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DOE/PC/51255-T1
(DE84007304)

Energy
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STUDIES ON TRANSITION METALS AND "ALLOY" FISCHER-TROPSCH CATALYSTS, THEIR ELECTRONIC AND BULK PROPERTIES

Final Report for the Period July 1, 1982—September 30, 1983

By
L. N. Mulay

November 1983

Work Performed Under Contract No. FG22-82PC51255

Pennsylvania State University
University Park, Pennsylvania

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DOE/PC/51255-T1
(DE84007304)
Distribution Category UC-90d

FINAL REPORT

Contract No. DE FG 22-82PC51255 (PETC)

STUDIES ON TRANSITION METALS AND "ALLOY" FISCHER-TROPSCH CATALYSTS, THEIR ELECTRONIC AND BULK PROPERTIES

(I: Fe/Mn ; II: Fe/TiO_2 III Fe/Mord.)

submitted by

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to

U.S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, PA 15236

November 1983

July 1, 1982 to Sept 30, 1983

(With No Cost Ext.Beyond June 30th)

STUDIES ON TRANSITION METALS AND "ALLOY" FISCHER-TROPSCH CATALYSTS, THEIR ELECTRONIC AND BULK PROPERTIES

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University Park, PA 16802

I. INTRODUCTION AND EXPERIMENTAL

As pointed out in the original proposal (funded on July 1, 1982) a number of Mössbauer spectroscopic and magnetic measurements were carried out to characterize Fe-Mn catalysts in the syngas reaction. The attention was focussed on "in-situ" characterization at various stages while the syngas reaction was taking place. In this final factual report, salient features of such experiments are outlined. We plan on writing a detailed paper with Dr. Diffenbach and coworkers at PETC) in the near future.

The Mössbauer drive unit and a transducer operating in a constant acceleration mode (Austin Science Associates, Inc.) was used with a ^{57}Co source in Rh matrix. Initially, a weak source was used which produced low count rate. A new 50 mCi ^{57}Co source was then installed and used for this study. The in-situ stainless steel Mössbauer cell (for use up to $\sim$4 atm. pressure) with external cylindrical "pencil" heaters connected in parallel to a three-mode temperature controller (Wistex 1542) was used in this study to obtain temperatures up to 900°K. Two reduction/syngas conditions were investigated: (a) the sample was reduced in H_2 (50 cc/min) at 250°C for 24 hrs and then kept in a syngas $CO/H_2 = 1:1$ (60 cc/min total gas flow) at 290°C for 24 hrs, (b) the sample was reduced in H_2 (30 cc/min) at 350°C for 24 hrs and then maintained in a $CO/H_2 = 1:1$ mixture (60 cc/min total gas flow) at 300°C for 24 hrs.

The magnetization measurements were carried out with a Vibrating Sample Magnetometer (Princeton Applied Research) which was appropriately modified for the present studies.

The sample (Iron Oxide 10%, Mn-Oxide 90%) was supplied by Dr. R. Diffenbach of PETC; hereafter, it will be referred to as D-1 ("as-received"), "reduced," "carbided," etc. All figures (1 to 10) are given at the end along with an Appendix describing research on the Fe/TiO_2 system. New results are given in Section IV, on samle D , 48% Fe-Mn. (see Chart I,P 5 A)

II. MÖSSBAUER SPECTROSCOPY

The room temperature spectrum of as-received (Fe-Mn) D-1 catalyst (Fig. 1) showed a doublet with isomer shift of 0.3 mm/sec (with respect to a standard NBS Fe foil) and a quadrupole splitting of 0.83 mm/sec arising from Fe^{3+} ions. The spectrum of the D-1 reduced in H_2 (50 cc/min) at 250°C for 24 hours, shown in Fig. 2 consisted of a sextet corresponding to metallic iron (∿46% reduction), a strong doublet corresponding to Fe^{2+} (∿49%), and a small doublet corresponding to Fe^{3+} (∿5%). The syngas reaction was carried out at 290°C with $CO:H_2$ ratio, 1:1 (60 cc/min total gas flow) for 24 hours. The spectrum for D-1 carbided, shown in Fig. 3 consisted of a mixture of Hägg carbide (χ-Fe_5C_2) and cementite (θ-Fe_3C) and Fe^{2+} ions. In addition, we also studied the reduction in H_2 (30 cc/min) at 350°C for 24 hours. As shown in Fig. 4, the spectrum consisted of a sextet corresponding to metallic iron (∿75%) and a doublet corresponding to Fe^{2+} ions. The Fe^{2+} probably arises from FeO or FeOOH. Higher reduction to Fe (∿80%) was achieved at a relatively high temperature (∿380°C). The spectrum shown in Fig. 5, collected after 24 hours syngas reaction at 300°C, consisted of Fe^{2+} and very small amount of carbides. This is probably due to the formation of coke which inhibits the formation of iron carbide. The deposition of coke also weakens the intensity of the spectra. Further investigation is in progress to interpret this spectrum.

Magnetic studies discussed in the next section seem to indicate the formation of Mn-ferrite ($MnFe_2O_4$(, which is generally formed with ease by substitution of Mn^{2+} at appropriate Fe sites in the spinel structure of γ-Fe_2O_3 . The presence of Mn-ferrite can be confirmed by Mössbauer Spectroscopy when further work is done with an "enriched" or a "concentrated" iron sample.

III. MAGNETIC STUDIES

This research consisted of two types of measurements: (a) magnetization (σ in emu/g of Fe) as a function of the field (H in Oersteds) and/or temperature (T in degrees K) to obtain information on average particle size from σ vs H/T curves in appropriate cases and (b) the thermomagnetic measurements; that is, measuring (saturation) magnetization (σ in emu/g of Fe) as a function of T. The thermomagnetic measurements are helpful in detecting the presence of two or more phases of Fe, and in appropriate cases these are helpful in identifying the phases via their Curie temperatures (T_c). Although T_c depends somewhat on the particle size and may get shifted because of the presence of other component(s), the apparent T_c values do provide an insight into solid-state reactions, or "strong metal support interactions (SMSI)," in the parlance of catalysis. Mössbauer spectroscopy is equally well-suited in detecting SMSI. Fig. 6 shows (saturation) σ vs H for the as-received D-1 sample. This indicated that the sample consisted of fine particles of γ-Fe_2O_3 and Mn-ferrite. The thermomagnetic measurements for the same sample shown in Fig. 7 displayed a T_c (at the inflection point) of about 280°C which agrees fairly well with that of Mn-ferrite. It appears that during the thermomagnetic measurements more of γ-Fe_2O_3 was converted to the Mn-ferrite.

The D-1 as-received sample was reduced at 250°C in a stream of H_2 (flow rate $\sim$30 cc/min) for 24 hurs. The saturation magnetization of the reduced sample (Fig. 8) was found to be 70 emu/g which showed $\sim$30% reduction. The extent of reduction was low because of "mild" reduction conditions. The thermomagnetic studies of the reduced D-1 sample (Fig. 9) showed no distinct T_c for metallic Fe. On the other hand, on sustained heating, the formation of Mn-ferrite could be confirmed.

The D-1 reduced sample when exposed to CO:H_2 (1:1) indicated the presence of Mn-ferrite and iron carbides (Fig. 10). The T_c of the suspected carbides was intermediate between the T_c of Fe_3C or Fe_5C_2 indicating the presence of both phases.

IV. NEW RESULTS ON MOSSBAUER SPECTROSCOPY

The spectra obtained for (48% Fe) Mn are shown in Figures 11 to 24 and are self-explanatory with respect to Chart I.

APPENDIX I Mössbauer Spectroscopy of Fe/TiO$_2$ System

In addition to the Fe/MnO work outlined before, Mössbauer spectra of samples NK-1 and NK-2 were obtained. The spectra and our (tentative) conclusions were sent to Dr. V.U.S. Rao of PETC on March 17, 1983. The spectra are not repeated in this report.

Weak intensities were observed due to the presence of TiO$_2$ as a substrate and a relatively weak source ∿10 mCi source [for about 7 days (experiments will be repeated with our new 50 mCi source, which was installed on March 17, 1983. Measurements will take approximately 8 weeks because of a backlog of several DOE and other samples]. Other workers have found that TiO$_2$ substrate absorbs considerable amounts of γ-ray radiation. Spectra were obtained relative to Fe foil using an Austin spectrometer and ND-100 MCA.

