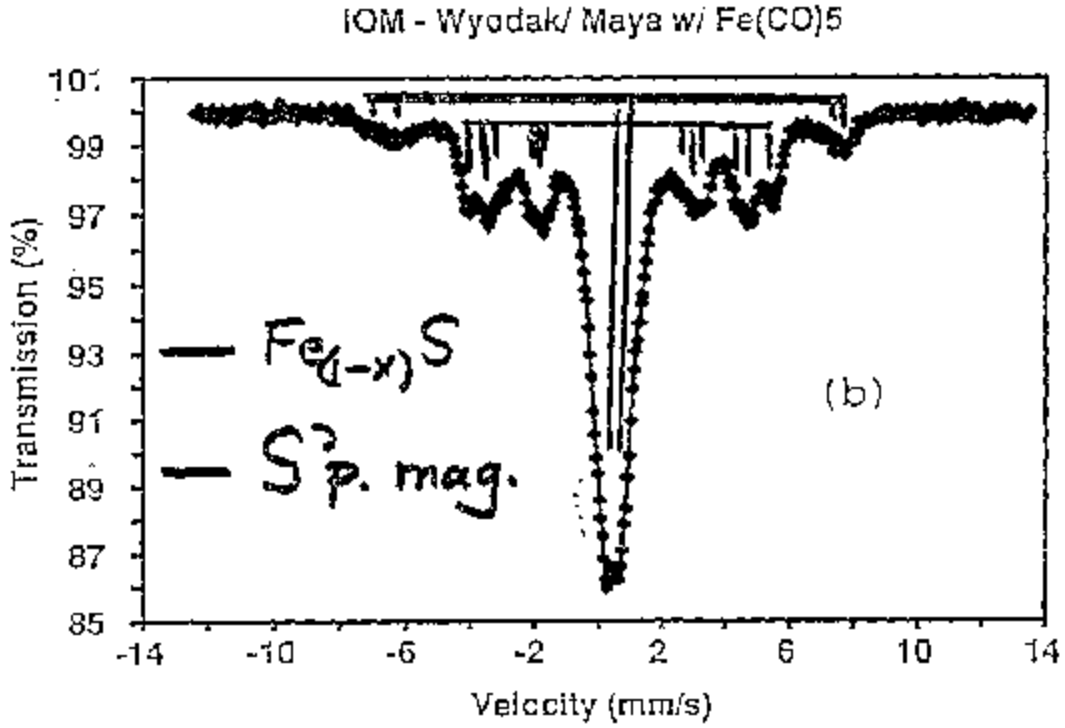
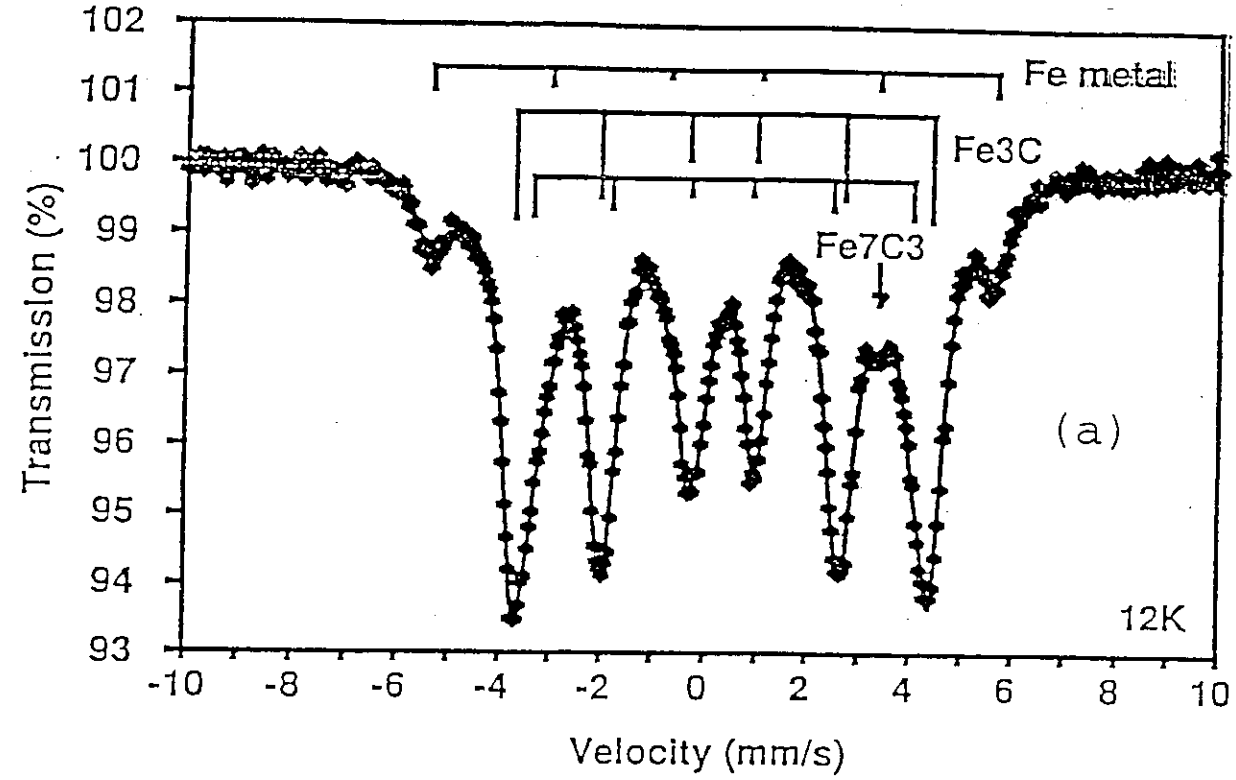


