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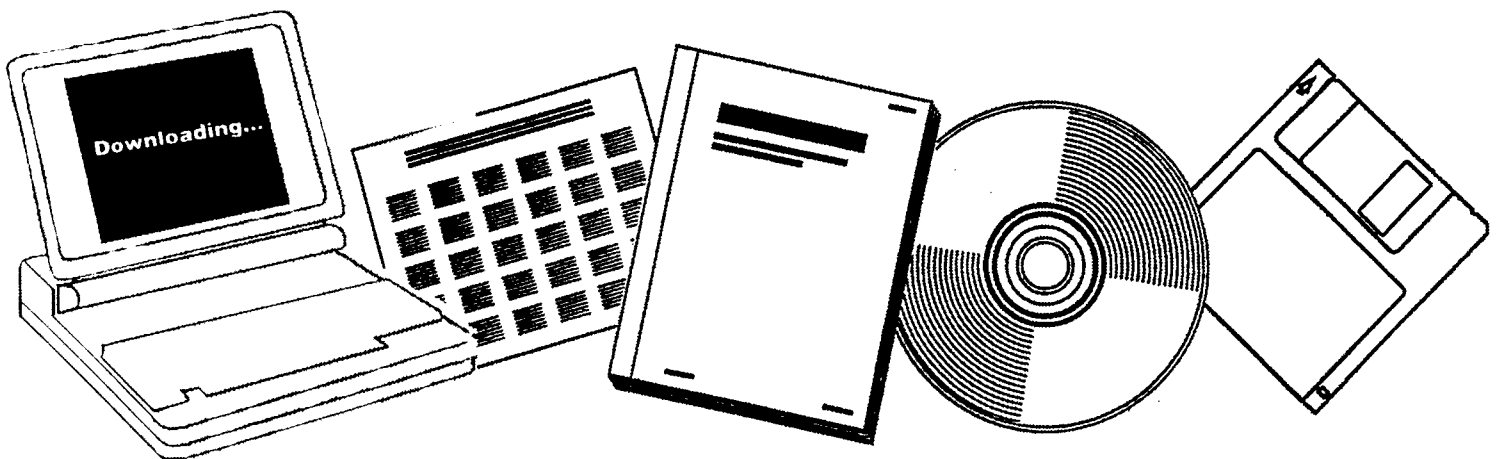
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MOESSBAUER SPECTROSCOPIC AND RELATED CHARACTERIZATION OF FISCHER-TROPSCH CATALYSTS. FINAL REPORT

PENNSYLVANIA STATE UNIV., UNIVERSITY
PARK. MATERIALS RESEARCH LAB

AUG 1982



U.S. Department of Commerce
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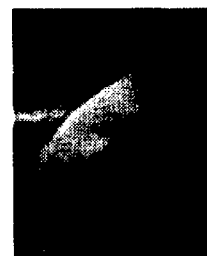
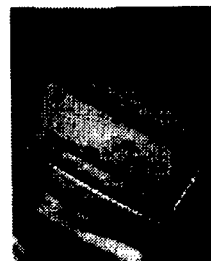
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DOE PC 41265--T1

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I. INTRODUCTION

As pointed out in our proposal, the work was undertaken using Mössbauer spectroscopy to characterize supported iron catalysts such as Fe/ZSM-5, Fe/Silicalite, and Fe/Mordenite in the synfuel gas reaction. As outlined in our May 1982 interim report, attention was focussed on Mössbauer in-situ characterization at various stages while the synfuel gas reaction was taking place. The fresh catalyst samples (impregnated using $\text{Fe}_3(\text{CO})_{12}$) were supplied by the Pittsburgh Energy Technology Center (PETC). In this report, salient aspects of Mössbauer spectra and interpretations are presented. The Mössbauer spectra at various reaction conditions such as gas flow rate, reduction time, and carbiding time are also reported to further understand the nature of catalyst and to derive optimum reaction conditions. Our work has resulted in several publications; a list of these and relevant papers is given at the end of this report.

II. PERSONNEL

Mr. Cary C. Lo (a Solid State Science student) was paid a half-time graduate assistantship for three terms and has assumed major responsibility for this project during the reporting period. Mr. Lo has also passed the candidacy and comprehensive examinations during this period and is proceeding with his related research under the direction of the principal investigator (P.I.), Prof. L. N. Mulay. The P.I. is pleased with the results obtained within the constraints of a limited budget and trust that the PETC-DOE scientists will also feel happy with the work accomplished.

III. NEW INSTRUMENTATION

A Mössbauer spectrometer for studies on the synfuel gas catalysts was set up and modified for temperature-dependent and/or applied external field work. A new 55 mCi Co^{57} source in Rh matrix supplied by the New England Nuclear (Boston, Mass.) was used in these studies. A block diagram of the Mössbauer spectrometer and its associated electronic units is shown in Fig. 1.

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The original Mössbauer drive transducer unit for vibrating the source in the constant acceleration mode was manufactured by the Nuclear Science and Engineering Company, Pittsburgh, PA. This drive unit is now replaced by a brand new Austin Associates drive unit with a helium-neon laser interferometer used for absolute velocity calibration. The gas proportional counter used to detect the 14.4 KeV gamma rays contained 90% krypton and 10% methane, and was made by the Reuter-Stokes Company, Cleveland, Ohio. The memory storage unit consists of a new ND-100 multichannel analyzer with 1024 channels, high voltage supply (ND-537), analog-to-digital converter (ND-570), and a preamplifier (ND-401); all such apparatus was supplied by the Nuclear Data, Inc., Chicago, IL. The teletype terminal was manufactured by the Teletype Corporation, Skokie, IL. The new Austin Associates Mössbauer spectrometer (S-600) provides (i) a sawtooth, (ii), a triangular and (iii) a sinusoidal mode with capabilities for "constant velocity" operation, and so on.

The in-situ cell for Mössbauer measurements [1] is shown in Fig. 2. This stainless steel cell with external cartridge heaters (Hot Watt 8215) was connected in parallel to a 3-mode temperature controller (Wistex 1542); this provided temperatures up to 800 K. Two Chromel/Alumel thermocouples were used to monitor the temperature. One was kept in contact with the bottom of the sample wafer while the other was connected to the surface of the sample holder. A uniform and stable temperature was achieved, with a temperature gradient less than 7 K, depending on the lower and higher operating temperatures. The air-cooled Beryllium windows (0.01" thick and 0.57" in diameter), supplied by Reuter Stokes Co. in 2x2" square plates, were vacuum brazed to Cu rings and then sealed by Varian ConFlat flanges. This Be window was analyzed using mass spectroscopy and Neutron Activation analysis which assured the iron impurity to be less than 50 ppm. The in-situ cell can be used at higher pressures, using thicker Be windows.

The flow rates of hydrogen and carbon monoxide were obtained using mass flow control valves (Brooks Model 5815). The hydrogen (99.999% pure from Airco) was further purified by passing it through a gas purifier and an Oxytrap (Alltech Associates, Inc.) to remove any H₂O and O₂ respectively. The carbon monoxide (99.99% pure from Matheson) was further purified by passing it through a gas purifier to remove any H₂O and carbonyls. A schematic diagram of the total reactor system is shown in Fig. 3.

IV. METHODS OF MEASUREMENT OF MÖSSBAUER PARAMETERS

Catalyst samples for Mössbauer measurements were mounted in the Mössbauer cell in a "porcus wafer" form, which allowed a free flow of gases over the catalyst. These self-supporting wafers of 0.57" diameter were made by pressing 0.2-0.3 g of powdered samples at a pressure of ~8000 psi. The velocity of the drive unit was set at ± 10 mm/sec so that all possible peaks arising from phases such as iron oxides, metallic iron, and iron carbides were well contained within the 512 channels of the multichannel analyzer. Calibration was performed using a standard NBS Fe foil for which the six-line spectrum was obtained. These six lines also allowed the calibration of the linearity of the drive unit, which was found to be within $\pm 0.5\%$. Since the channels for the peaks of the iron standard could be found from the printout spectra, a calibration constant in mm/sec/channel was calculated so that any channel number could be converted to the corresponding velocity.

The catalyst samples supplied by PETC were prepared in the following manner. The transition metal Fe was introduced into the zeolite by impregnation with the iron carbonyl $\text{Fe}_3(\text{CO})_{12}$ by using an extraction technique with cyclohexane as the solvent [2]. The weight percent of impregnated iron, normally in the range 10-16%, was determined by atomic absorption techniques. In general, in-situ Mössbauer measurements were carried out at four stages: (a) as-impregnated fresh samples, (b) samples reduced in H_2 (50 cc/min) at 450°C , (c) those carburized in $\text{CO}/\text{H}_2 = 1:1$ (100 cc/min total gas flow) at 250°C and (d) those run in $\text{CO}-\text{H}_2$ (1:1 syngas mixture) (100 cc/min total gas flow) at 280°C and then 300°C . The spectra were obtained at room temperature under various stages as shown in Fig. 4.

All Mössbauer measurements below room temperature were performed using a Model LT-3-110 liquid transfer "Heli-Tran." The "Heli-Tran" was used in conjunction with an APD-E digital temperature controller, both of which were made by Air Products and Chemicals, Inc., Allentown, Pa. The aluminum foil containing the sample measurement was attached to a special sample holder supplied by Air Products and Chemicals, Inc., which was then screwed into the tip of the cold finger. The sample temperature could be maintained to ± 0.10 K with this cryostat. The thermocouple was calibrated by Air Products and Chemicals Inc. For a detailed description of the theory and method of

operation of the cryostat, the reader should consult several excellent manuals written by Air Products and Chemicals, Inc.

V. ANALYSIS OF MÖSSBAUER DATA

The Mössbauer data were recorded from the spectrometer in the form of a punched paper tape printed on the teletype and, when necessary, recorded on the X-Y plotter. A computer program has been used in several cases to convert the contents of the paper tape onto a Cal-comp graphic converter. A least squares computer program obtained from the Quantum Chemistry Program Exchange and other groups was used to fit the Mössbauer data. Single Lorentzian lines were used in fitting the spectra. The program was capable of varying the line positions, line widths and intensities in order to obtain the best fit. A fit was considered to be good when the chi (χ) squared value was approximately equal to the number of channels in the spectrum. In some cases, after an initial fit was obtained, the line widths were constrained and the fitting procedure was repeated. A subroutine for the calculation of χ square and MISFIT, developed by S.L. Ruby [3] of the Argonne National Laboratory, was also included in the main computer program to compute the quality of the fitting obtained. The line widths were usually constrained to be within 0.30 to 0.35 mm/sec, which is appropriate for Fe⁵⁷. For further details pertaining to the computer program used to fit Mössbauer data, the reader should consult Write Up No. 276 of Quantum Chemistry Program Exchange, Indiana University.

Several numerical methods have been developed for determining the hyperfine parameters from an observed Mössbauer spectrum; these being, in general, synthetic methods requiring a computer. As Hoy and Chandra [4] have pointed out, these approaches are unsatisfactory because they necessitate making successive fits to the observed spectrum, using trial and error values of the parameters. In view of these arguments, an analytical technique was adopted, which is discussed by Williams and Bancroft [5].

VI. SYNOPSIS OF THE WORK CARRIED OUT ON THE "1981"—SAMPLES SENT BY PETC

The Mössbauer measurements of catalysts containing ZSM-5, silicalite or Mordenite as the shape selective component, and Fe (using Fe₃(CO)₁₂) as a

transition metal component have been systematically studied. The general findings of our study are outlined below:

(1) Fe^{3+} ions were found to exist in the as-impregnated catalysts, as expected. A very interesting and significant result indicated that the carbonyl impregnated sample contained ultrafine $\gamma\text{-Fe}_2\text{O}_3$ of $d = 60\text{--}66 \text{ \AA}$ in agreement with x-ray diffraction line broadening. In contrast, the nitrate impregnated sample showed $\alpha\text{-Fe}_2\text{O}_3$ of approximate particle size of 100 \AA from a comparison with Mössbauer studies on $\alpha\text{-Fe}_2\text{O}_3$ by Kundig [6].