NK-1 (Fresh, 300 K) Isomer Shift (δ) is small, possibly due to (i) the presence of Fe^{3+} (high valence), (ii) (CO) groups from Ligands and (iii) Fe-Ti bonding (metal support interaction--resembling an ilmenite structure, i.e., iron titanate--FeTiO$_3$). Asymmetry of the central doublet may be ascribed to the anisotropy of particles and their small size.

Small shoulders are indicative of magnetic ordering in bulk material. This aspect may be studied further at a later date, which is expected to reveal SMSI.

NK-2 (Fresh 300 K) Spectrum is less discernible than NK-1. The spectrum at first glance is similar to that of NK-1; the central doublet, however, is more symmetrical. Other aspects are similar to that of NK-1.

Unfortunately, information was not given on the Fe content in NK-1 and NK-2, which has prevented us from making prudent interpretations. If this work is to be continued at a modest level, more analytical information on the two samples, XRD, etc. should be given, and the requested funding level should be maintained. It should be noted that the Mössbauer spectroscopy, which is a powerful probe for structural analysis at the microscopic level is rather expensive. It takes about 25 days to obtain a good spectrum under "in-situ" conditions from the time one prepares a thin disc of the sample, records the spectrum, transfers it on a Cal-comp plotter and does computer fitting so as to arrive at reliable interpretations.

Fe / Mn CATALYSTS

Dr. R. Diff } PETC July 82 - ON
Dr. Tisher }

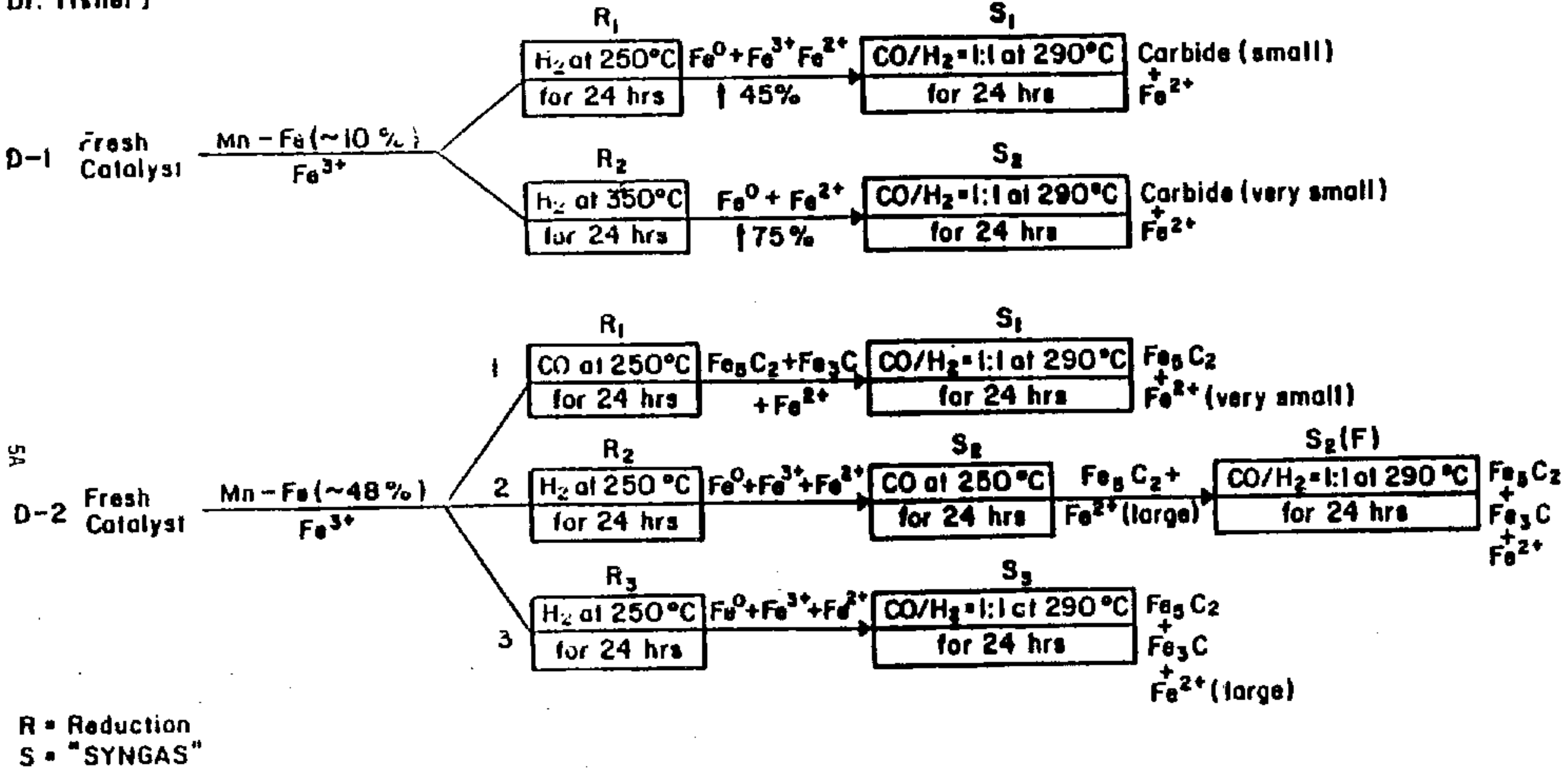


CHART : I Showing sequence of Reduction (R_1 , R_2 , etc.) and Syngas (S_1, S_2 , etc.) conditions. These codes are used in Figs 1 to 24.