Fig. 13(a) Mössbauer spectrum of IOM of ILL # 6/Maya/w Fe_2O_3/SO_4 (sample 1)

(b) Mössbauer spectrum of IOM of ILL # 6/Maya/w Fe_2O_3/SO_4 (sample 2)



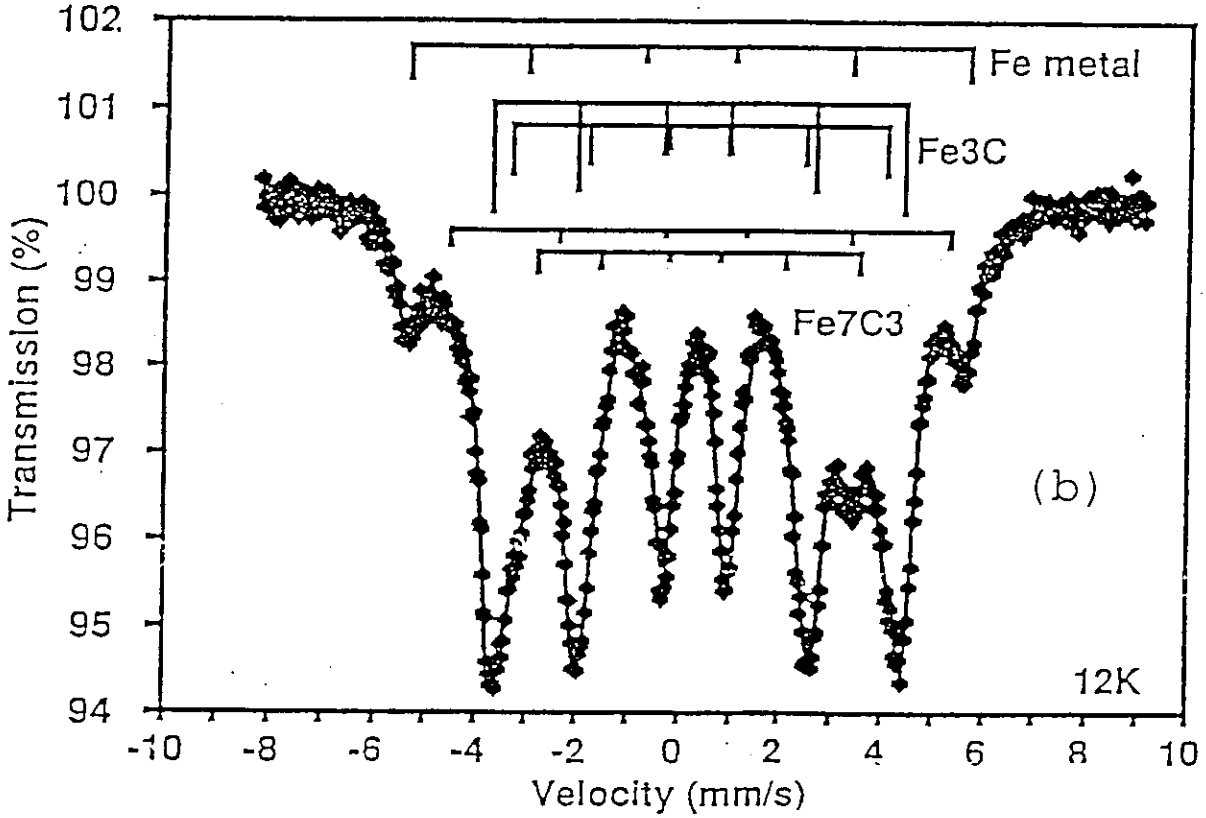


Fig. 14(a) Mössbauer spectrum of Fe carbide made from laser pyrolysis (sample 1)

(b) Mössbauer spectrum of Fe carbide made from laser pyrolysis (sample 2)