(2) All the catalysts on reduction were found to contain Fe metal ($\sim 80\%$), Fe_3O_4 , and Fe^{3+} ions. It should be noted that the reduction was completed in two hours since identical Mössbauer spectra were obtained from runs ranging from 2 hours to 24 hours. In addition, we also studied the reduction at various H_2 flow rates (10 cc/min, 40 cc/min, and 50 cc/min). As the H_2 flow rate increased from 10 cc/min to 50 cc/min, less amount of Fe_3O_4 was obtained.

(3) On carburization, the ZSM-5 (Fe) samples at 250°C with CO/H_2 ratio 1:1 (100 cc/min total gas flow) showed the presence of χ -carbide (Fe_5C_2), cementite (Fe_3C), and Fe_3O_4 . It was found that the $\chi\text{-Fe}_5\text{C}_2$ is dominant compared with the cementite phase. It should be stressed that the carbiding was found to be completed at 16 hours.

(4) The used catalysts (at 280°C for 48 hours) originally prepared by carbonyl impregnation showed the same spectra as obtained with the carbided catalysts. This showed that the catalyst displayed steady catalytic activity and selectivity as the reaction proceeded. When the reaction temperature was changed to 300°C , no major change was found but a slightly increased $\theta\text{-Fe}_3\text{C}$ (cementite) was obtained over a period of 3 days. This confirms that the catalyst was fairly stable at different reaction temperatures. In contrast, as the reaction time was extended, the used catalysts derived from nitrate impregnation showed relatively more cementite as compared to the χ -carbide. Previously, we have shown [7] that the χ -carbide is more active than cementite. Thus, it is evident that the nitrate impregnated catalyst exhibited unsteady activity and selectivity to liquid hydrocarbons.

(5) A significant metal-support interaction was found in the case of fresh catalysts prepared by carbonyl impregnation on Mordenite with various $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios.

In the following sections we describe the specific details of Mössbauer in-situ studies obtained for samples 81-3 ($\text{Fe}_3(\text{CO})_{12}$ on ZSM-5) and 81-12 ($\text{Fe}_3(\text{CO})_{12}$ on Mordenite).

(A) The room temperature Mössbauer spectrum (Fig. 5) of impregnated sample of $\text{Fe}_3(\text{CO})_{12}$ on ZSM-5 shows a strong doublet with isomer shift of 0.4 mm/sec and quadrupole splitting of 0.95 mm/sec similar to that observed by Coey and Khalafalla [8], and associated with ultrafine particles that were identified as ferrimagnetically ordered superparamagnetic $\gamma\text{-Fe}_2\text{O}_3$. This aspect was confirmed by x-ray diffraction as well as magnetic measurements [9]. Particle size calculations from magnetic measurements of this finely dispersed catalyst, assuming spherical particles, yield an average particle size in the range 60-66 Å, in agreement with x-ray diffraction line broadening. However, the room temperature Mössbauer spectrum (Fig. 6) of impregnated $\text{Fe}_3(\text{CO})_{12}$ on Mordenite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 11.4$) shows a doublet with isomer shift of 0.375 mm/sec and quadrupole splitting of 0.741 mm/sec due to Fe^{3+} from antiferromagnetically ordered superparamagnetic $\gamma\text{-Fe}_2\text{O}_3$. This was also confirmed by magnetic measurements. It should be noted that as the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio increased from 11.4 to 17.4, the isomer shift increased to 0.383 mm/sec and then decreased to 0.331 mm/sec at a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 20.4. As the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio further increased to 61.82, an isomer shift of 0.191 mm/sec was obtained along with a small sextet arising from bulk iron oxide.

(B) The room temperature Mössbauer spectrum of the catalyst (sample 81-3) reduced in H_2 (50 cc/min) at 450°C for 30 minutes shown in Fig. 7 consisted of a sextet corresponding to metallic iron (Fe^0), two small sextets corresponding to Fe_3O_4 , and a central doublet corresponding to Fe^{3+} which showed incomplete reduction (see arrow shown in Fig. 7). As shown in Fig. 8, when the catalyst was reduced for 24 hours, the central doublet was decreased (see arrow shown in Fig. 8). However, the reduction was completed in 2 hours since the same Mössbauer spectra were obtained from 2 hours to 24 hours. As mentioned

previously, relatively more Fe_3O_4 was obtained when the H_2 flow rate was decreased. A typical spectrum of catalyst reduced for 2 hours at $\text{H}_2 = 10$ cc/min is shown in Fig. 9.

The room temperature spectrum of the sample 81-12 reduced in H_2 (10 cc/min) at 450°C for 4 hours shown in Fig. 10 consisted of metallic iron, Fe_3O_4 and Fe^{2+} . However, the more Fe_3O_4 content was observed in this case.

(C) The carbiding was carried out at 250°C with CO/H_2 ratio 1:1 (100 cc/min total gas flow) for 24 hours. The spectrum of carbided 81-3 shown in Fig. 11, collected after 9 hours of carbiding, consisted of Fe_3O_4 , $\theta\text{-Fe}_3\text{C}$, $\chi\text{-Fe}_5\text{C}_2$, and Fe^0 which indicates that the carbiding was not completed. As shown in Fig. 12, when the catalyst was carbided for 19 hours, the carbiding was completed with no iron shown in the spectrum. It should be noted that the carbiding was completed at 16 hours. However, the spectrum of catalyst carbided for 24 hours is shown in Fig. 13 which shows no major change from Fig. 12.

The spectrum of catalyst 81-12 carbided at 250°C with CO/H_2 ratio 1:1 (20 cc/min total gas flow) for 20 hours shown in Fig. 14 consisted of $\gamma\text{-Fe}_2\text{O}_3$ and Fe_3O_4 . No iron carbide (in any phase) was found in the carbided sample.

(D) The synfuel gas reaction was first carried out with $\text{CO}/\text{H}_2 = 1:1$ (100 cc/min total gas pressure) at 280°C for 48 hours. The spectrum (see Fig. 15) obtained after a 12-hour run shows similar to that observed at carbiding stage. The reaction temperature was then increased to 300°C for 72 hours. Similar spectra shown in Figs. 16 and 17 were obtained after a 12-hour run and 48-hour run, respectively. This indicated that the catalyst was fairly stable at various temperatures as the reaction time went on.

VIII. CONCLUSIONS

(1) The catalysts prepared using $\text{Fe}_3(\text{CO})_{12}$ impregnation on ZSM-5 showed $\gamma\text{-Fe}_2\text{O}_3$ with better dispersion and smaller particle size which led to high surface area.

(2) The H_2 flow rate varied the Fe_3O_4 content at the reduction stage. Under normal reduction conditions, the reduction is completed in two hours. High H_2 flow is suggested in order to obtain complete reduction.

(3) The carbided catalyst with carbonyl impregnation showed no phase change in the synfuel gas reaction. This confirmed that the catalysts were very stable and the activity obtained from PETC samples at $300^\circ C$ was mainly due to the temperature effect.

(4) Low activity of iron on Mordenite catalyst resulted possibly from the extensive oxidation of the carbided catalyst.

(5) The catalysts prepared using $Fe_3(CO)_{12}$ impregnation on Mordenite with various SiO_2/Al_2O_3 ratio showed $\gamma-Fe_2O_3$ with various isomer shift arising from the change of chemical environment. This is an evidence of strong metal support interaction (SMSI) due to the acidity of the catalyst support.

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6. W. Kundig, K.J. Ando, R.H. Lindquist, and G. Constabaris, Czech. J. Phys., 17, 467 (1967).
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9. R.T. Obermyer, L.N. Mulay, C. Lo, M. Oskooie-Tabrizi, and V.U.S. Rao, J. Appl. Phys., 53, 2683 (1982).

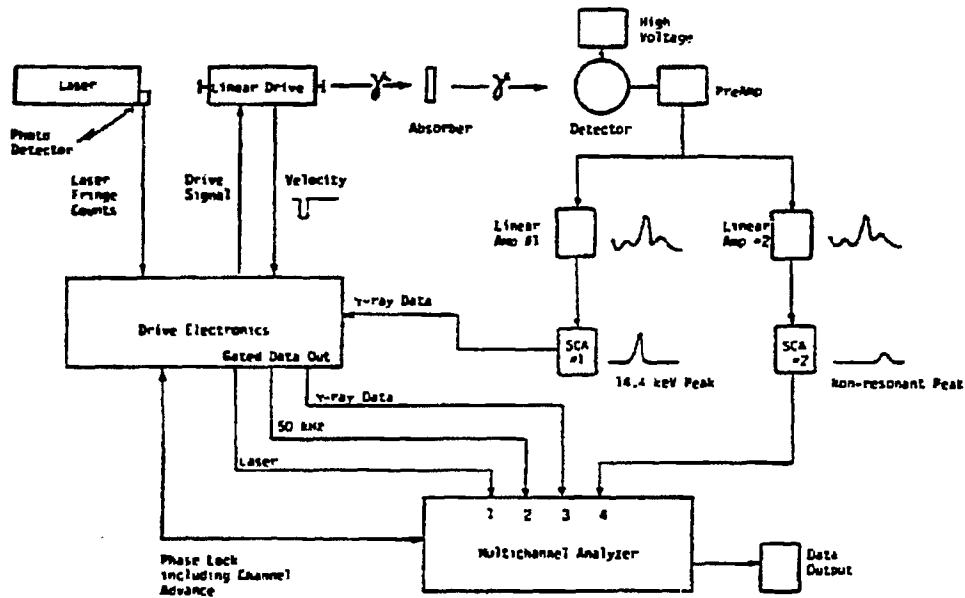


Fig. 1 Schematic of Mössbauer spectrometer configuration (with laser).

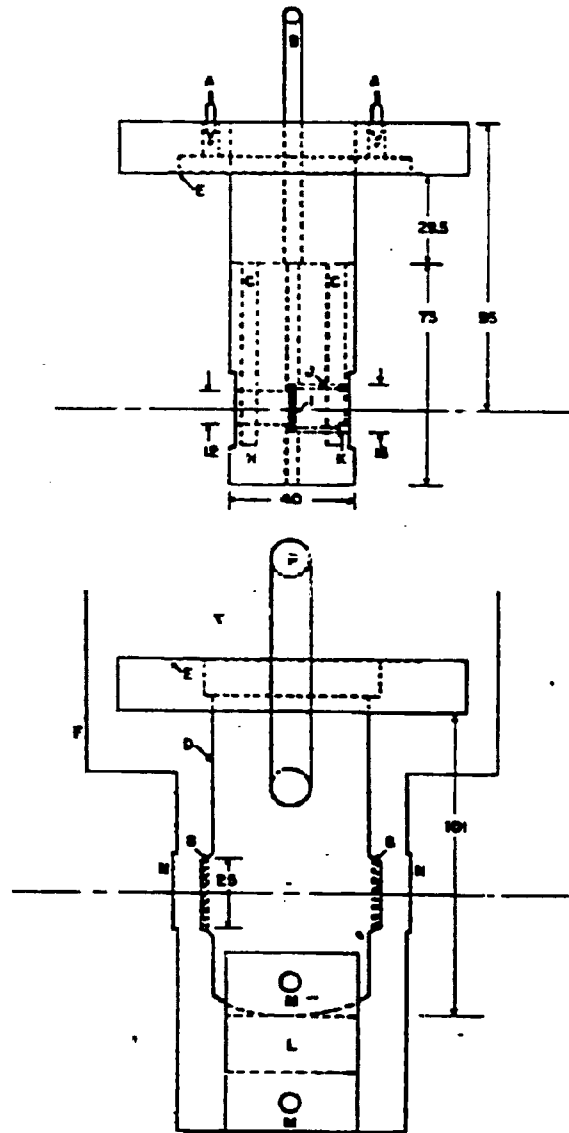


Fig. 2 Mössbauer absorber cell with the sample holder assembly raised and thermocouples, flange bolts, and bolt holes omitted. Dimensions in mm. (A) Thermocouple feedthroughs; (B) gas inlet tubing; (C) heater wells; (D) outer shell; (E) gasket for ConFlat flange; (F) copper heat shield; (G) Be window; (H) sample holder block; (I) sample; (J) retaining ring; (K) hollow boron nitride screw; (L) cell mount; (M) screws to secure cell and mount; (N) Be window; (P) gas outlet.