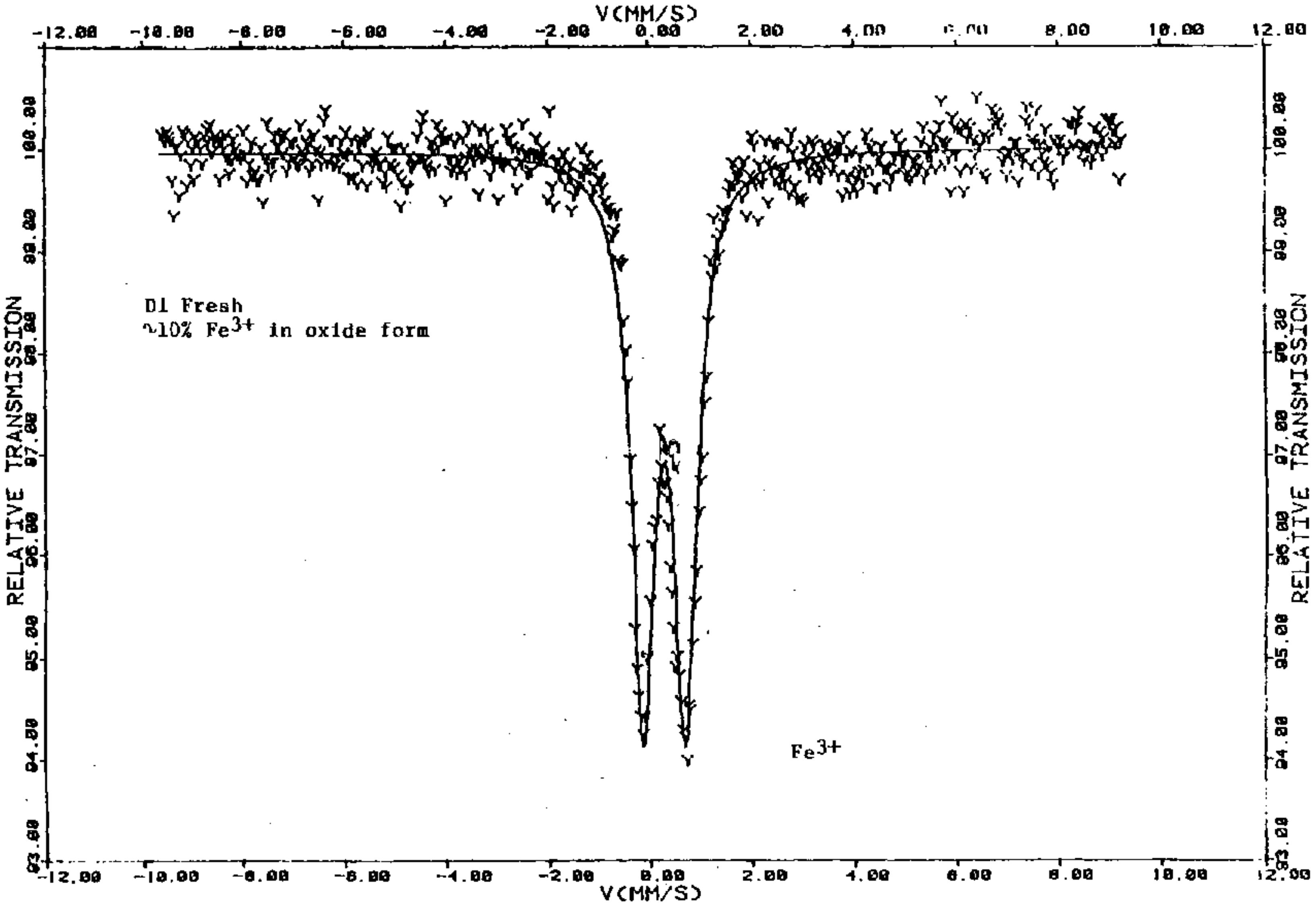


Fig. 1 Room temperature Mössbauer spectrum of as-received Fe-oxide/Mn-oxide [Fe ~10%] - D1.

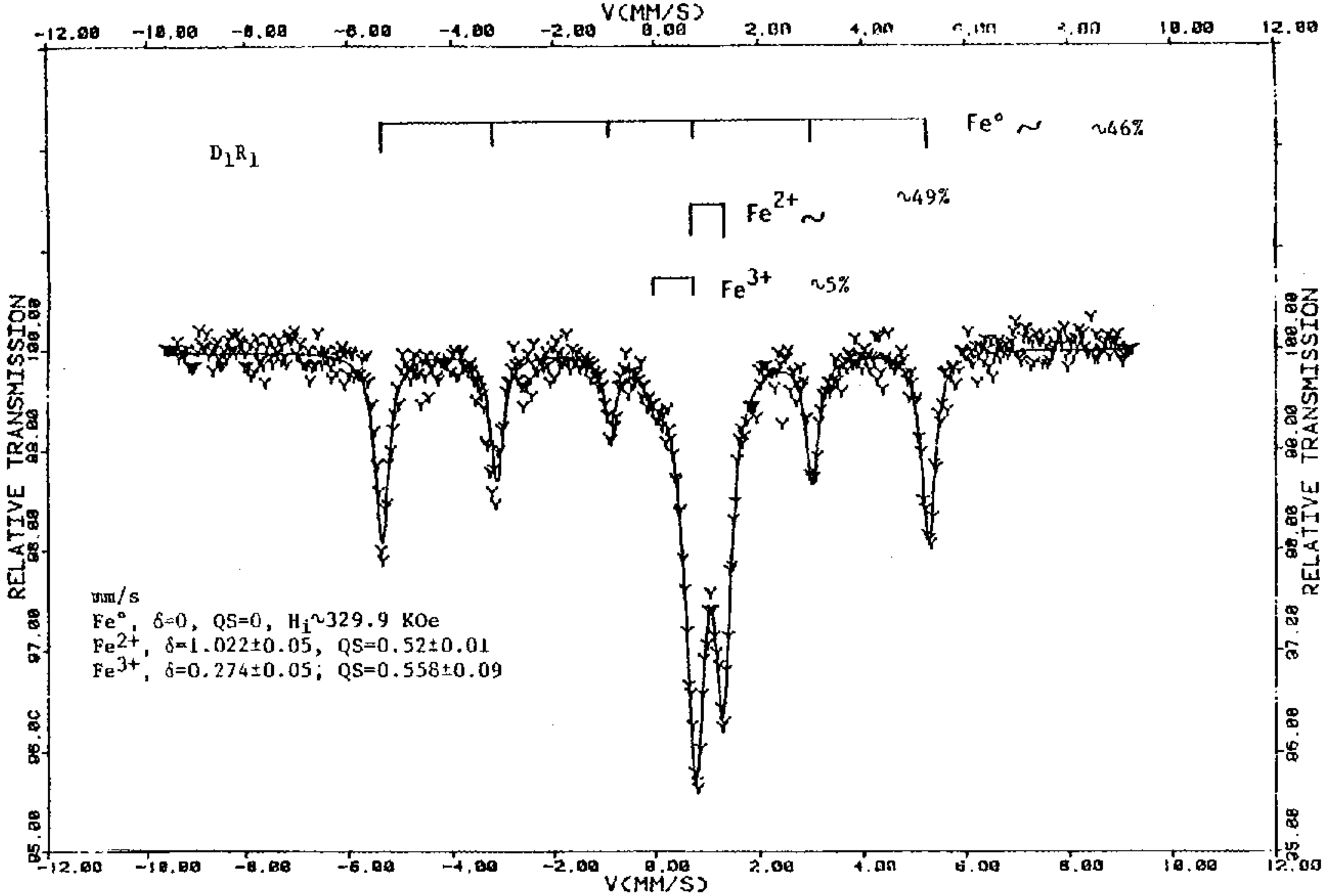


Fig. 2 Room temperature Mössbauer spectrum of reduced sample D-1 in H_2 (50 cc/min) at 250°C for 24 hours, showing ∿46% reduction.

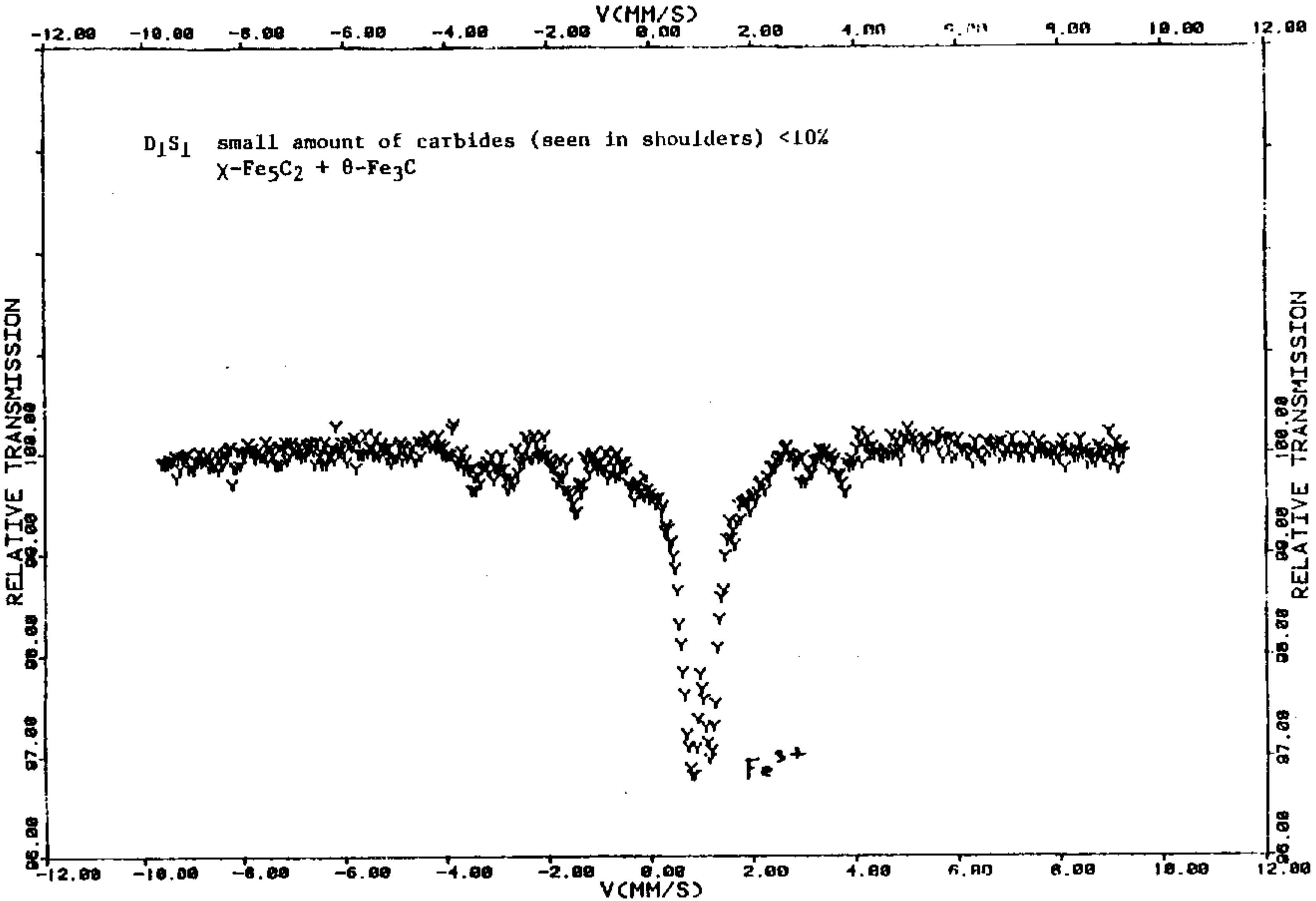


Fig. 3 RT spectrum of sample D-1 after syngas reaction at 290°C with CO/H$_2$ (1:1) for 24 hours.