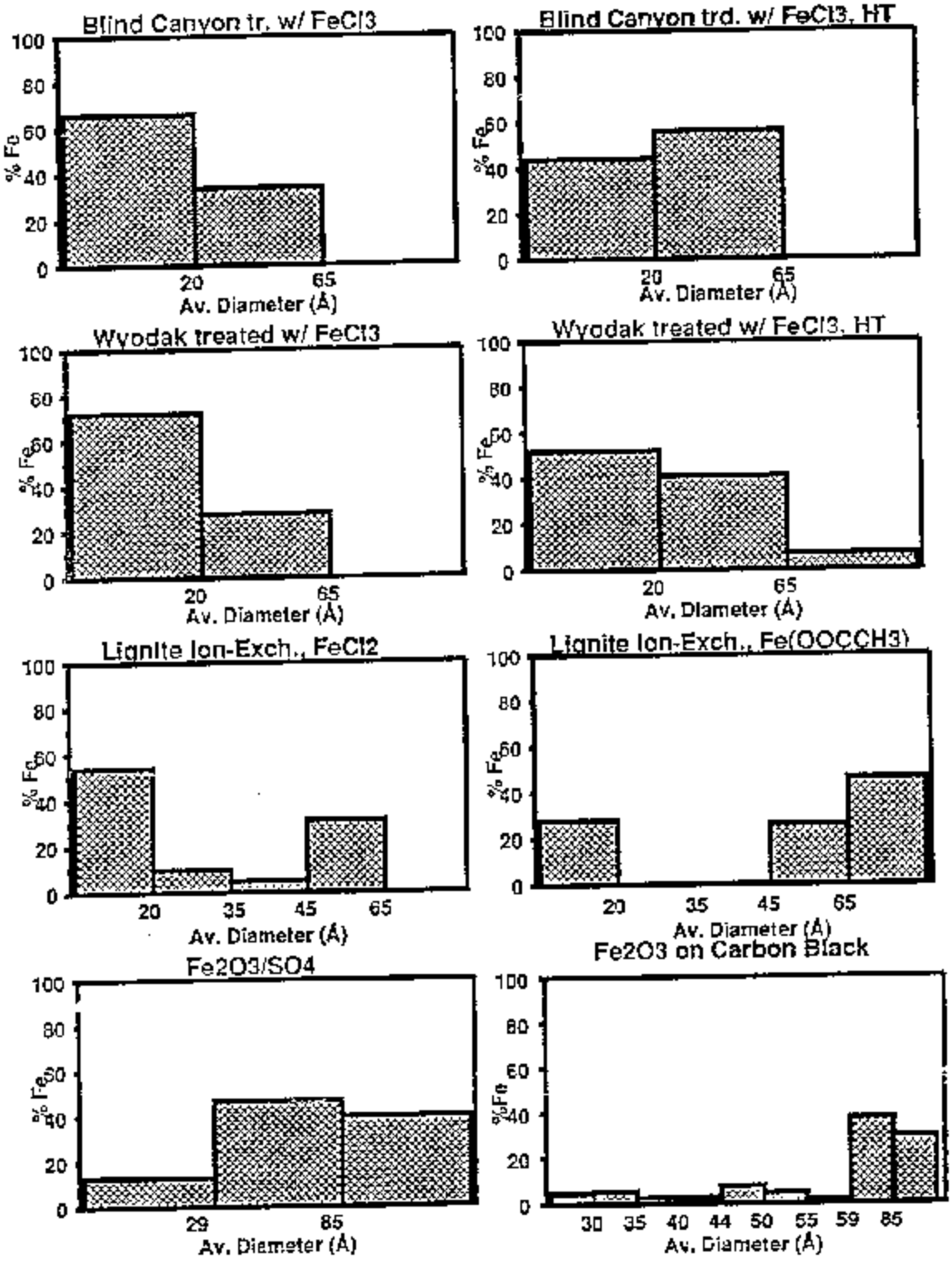


Fig. 15 The size distribution for various as-dispersed iron DCL catalysts derived from Mössbauer data