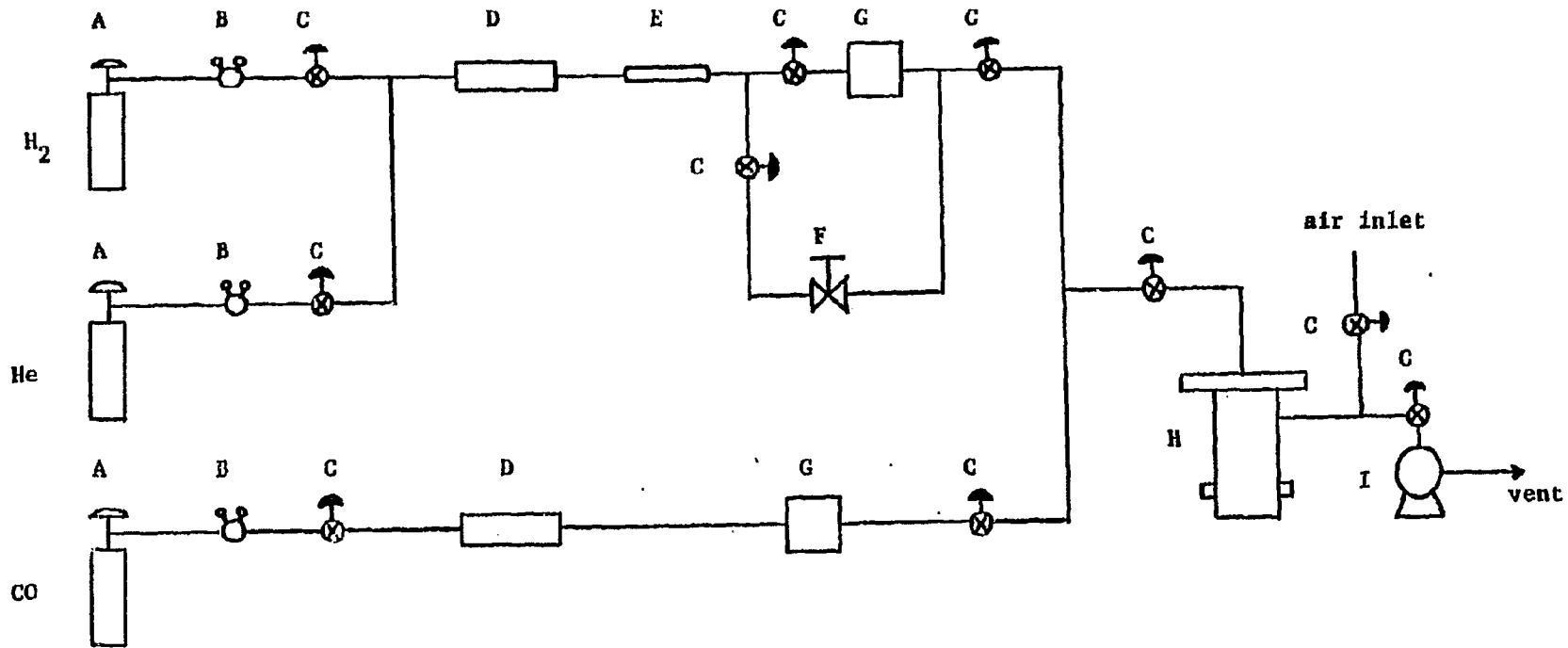


Fig. 3 Gas flow and reactor system for Mössbauer in-situ study.

(A) gas tank; (B) two-stage regulator; (C) bellow valve; (D) gas purifier; (E) Oxy trap;
 (F) needle valve; (G) gas flow control valve; (H) Mössbauer cell; (I) vacuum pump.

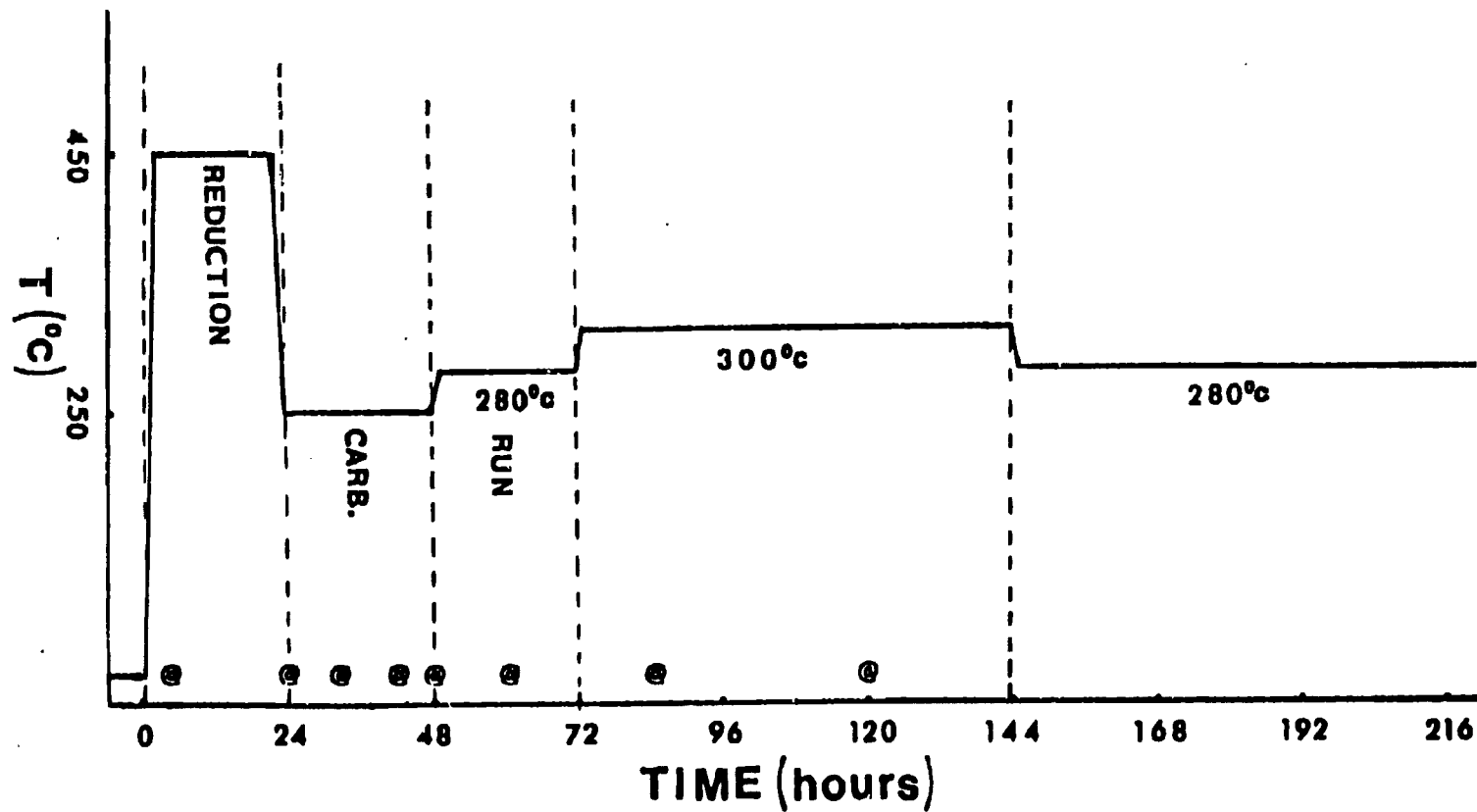


Fig. 4 Mössbauer spectra (•) obtained at room temperature under various stages.

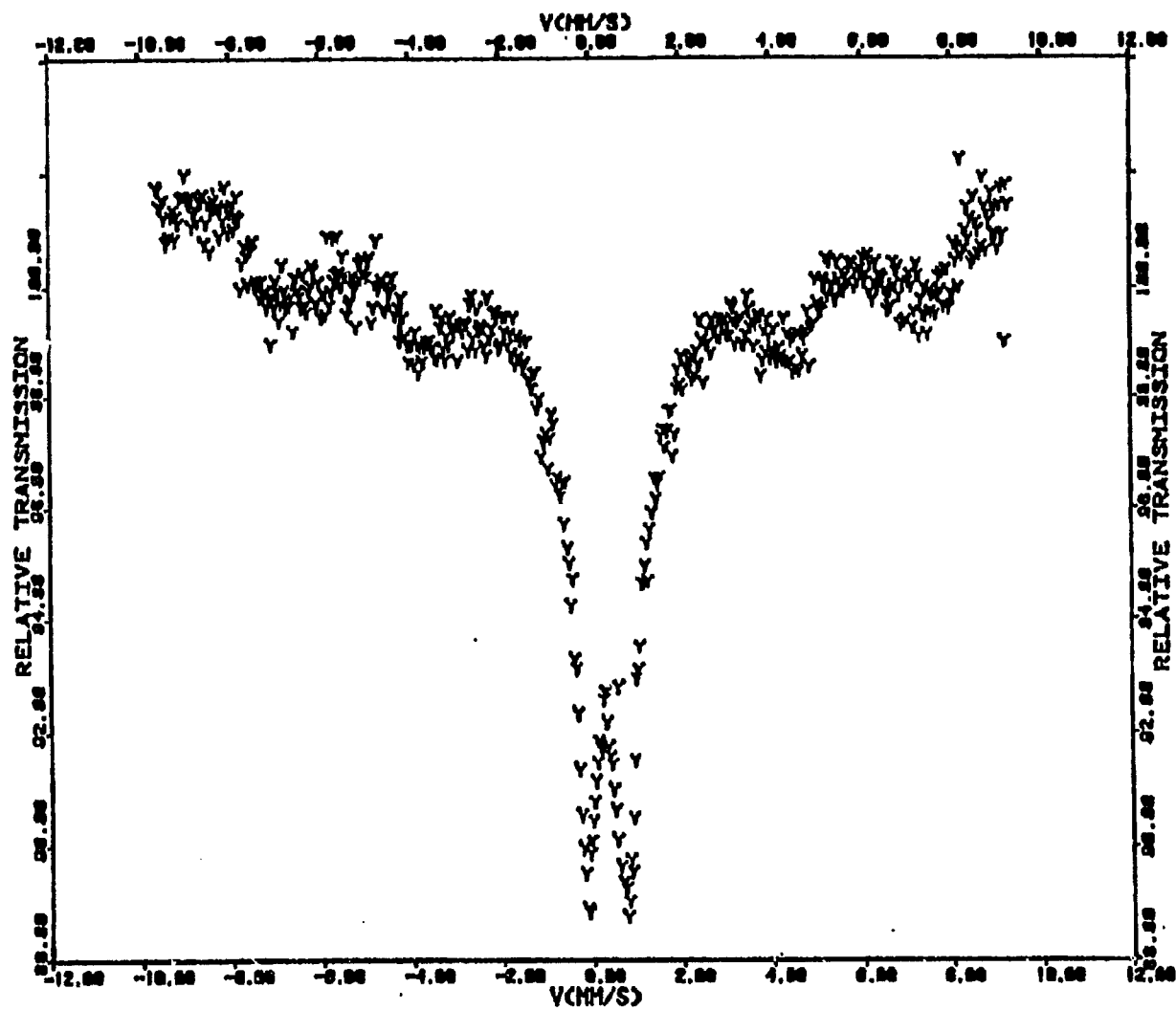


Fig. 5 ZSM-5 (15.2%) Fresh catalyst impregnated using $\text{Fe}_3(\text{CO})_{12}$ (Fresh 359-J).