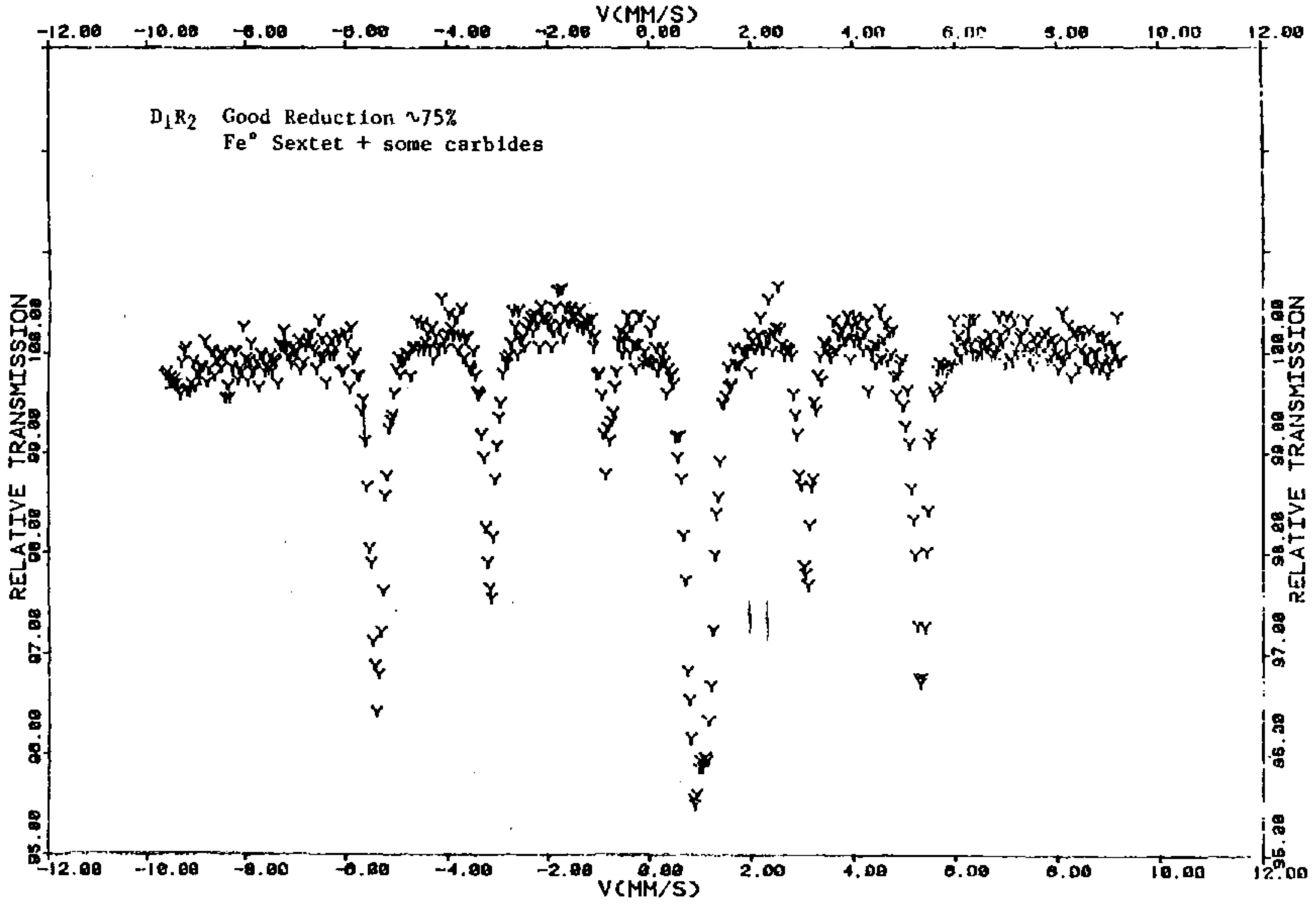


Fig. 4 RT spectrum of reduced sample D-1 in H_2 (30 cc/min) at 350°C for 24 hours, showing ∿75% reduction.

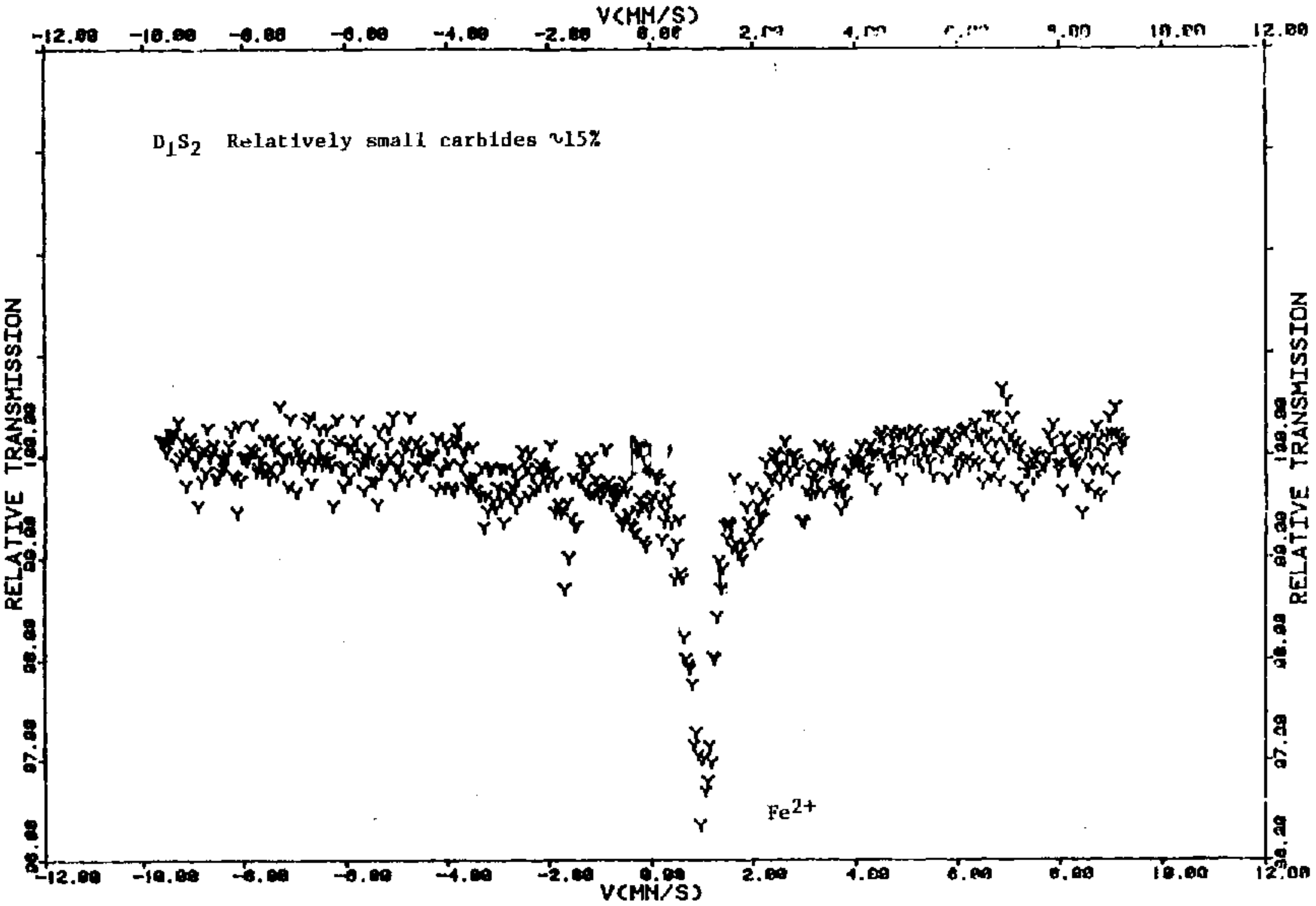


Fig. 5 RT spectrum of sample D-1 after syngas reaction at 300°C with CO/H_2 (1:1) for 24 hours.