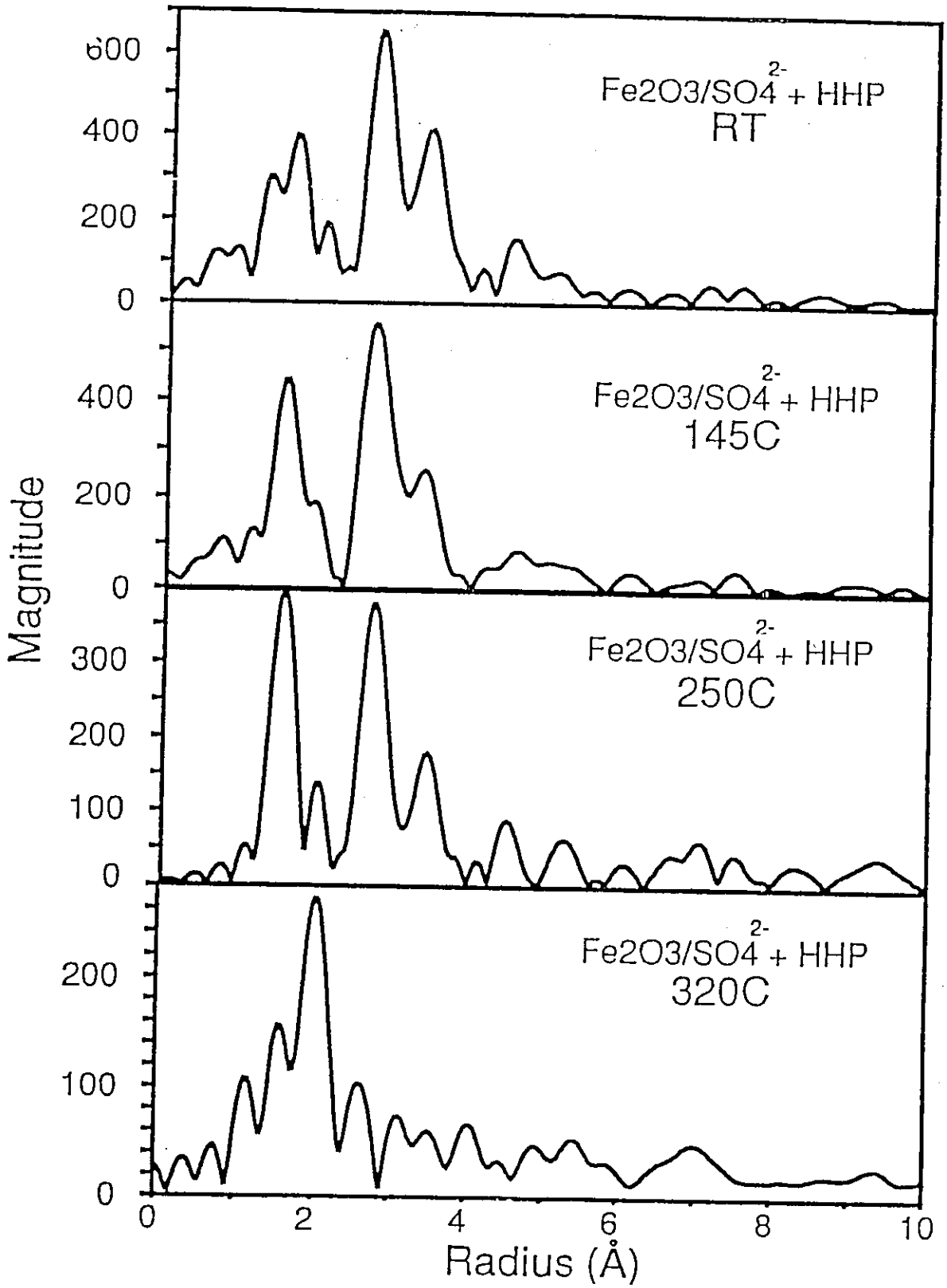


Fig. 16 **In situ radial distribution functions (RDFs) of Fe_2O_3/SO_4 catalyst mixed with hexahydropyrene at indicated temperatures**