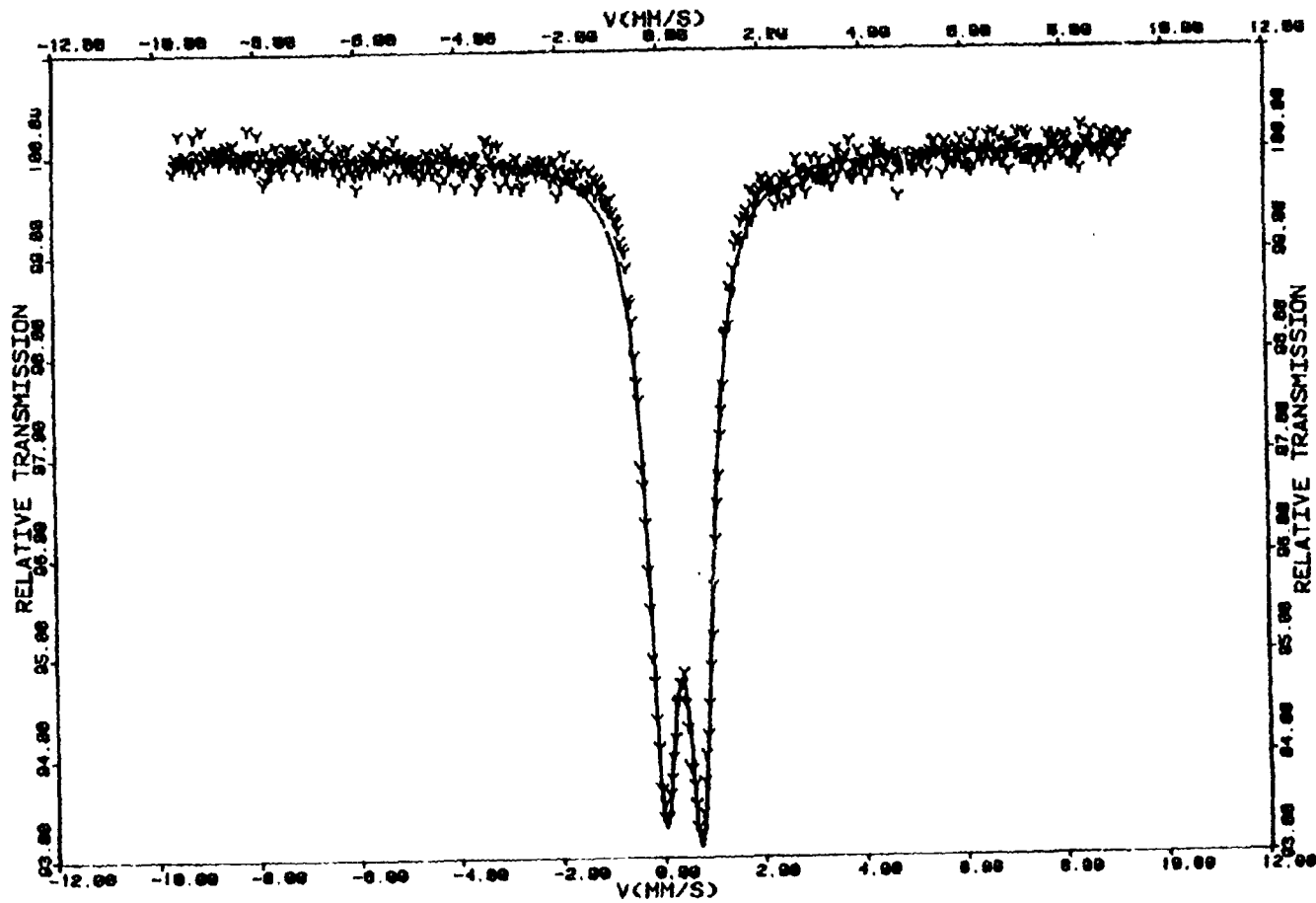


Fig. 6 81-12, Hordenite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 11.4$) with 15.11% Fe impregnated using $\text{Fe}_3(\text{CO})_{12}$.

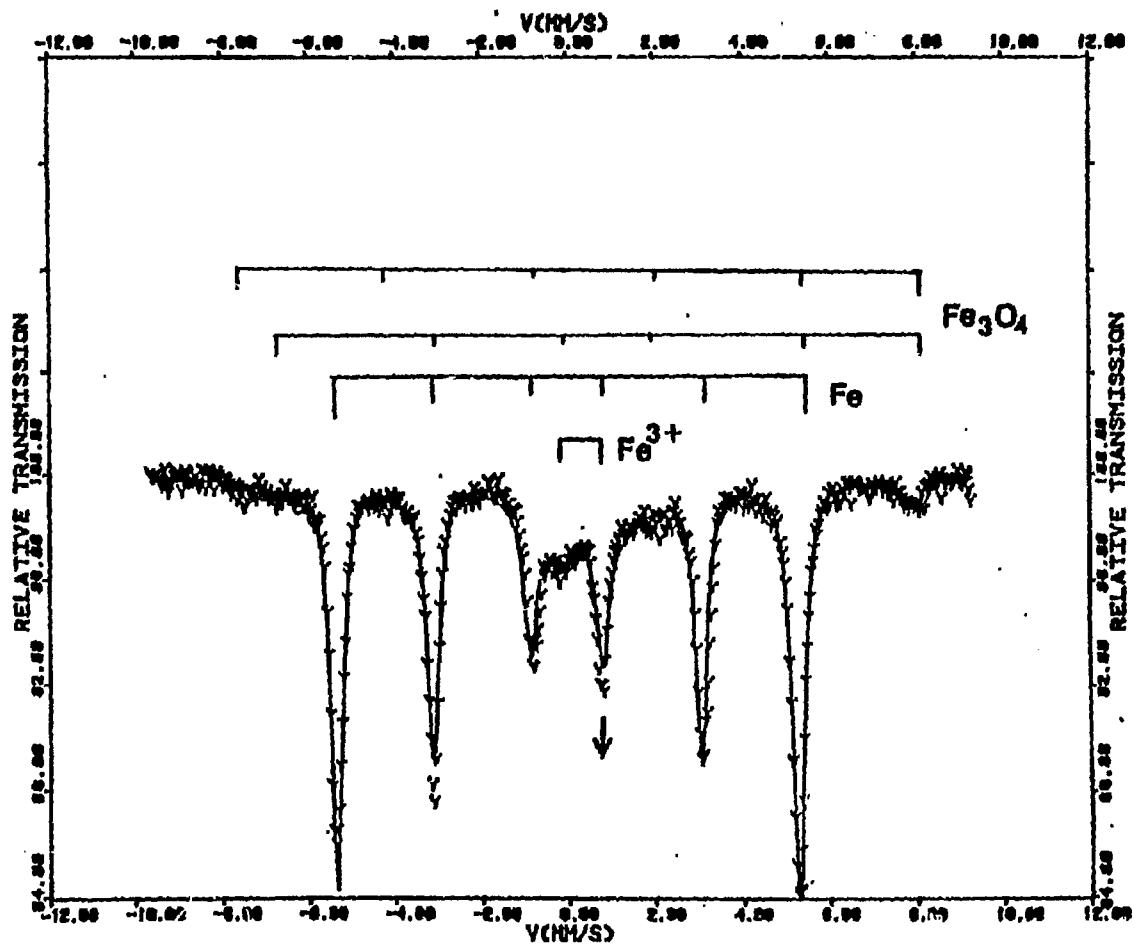


Fig. 7 81-3, Reduction for 30 min with H₂ = 50 cc/min at 450°C.

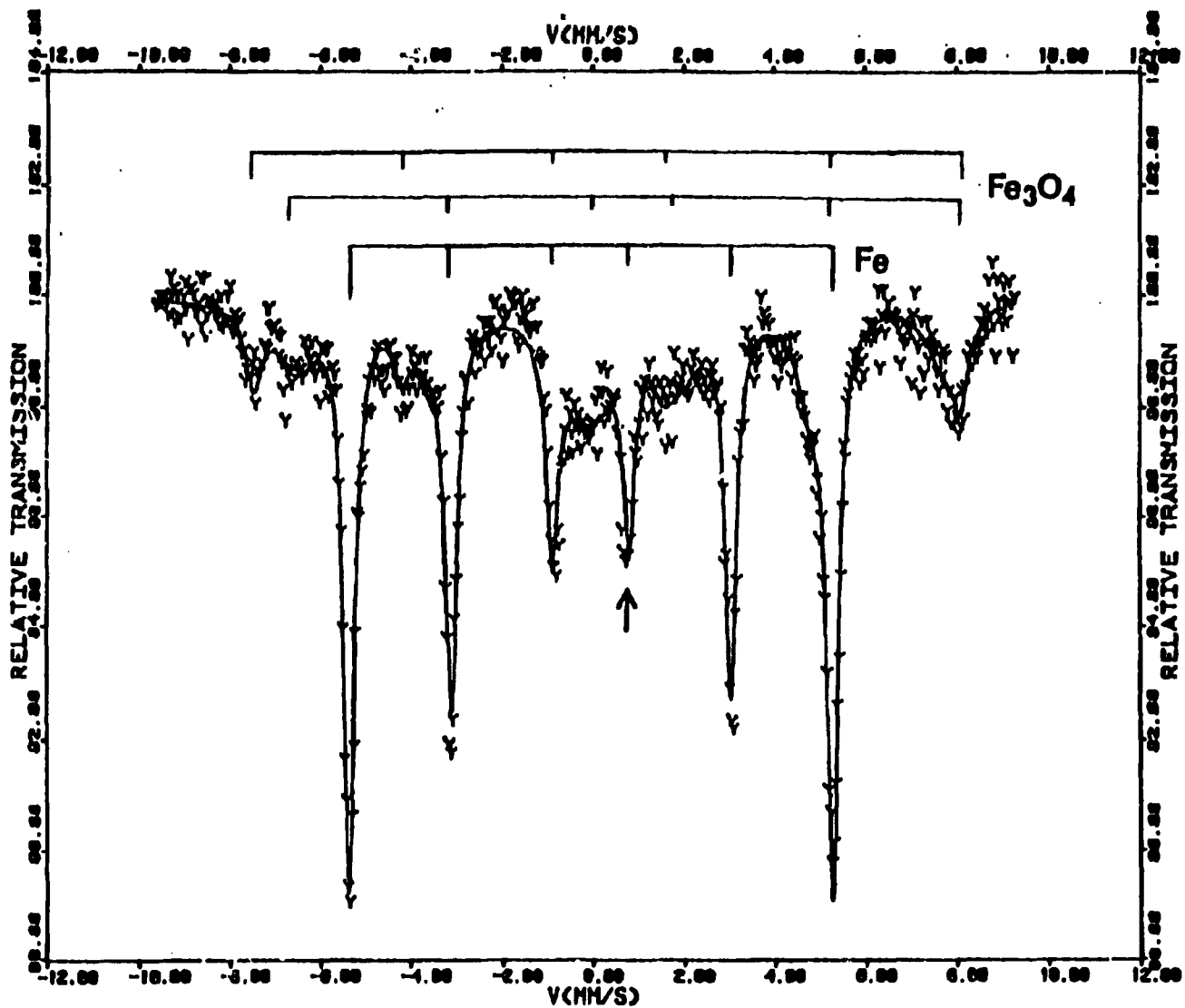


Fig. 8 81-3, Reduction for 24 hrs with H₂ = 50 cc/min at 450°C.