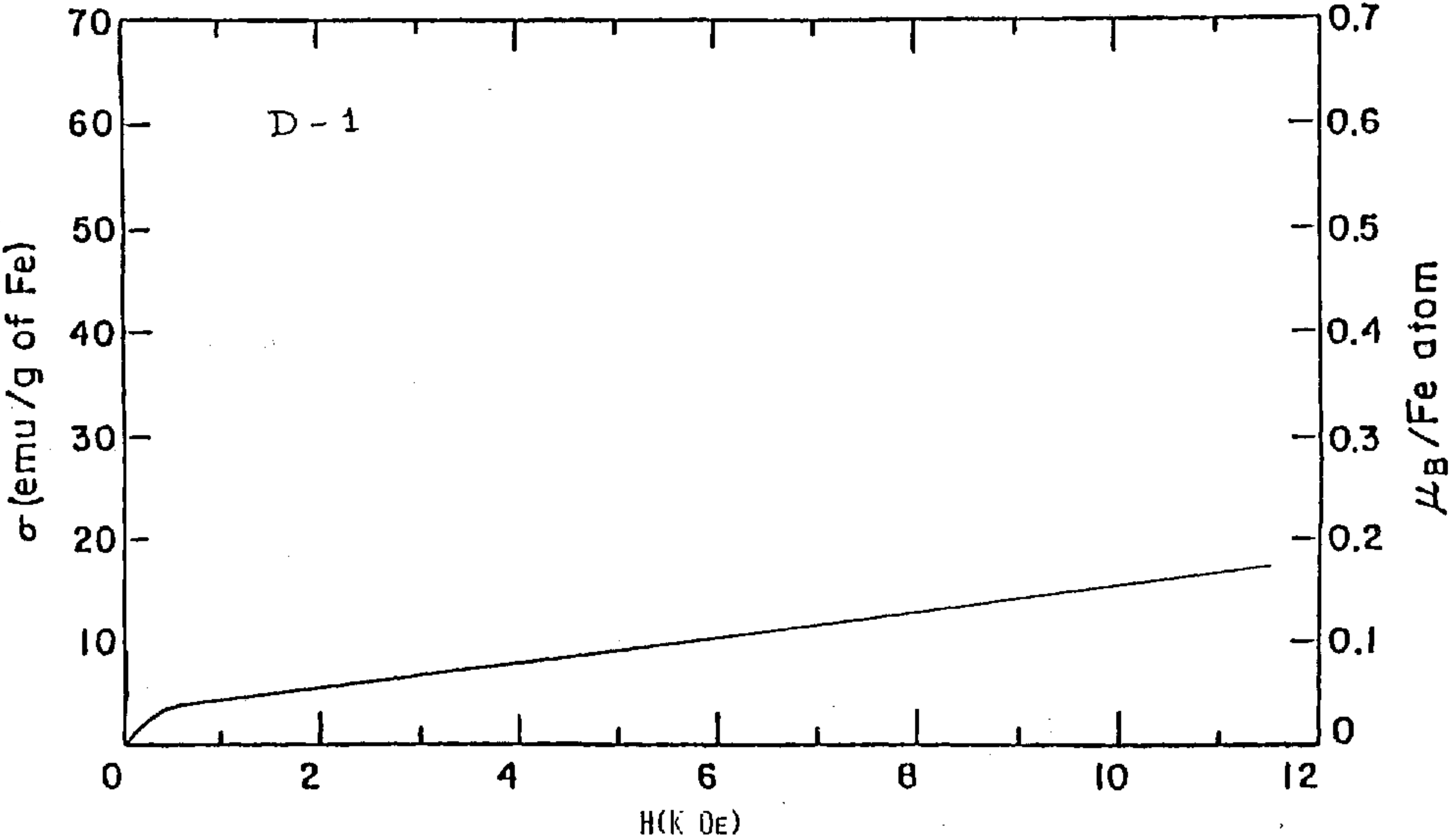


Fig. 6 Magnetization as a function of the field for the as-received Fe-oxide/Mn-oxide [Fe ~ 10%] - D1

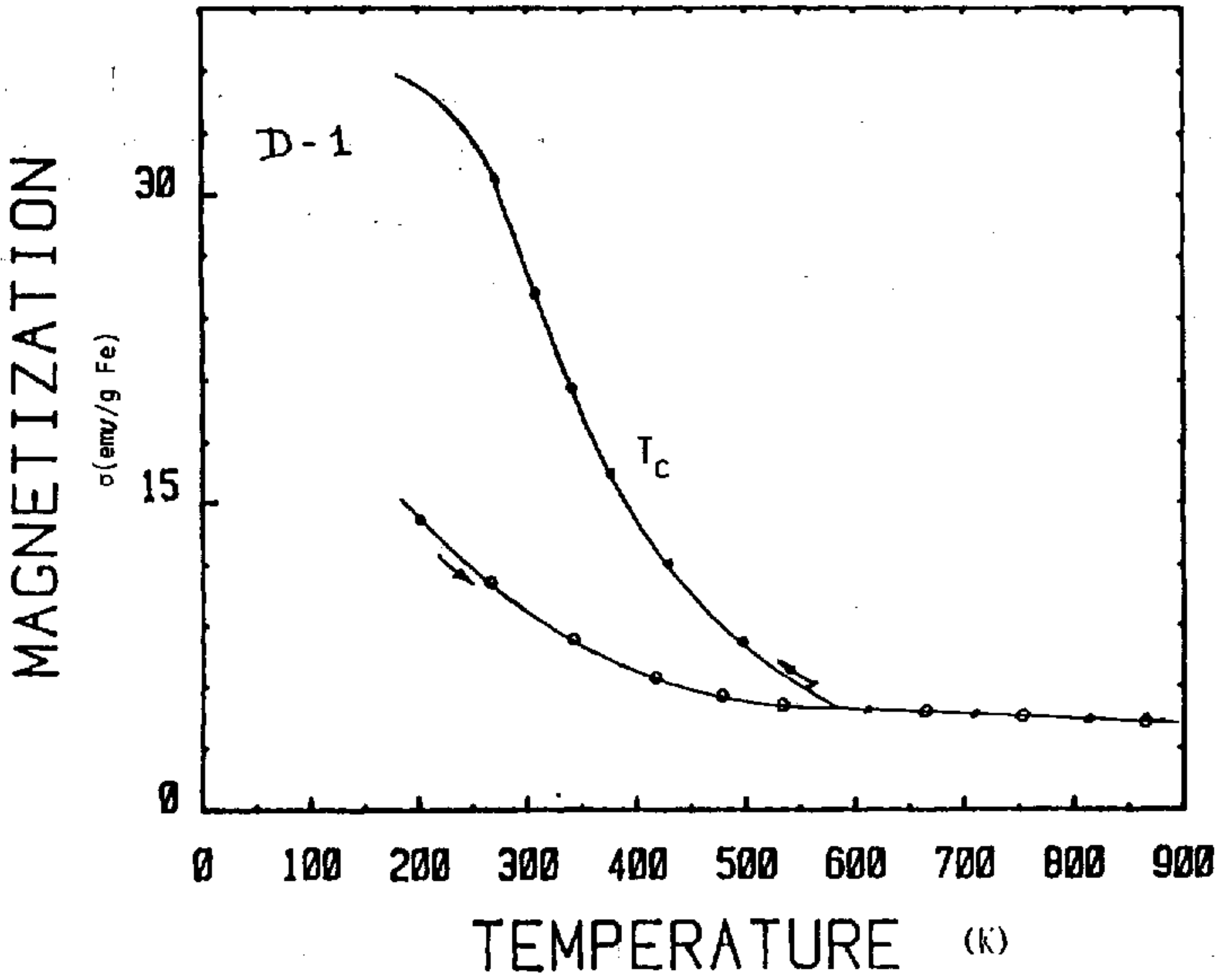


Fig. 7 Thermomagnetic measurements for sample D-1 (see Fig. 6).