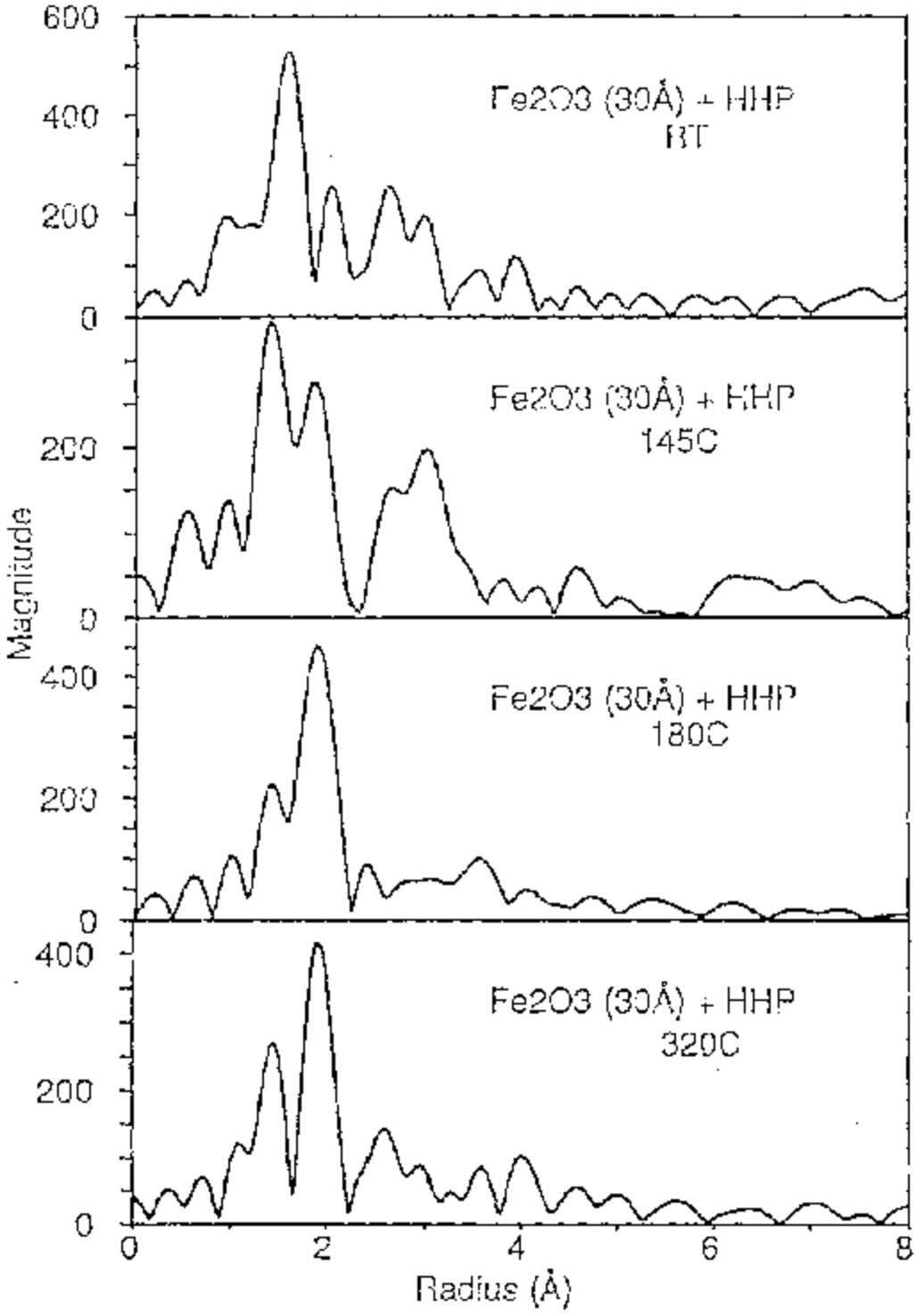


Fig. 17 **In situ radial distribution functions (RDFs) of Fe_2O_3(30 Å) from United Catalyst mixed with hexahydropyrene at *indicated temperatures***