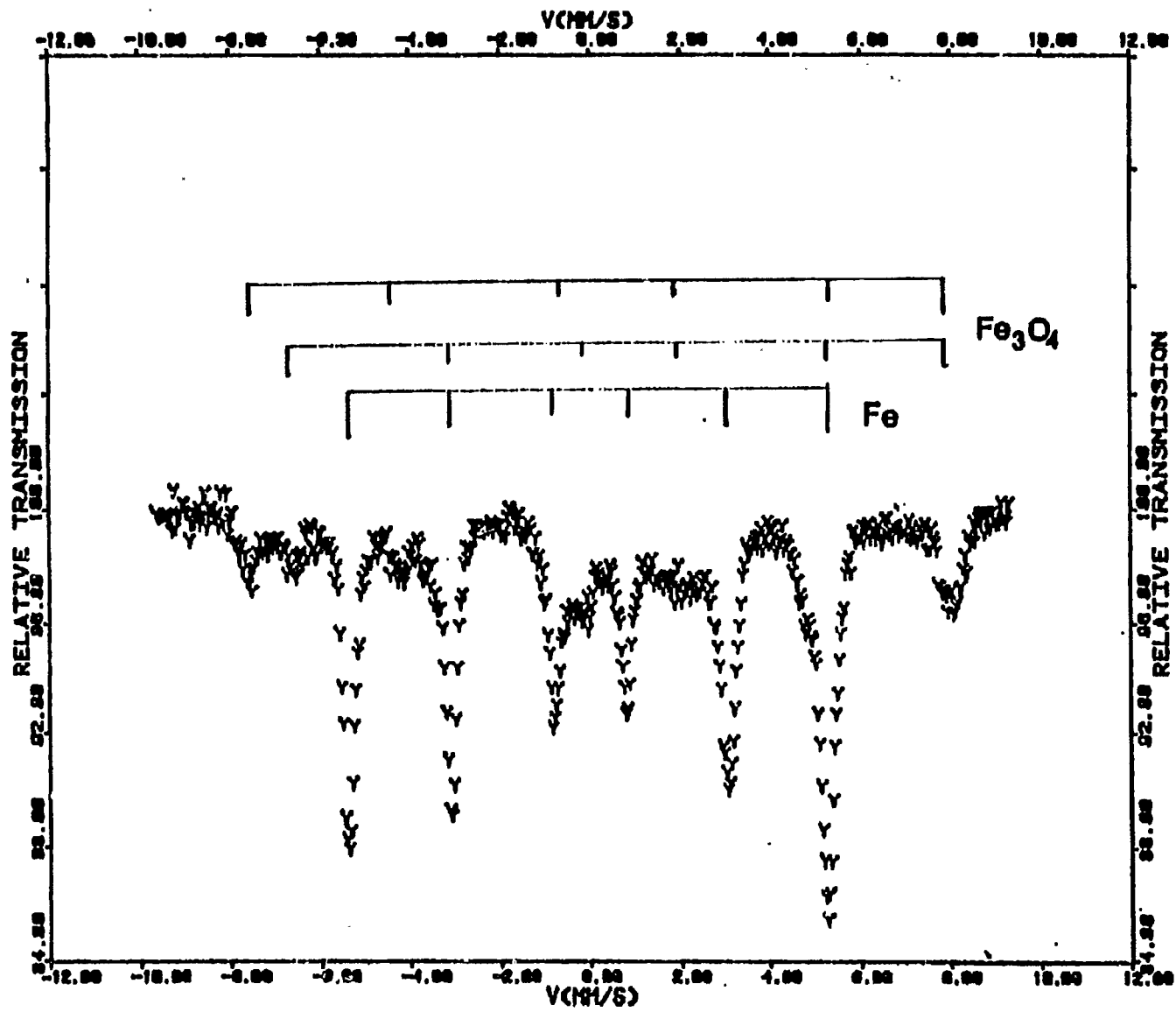


Fig. 9 81-3, Reduction for 2 hrs with $H_2 = 10$ cc/min at $450^\circ C$.

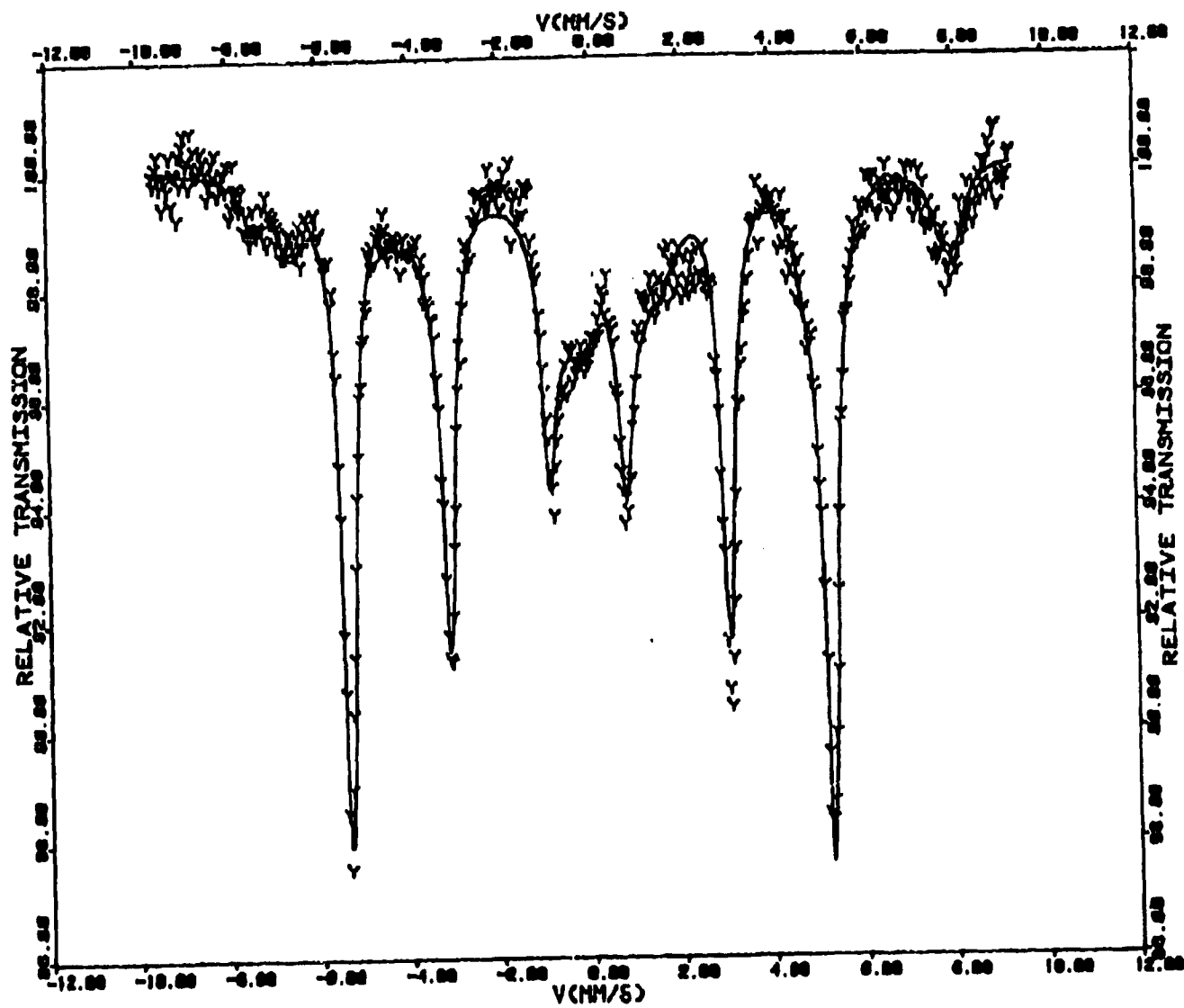


Fig. 10 87-12, Reduction for 4 hrs with $H_2 = 10$ cc/min at $450^\circ C$.

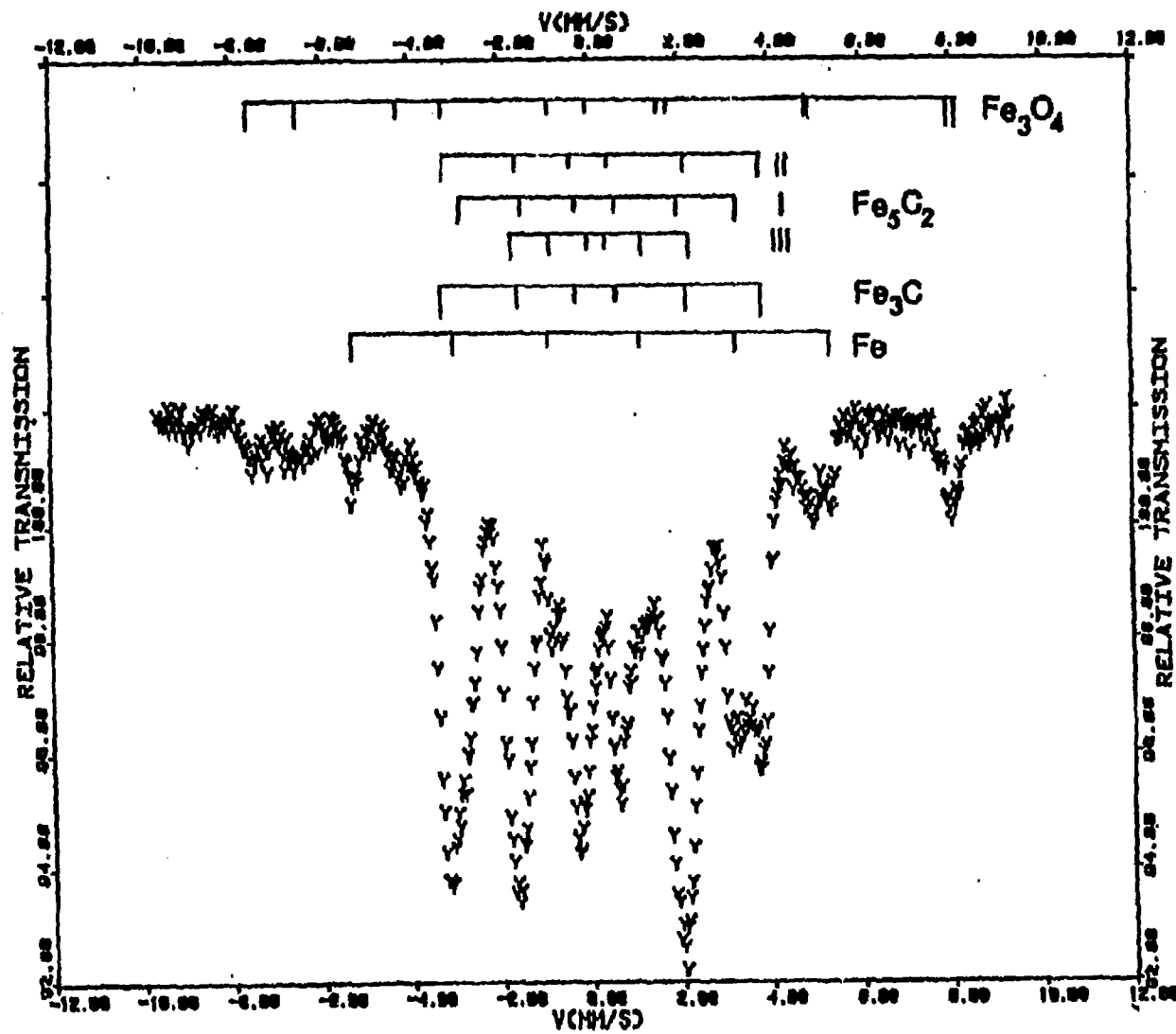


Fig. 11 81-3, carbiding with $H_2/CO = 1:1$, 50 cc/min, at 250°C for 9 hrs.