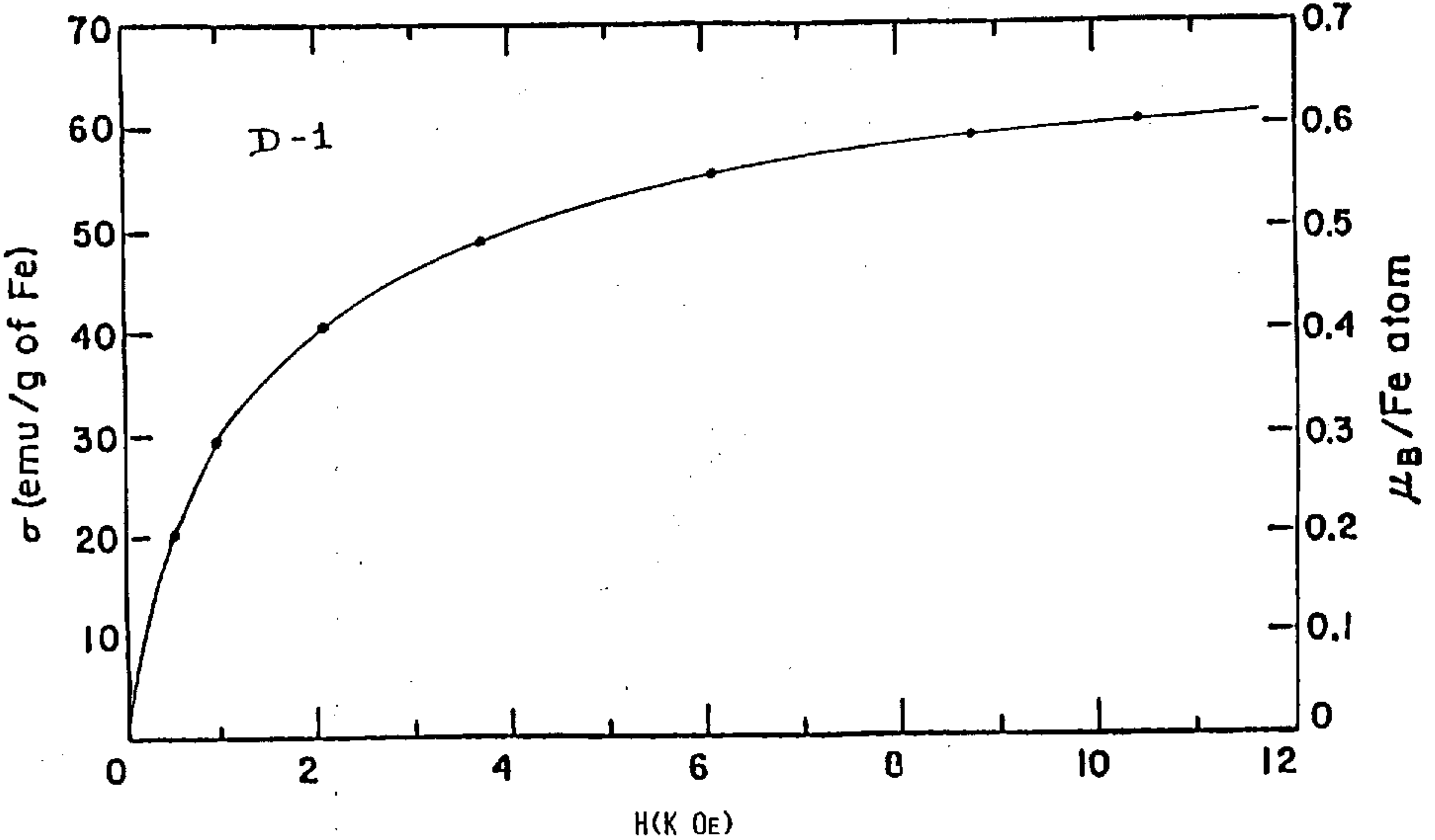


Fig. 8 Magnetization as a function of the field for reduced sample D-1, showing ~30% reduction to Fe under "mild" conditions (see text).

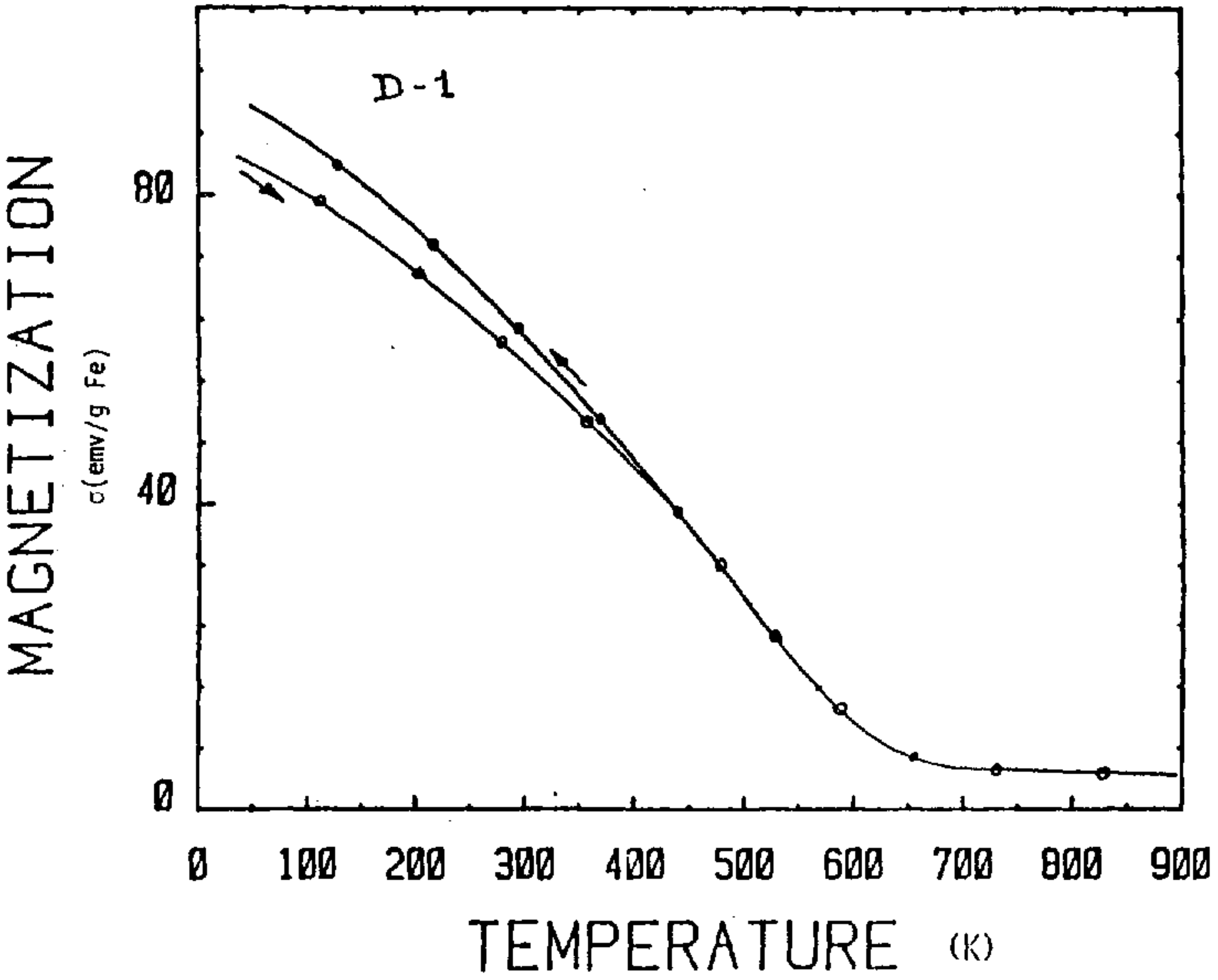


Fig. 9 Thermomagnetic measurements for reduced sample D-1. On coolong the σ_s is seen to correspond to Mn-ferrite.