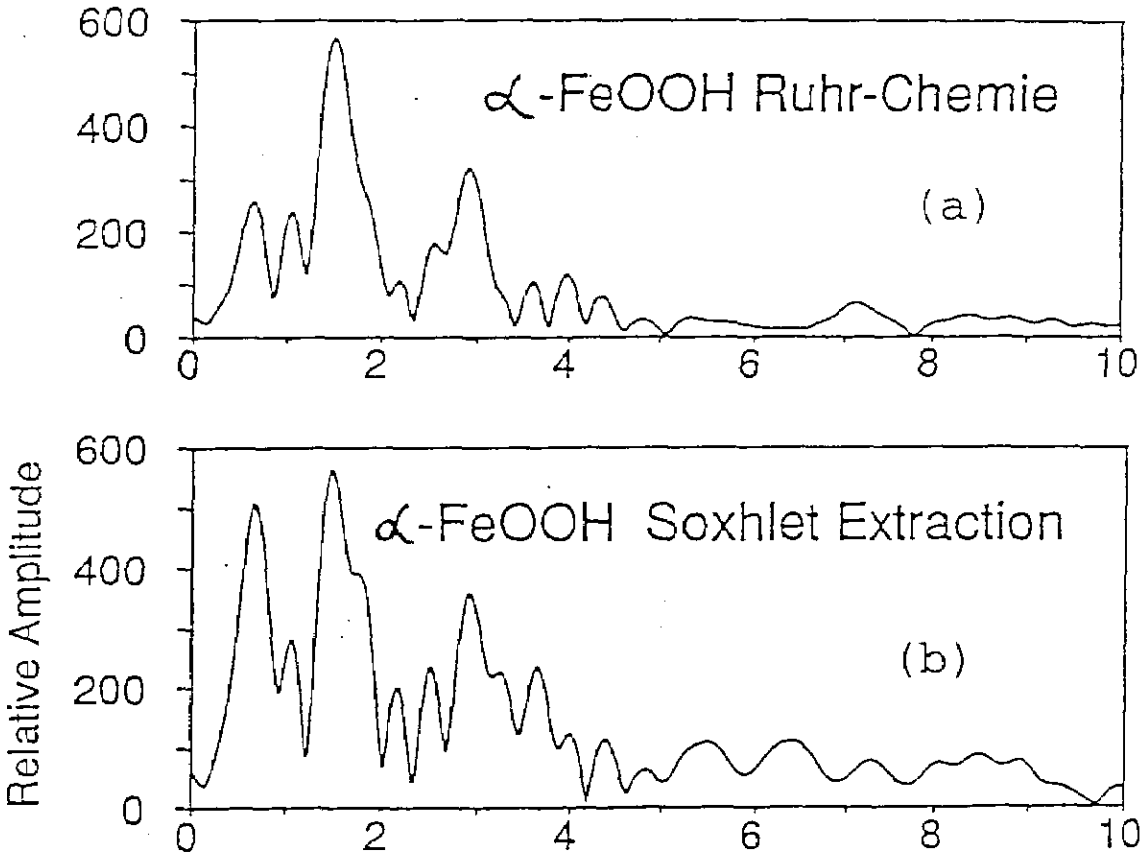


Fig. 18 (a) **EXAFS spectrum of α-FeOOH (Ruhr-Chemie sample)**
(b) **EXAFS spectrum of α-FeOOH *obtained by soxhlet* extraction**