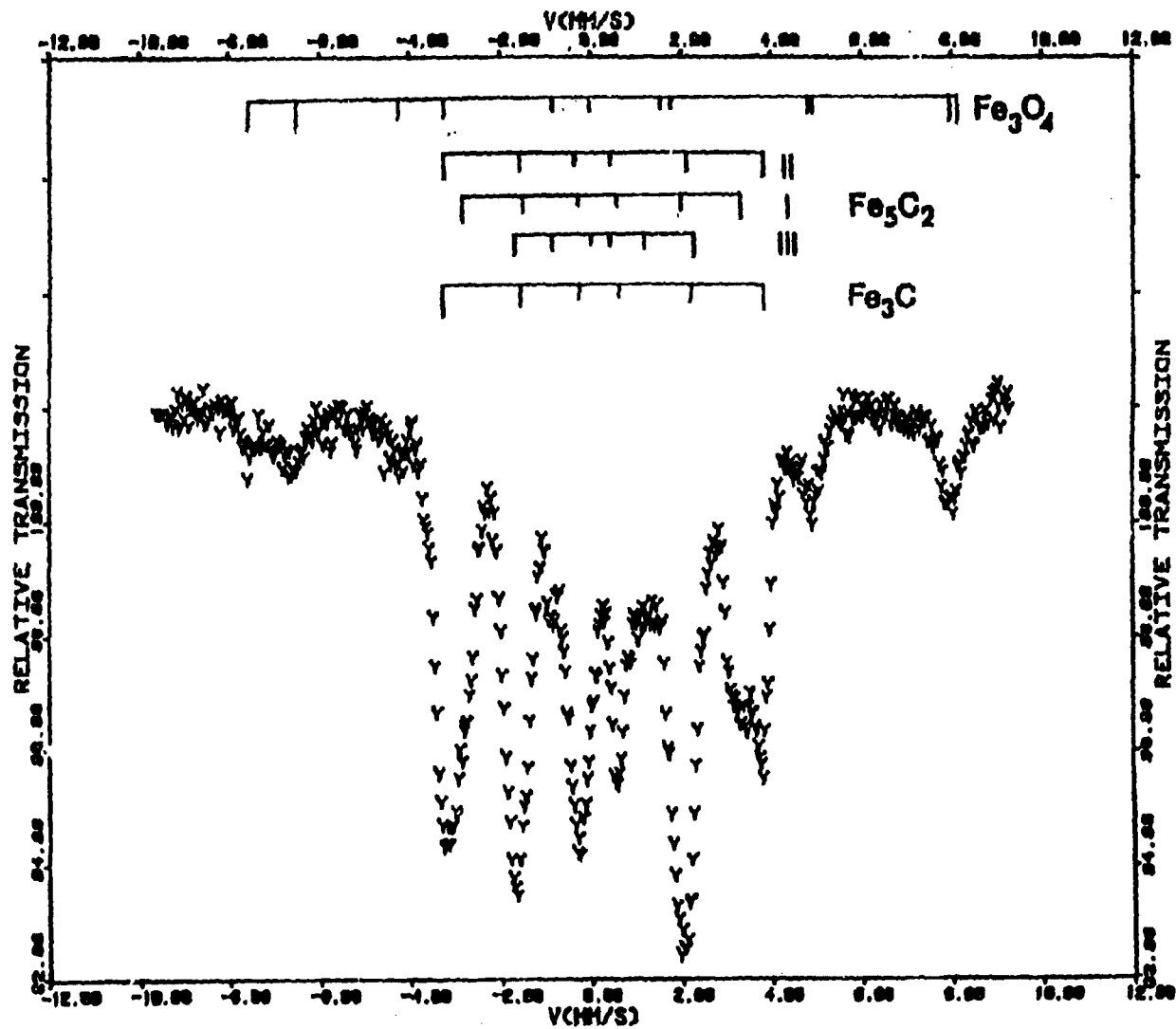


Fig. 12 81-3, carbidi ; with $H_2/CO = 1:1$, 50 cc/min, at 250°C for 19 hrs.

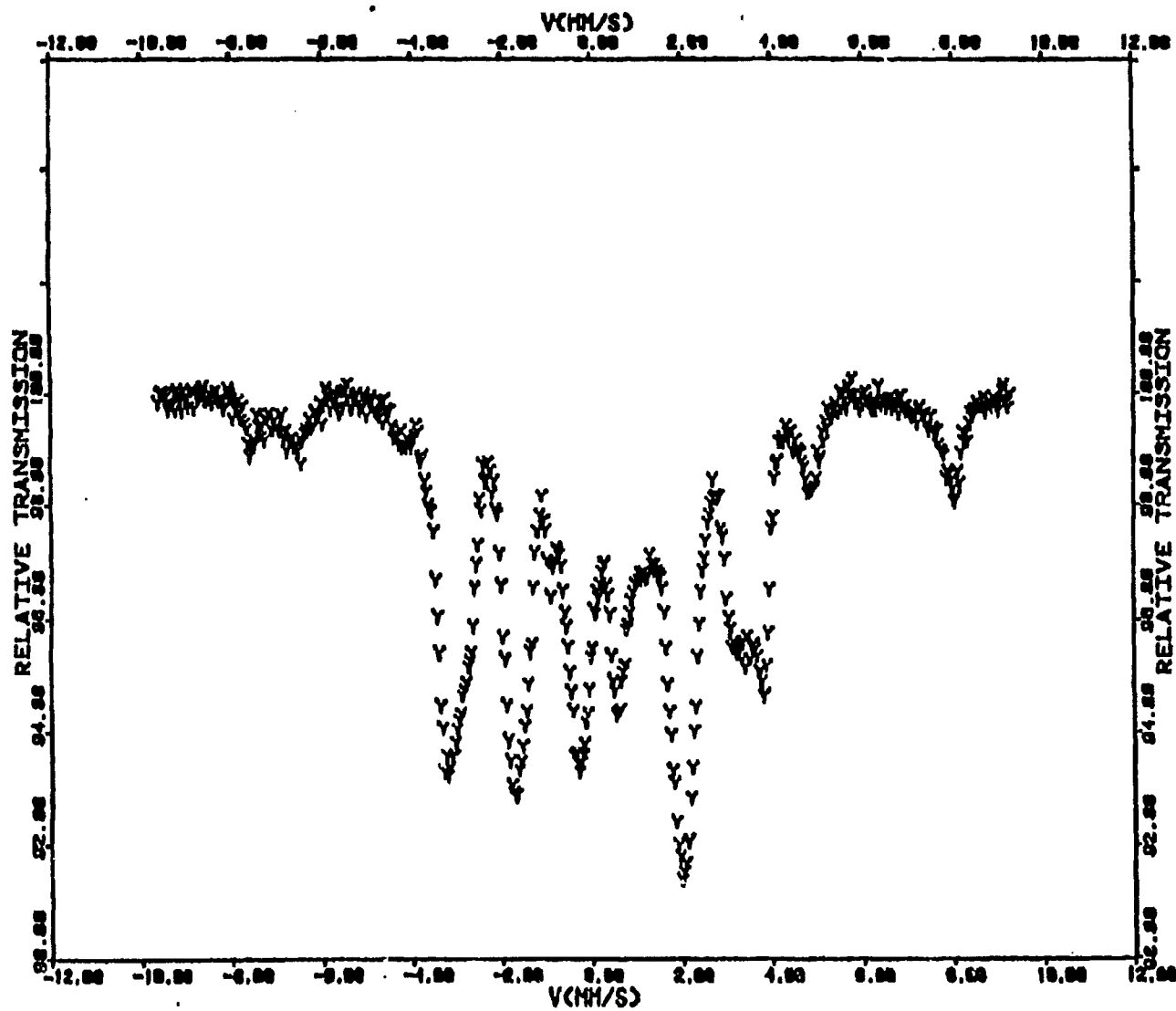


Fig. 13 81-3, carbiding with $H_2/CO = 1:1$, 50 cc/min, at 250°C for 24 hrs.

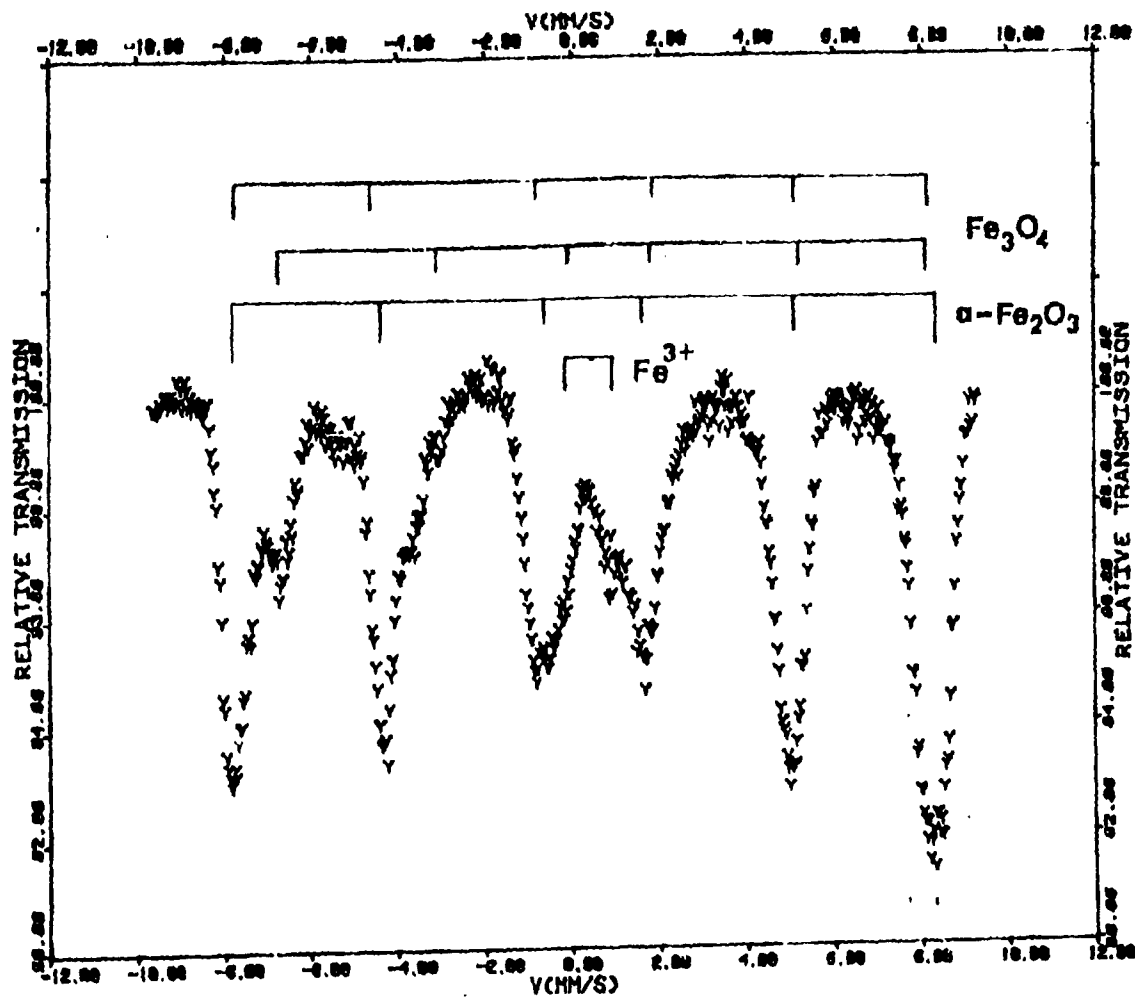


Fig. 14 81-12, carbiding with $\text{H}_2/\text{CO} = 1:1$, 10 cc/min, at 250°C for 20 hrs.