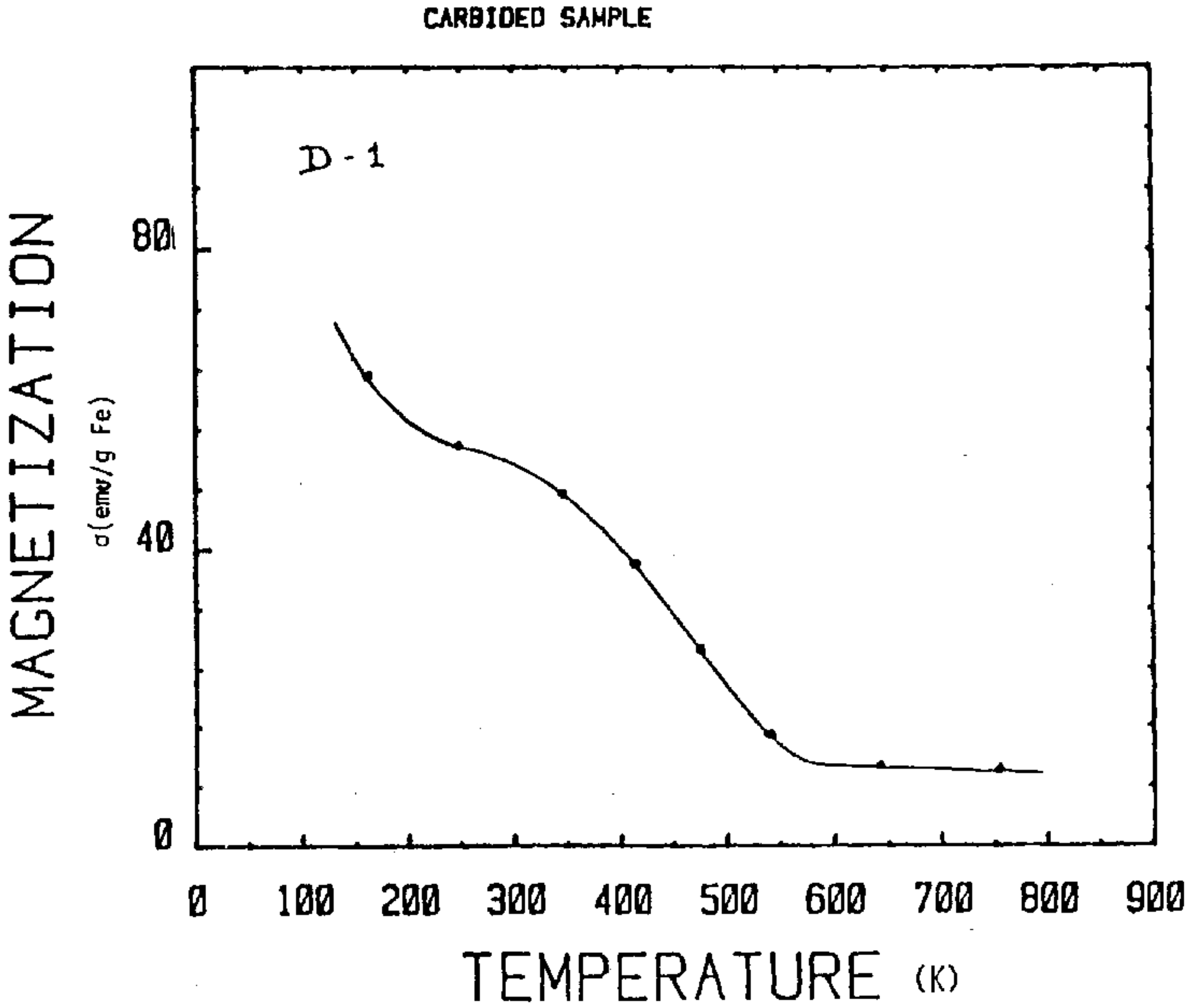


Fig. 10 σ vs T curves for reduced sample D-1 exposed to CO + H_2 (1:1). Presence of Mn-ferrite and a mixture of "Fe-carbides" is inferred.

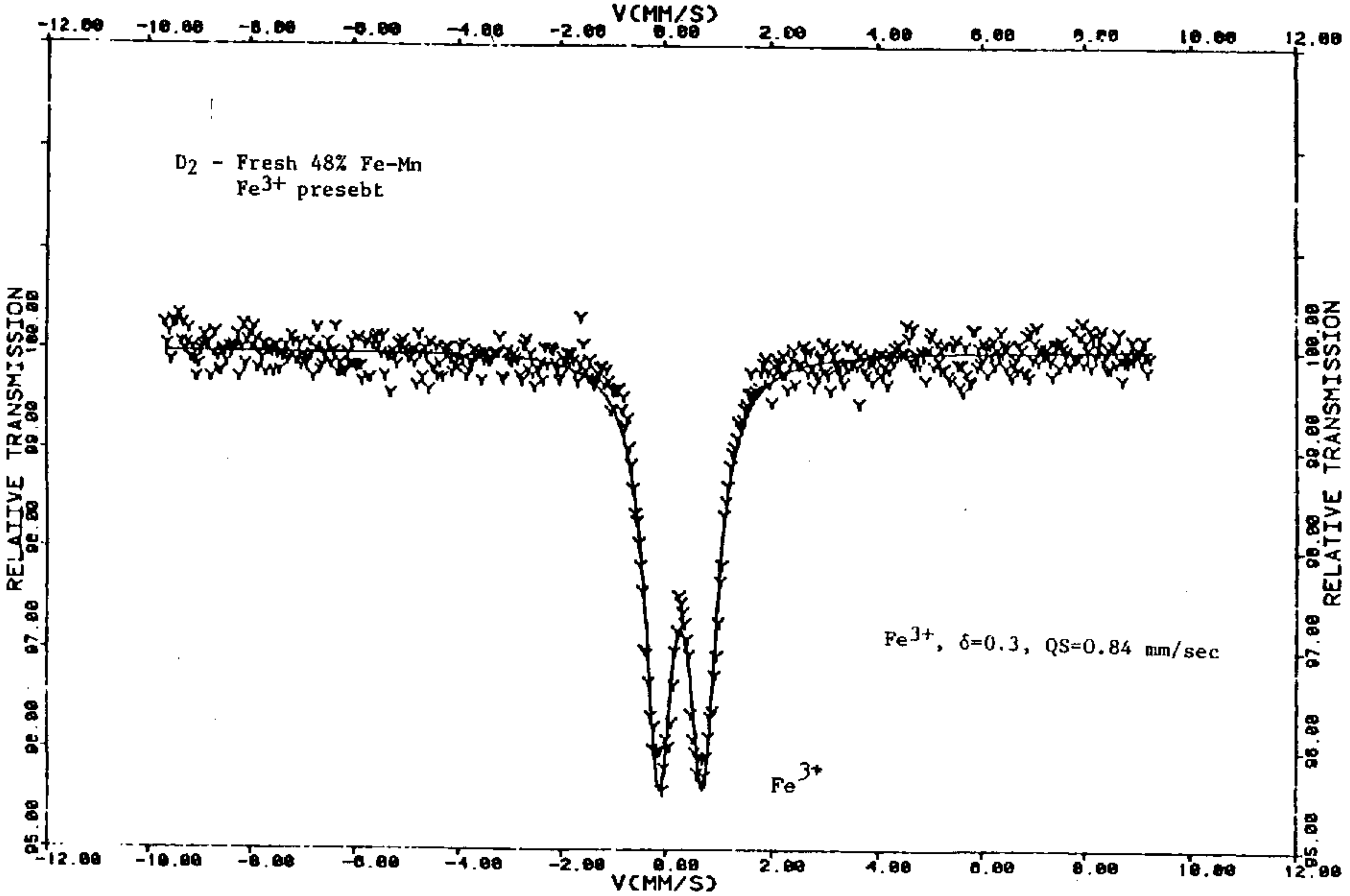


Figure 11. Mn-Fe (~48%) Fresh catalyst.