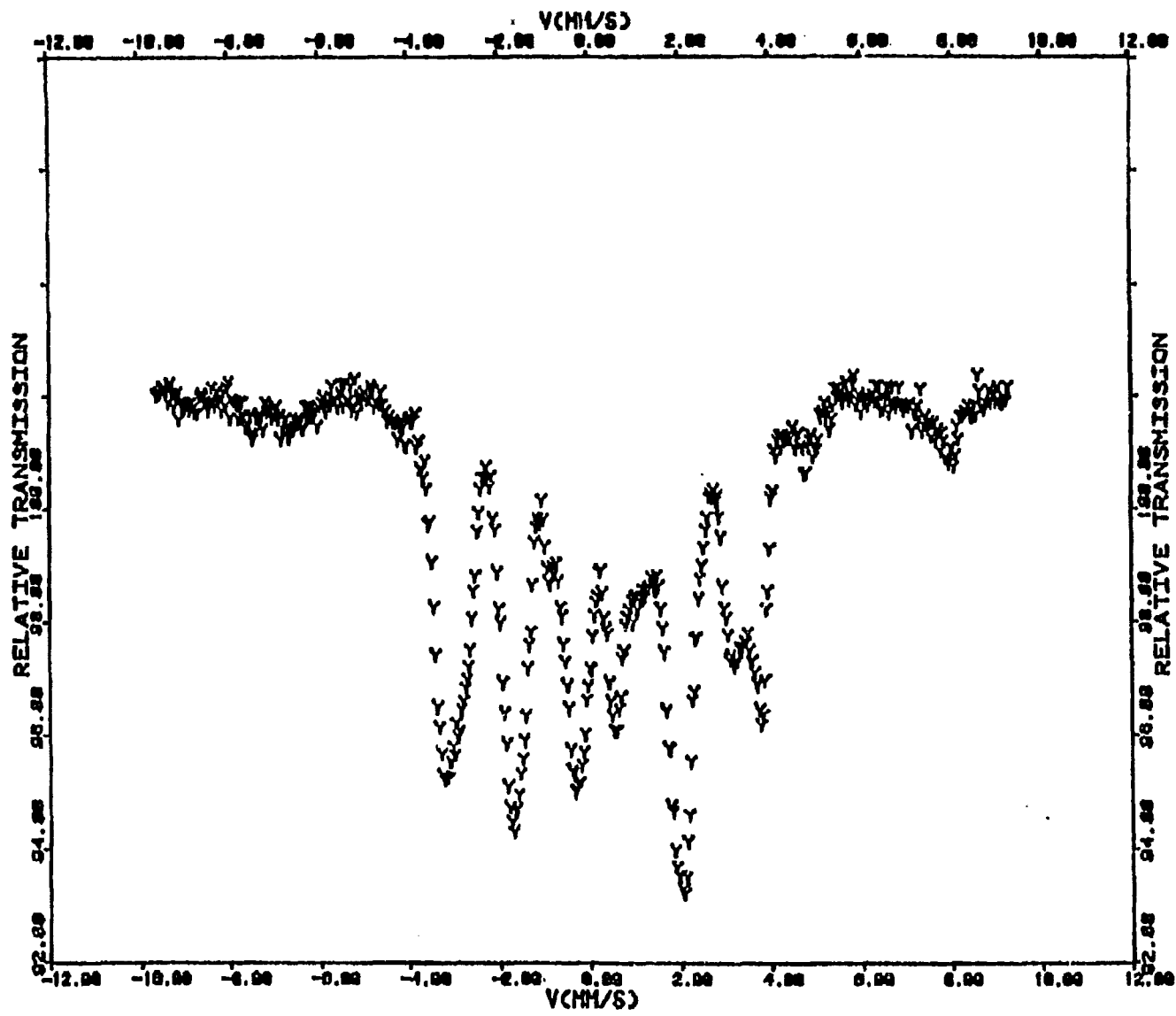


Fig. 15 81-3, Run with $H_2/CO = 1:1$, 50 cc/min, at $280^\circ C$ for 12 hrs.

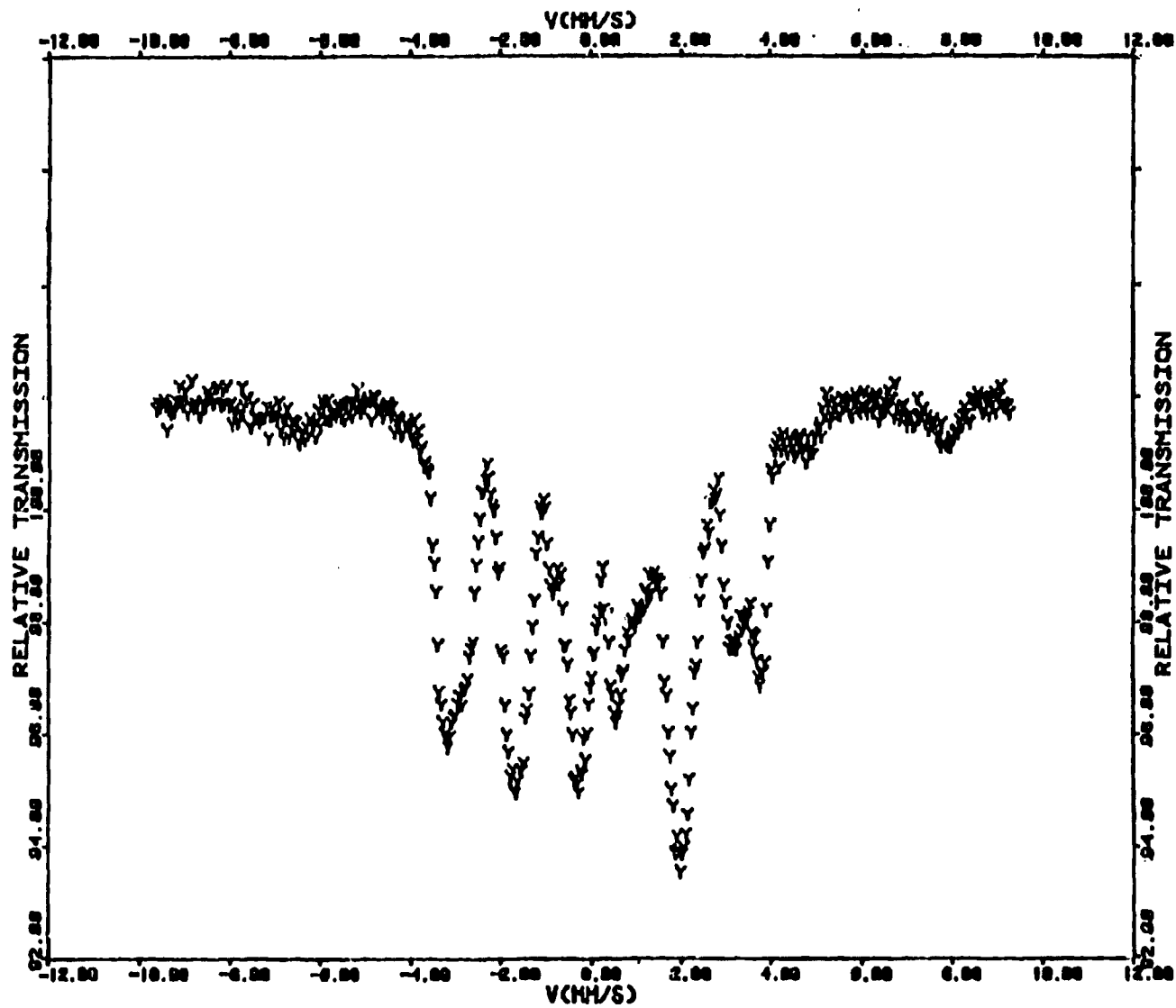


Fig. 16 81-3, Run with $H_2/CO = 1:1$, 50 cc/min, at 300°C for 12 hrs.

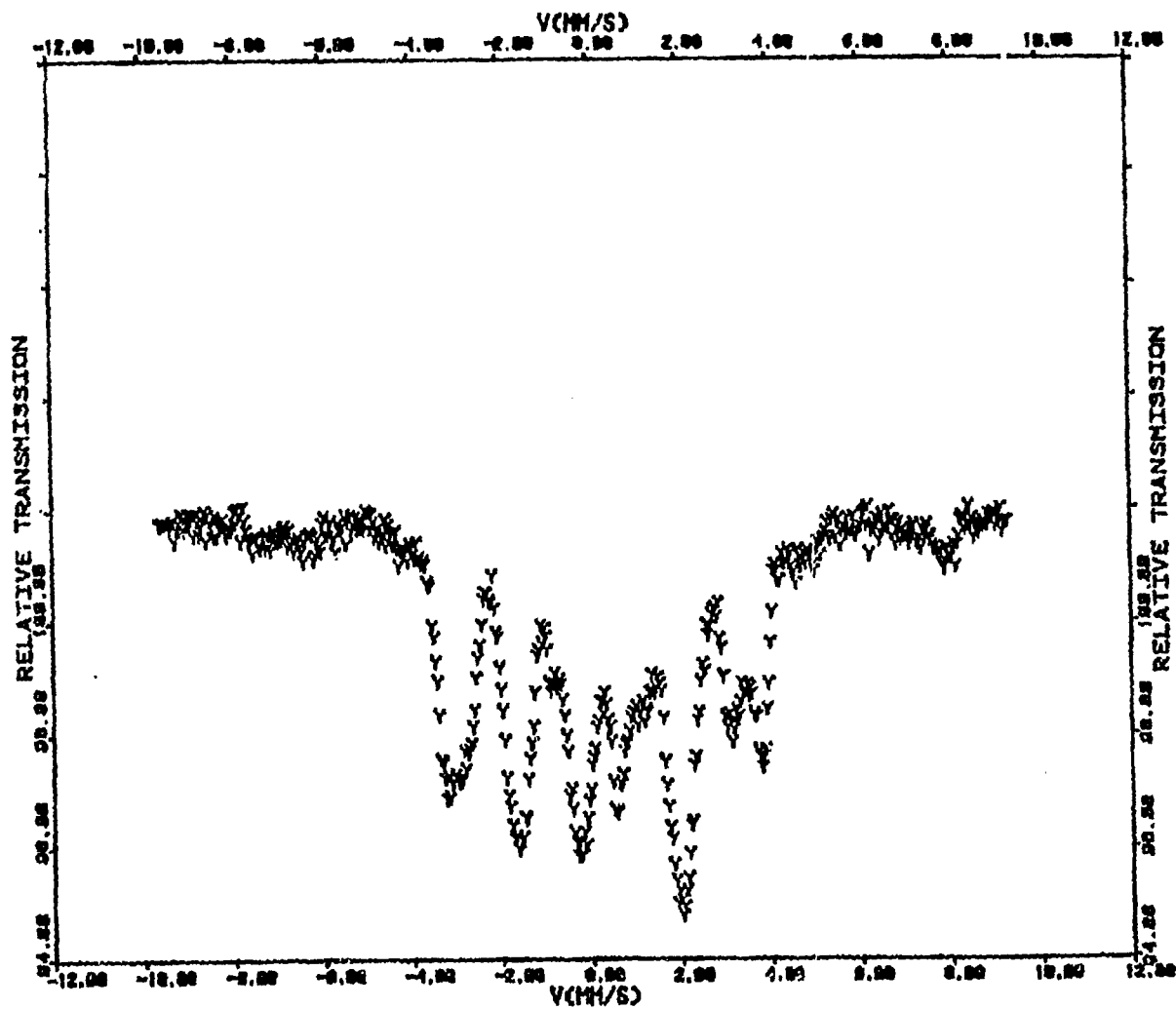


Fig. 17 81-3, Run with $H_2/CO = 1:1$, 50 cc/min, at $300^\circ C$ for 48 hrs.

LIST OF PUBLICATIONS

Based on the work supported by DOE-PETC

1. Synthesis of Iron-Nitrogen Compounds by RF-Sputtering: Mossbauer Studies. *Mat. Res. Bull.* 15, 1267(1980).
2. Mossbauer and Magnetic Studies of Bifunctional Medium-Pore Zeolite-Iron Catalysts Used in Synthesis Gas Conversion. Chapter 27 in "Mossbauer Spectroscopy and Its Chemical Applications." J. G. Stevens and G. K. Shenoy, eds. Adv. in Chem. Series. No.194, Am. Chem. Soc., Washington, DC (1981).
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I MOSSBAUER SPECTROSCOPY RESULTS

DOE Contract DE-AC-22-81PC41265. Principal Investigator Prof. L.N. Mulay, 136 Mat. Res. Lab., The Pennsylvania State University, University Park, PA 16802

Sample No.	Sample	State	Description of Mossbauer Spectra and Interpretation
81-1	ZSM-5 (16% Fe)	Used	large amount of Fe_3O_4 , Fe_5C_2 , and a strong doublet
81-2	ZSM-5 (Fe) added with Fe_3O_4	Used	Fe_5C_2 , Fe_3C , no presence of Fe_3O_4
81-3	ZSM-5 (15.2% Fe)	Fresh	strongly unresolved doublet corresponding to $\gamma-Fe_2O_3$
81-4	ZSM-5 (15.2% Fe)	Reduced	six peaks corresponding to iron metal and small central doublet due to Fe^{3+}
81-5	ZSM-5 (15.2% Fe)	Carbided	Fe_5C_2 , small amount of Fe_3O_4 , and doublet corresponding to Fe^{3+}
81-6	Silicalite (10% Fe)	Fresh	doublet due to Fe^{3+}
81-7	Silicalite (20% Fe)	Fresh	doublet due to Fe^{3+}
81-8	ZSM-5 (14.7% Fe)	Fresh	doublet due to Fe^{3+}
81-9	ZSM-5 (14.7% Fe)	Used	Fe_5C_2 , large amount of Fe_3C , and doublet due to Fe^{3+}
81-10	ZSM-5 (15.2% Fe)	Reduced	Fe-metal (~85%) and doublet due to Fe^{3+}
81-11	ZSM-5 (15.2% Fe)	Carbided	Fe_5C_2 , Fe_3O_4 , and doublet due to Fe^{3+}

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Submitted by:

L. N. Mulay

L.N. Mulay

Professor of Solid State Science

Date: November 2, 1981

II

MÖSSBAUER SPECTROSCOPY RESULTS

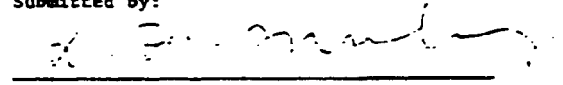
DE Contract DE-AC-22-81PC41265. Principal Investigator Prof. L.N. Mulay, 136 Mat. Res. Lab., The Pennsylvania State University, University Park, PA 16802

Sample No.	Sample and Its State	Description of Mössbauer Spectra and Interpretation
81-12	Mordenite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 11.4$) with 15.11% Fe impregnated using carbonyl. Fresh catalyst. Fe 3-356/H-Mordenite AR	Strong asymmetric doublet due to Fe^{3+} from (ferrimagnetically ordered superparamagnetic) $\gamma\text{-Fe}_2\text{O}_3$ [I.S. = 0.375 mm/s, Q.S. = 0.741 mm/s].
81-15	Sample 81-12 calcined in air at 500°C. Fe 3-356/H-Mordenite 500°C.	Small asymmetric doublet due to Fe^{3+} from (antiferromagnetically ordered superparamagnetic) $\alpha\text{-Fe}_2\text{O}_3$ and a six-peak magnetically ordered $\alpha\text{-Fe}_2\text{O}_3$ [I.S. = 0.438 mm/s, H.F. = 512 KOe].
81-18	Mordenite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 17.4$) with 17.08% Fe impregnated using carbonyl. Fresh catalyst. Fe 3-354/H-Mordenite AR.	Strong asymmetric doublet due to Fe^{3+} from (ferrimagnetically ordered superparamagnetic) $\gamma\text{-Fe}_2\text{O}_3$ [I.S. = 0.382 mm/s, Q.S. = 0.744 mm/s].
81-21	Sample 81-18 calcined in air at 500°C. Fe 3-354/H-Mordenite 500°C.	Small asymmetric doublet due to Fe^{3+} from (antiferromagnetically ordered superparamagnetic) $\alpha\text{-Fe}_2\text{O}_3$ and a six-peak magnetically ordered $\alpha\text{-Fe}_2\text{O}_3$ [I.S. = 0.430 mm/s, H.F. = 511 KOe].
81-24	Mordenite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 20.4$) with 16.13% Fe impregnated using carbonyl. Fresh catalyst. Fe 3-357/H-Mordenite AR.	Strong doublet from Fe^{3+} and a small peak (due to Fe^{2+}) with positive I.S. and large Q.S. from superparamagnetic iron-oxide. The acidic H in the latter plays an important role in the reduction process.
81-27	Sample 81-24 calcined in air at 500°C. Fe 3-357/H-Mordenite 500°C.	Small asymmetric doublet due to Fe^{3+} from (antiferromagnetically ordered superparamagnetic) $\alpha\text{-Fe}_2\text{O}_3$ and a six-peak magnetically ordered $\alpha\text{-Fe}_2\text{O}_3$.
81-28	Mordenite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 61.82$) with 14% Fe impregnated using carbonyl. Fresh catalyst. Fe 3-361/H-Mordenite AR.	Six small peaks with a (coalesced doublet) strong peak at the center arising from magnetically ordered iron-oxide(s). Increase in $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio gives rise to complex spectrum.
81-3A	ZSM-5 (Fe). Fresh catalyst impregnated using $\text{Fe}_3(\text{CO})_{12}$. (Fresh 359-J). Calcined in air at 600°C in our lab. (This work was done to check the calcining effect at higher temperature using an acidic ZSM-5 structure).	The complex spectrum corresponds to mostly Fe_3O_4 , with a trace of a doublet as seen in previous cases. The acidity and "crystal field" effects are responsible for the complexity of the spectrum.

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E: January 13, 1982

Submitted by:



L.N. Mulay
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III MOSSBAUER SPECTROSCOPY RESULTS

DOE Contract DE-AC-22-81PC41265. Principal Investigator Prof. L.N. Mulay, 136 Mat. Res. Lab., The Pennsylvania State University, University Park, PA 16802

Sample No.	Sample and Its State	Description of Mossbauer Spectra and Interpretation
81-3	ZSM-5 (15.2% Fe) Fresh catalyst impregnated using Fe ₃ (CO) ₁₂ (Fresh 359-J)	strong doublet corresponding to superparamagnetic γ -Fe ₂ O ₃ (I.S.=0.4 mm/sec, Q.S.=0.95 mm/sec)
81-3-1	81-3, Reduction for 2 hrs with H ₂ =10 cc/min at 450°C	six peaks corresponding to Fe ⁰ plus large amount of Fe ₃ O ₄ (~40%)
81-3-2	81-3, Reduction for 2 hrs with H ₂ =40 cc/min at 450°C	six peaks corresponding to Fe ⁰ plus Fe ₃ O ₄ (~20%)
81-3-3	81-3, Reduction for 20 min with H ₂ =50 cc/min at 450°C	six peaks corresponding to Fe ⁰ , two small sextets corresponding to Fe ₃ O ₄ , and central doublet (Fe ³⁺) shows incomplete reduction. We conclude at this point that the flow rate of H ₂ is very important.
81-3-4	81-3, Reduction for 24 hrs with H ₂ =50 cc/min at 450°C	six peaks corresponding to Fe ⁰ , two small sextets corresponding to Fe ₃ O ₄ , and central doublet (Fe ³⁺) is reduced comparing to 81-3-3. The reduction is completed in 2 hrs. Same Mossbauer spectra were obtained from 2 hrs to 24 hrs.
81-3-5	81-3, carbiding with H ₂ /CO=1:1, 50 cc/min, at 250°C for 9 hrs.	complex spectrum consists of three sites corresponding to χ -Fe ₅ C ₂ , small six peaks corresponding to Fe ⁰ , and very small Fe ₃ O ₄ . The carbiding is incomplete at this stage.
81-3-6	81-3, carbiding with H ₂ /CO=1:1, 50 cc/min, at 250°C for 19 hrs.	carbiding is completed at this stage. χ -Fe ₅ C ₂ plus small Fe ₃ O ₄ . No Fe was found in the spectrum. We conclude at this point that the carbiding need not be carried out for 24 hrs.
81-3-7	81-3, carbiding with H ₂ /CO=1:1, 50 cc/min, at 250°C for 24 hrs.	spectrum shows no change from 81-3-6 but with slightly reduced line width due to sintering, very small amount of Fe ₃ C is possibly formed.
81-3-3	81-3, Run with H ₂ /CO=1:1, 50 cc/min, at 280°C for 12 hrs.	mostly χ -Fe ₅ C ₂ , small Fe ₃ O ₄ , and very small θ -Fe ₃ C possibly formed
81-3-9	81-3, Run with H ₂ /CO=1:1, 50 cc/min, at 280°C for 24 hrs.	mostly χ -Fe ₅ C ₂ , small Fe ₃ O ₄ and θ -Fe ₃ C identical to spectrum obtained from 81-3-8
81-3-10	81-3, Run with H ₂ /CO=1:1, 50 cc/min, at 300°C for 12 hrs.	χ -Fe ₅ C ₂ is dominant in this spectrum and no major change as the reaction temperature is raised from 280°C to 300°C. But peak intensity ratio slightly changes. This shows that unresolved phase is possibly removed.
81-3-11	81-3, Run with H ₂ /CO=1:1, 50 cc/min, at 300°C for 24 hrs.	A similar spectrum as above is obtained, showing no major change.
81-3-12	81-3, Run with H ₂ /CO=1:1, 50 cc/min, at 300°C for 48 hrs.	The same spectrum as above was observed.
81-3-13	81-3, Run with H ₂ /CO=1:1, 50 cc/min, at 300°C for 72 hrs.	The spectrum remains the same as above. This confirms that the catalyst is very stable at this stage.
81-3-14	81-3, Run with H ₂ /CO=1:1, 50 cc/min, at 280°C for 24 hrs.	The spectrum has no major change as the temperature is decreased to 280°C. Slightly increased θ -Fe ₃ C is seen due to intensity change.
81-3-15	81-3, Run with H ₂ /CO=1:1, 50 cc/min, at 280°C for 48 hrs.	The similar spectrum is obtained as above. The catalyst is still stable at this stage.

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DATE:

Apr 22, 82

(16)
Five of the above were reported measurements.

L. N. Mulay

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