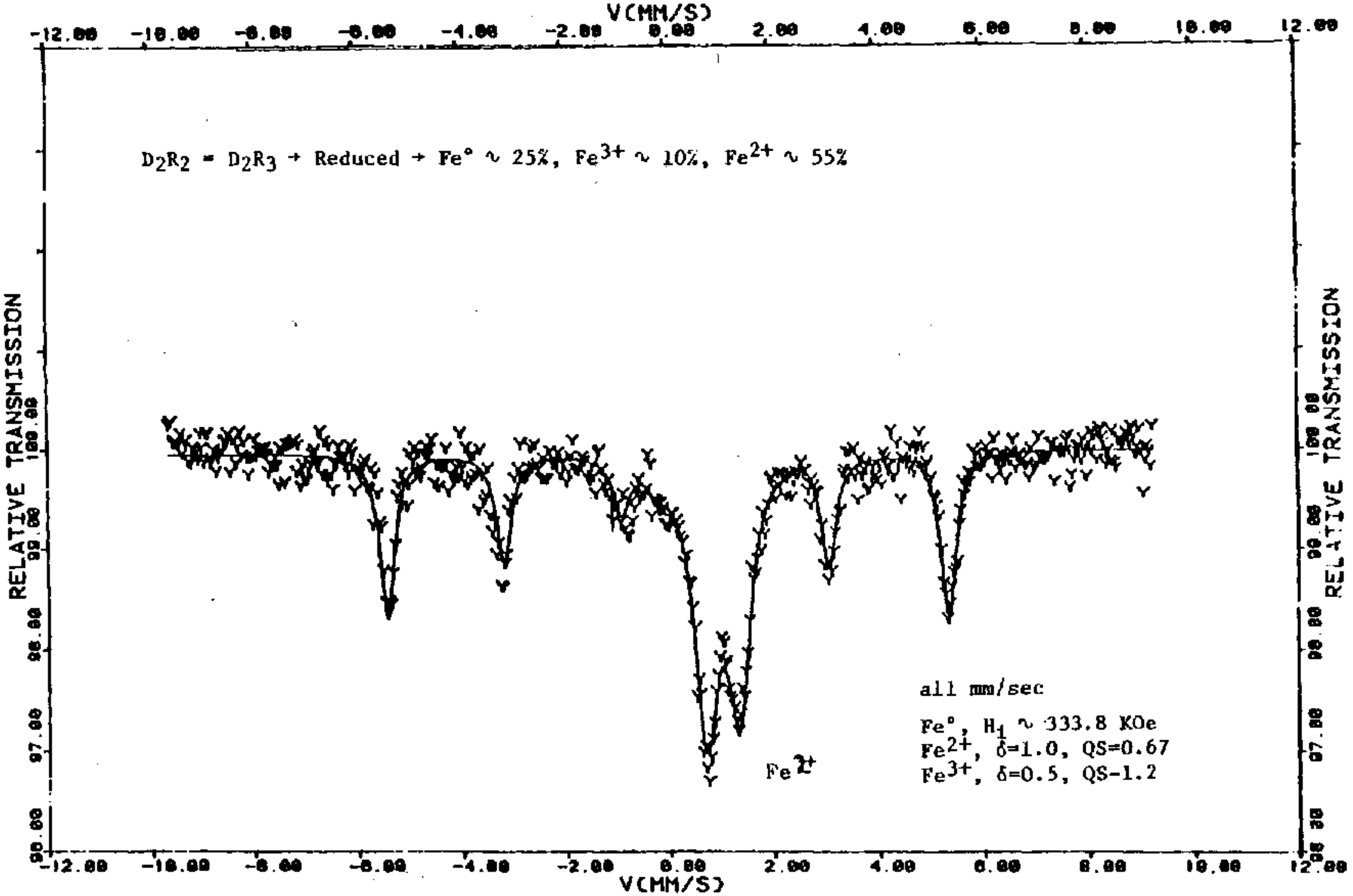


Figure 12. Mn-Fe (-48%) reduced at 250°C, 24 hrs, H_2 = 30 cc/min.

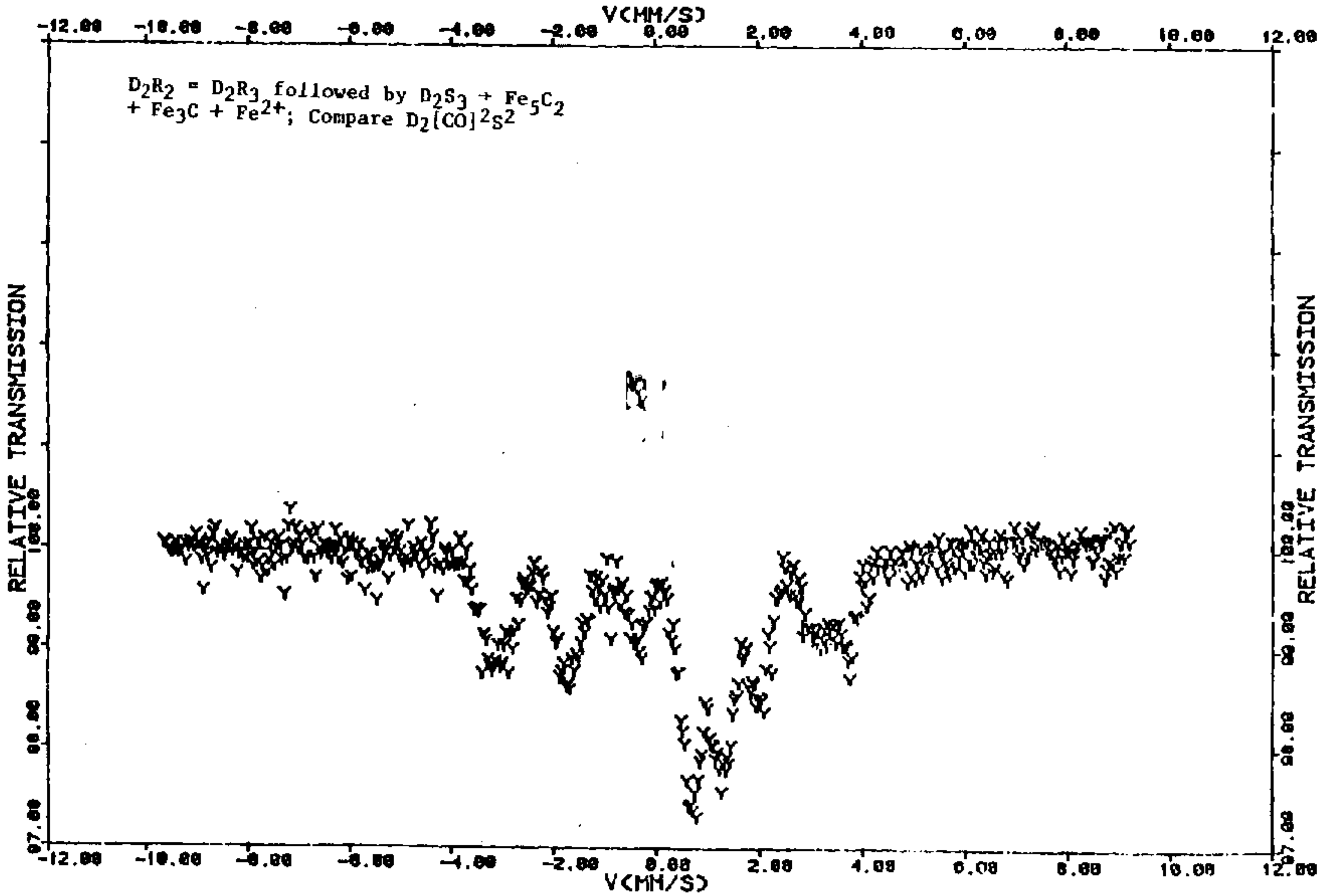


Figure 13. (~48%) Fe-Mn Syngas CO/H_2 = 1:1 (60 cc/min total) at 290°C for 24 hrs. (This sample was first reduced by H_2 at 250°C for 24 hrs.)

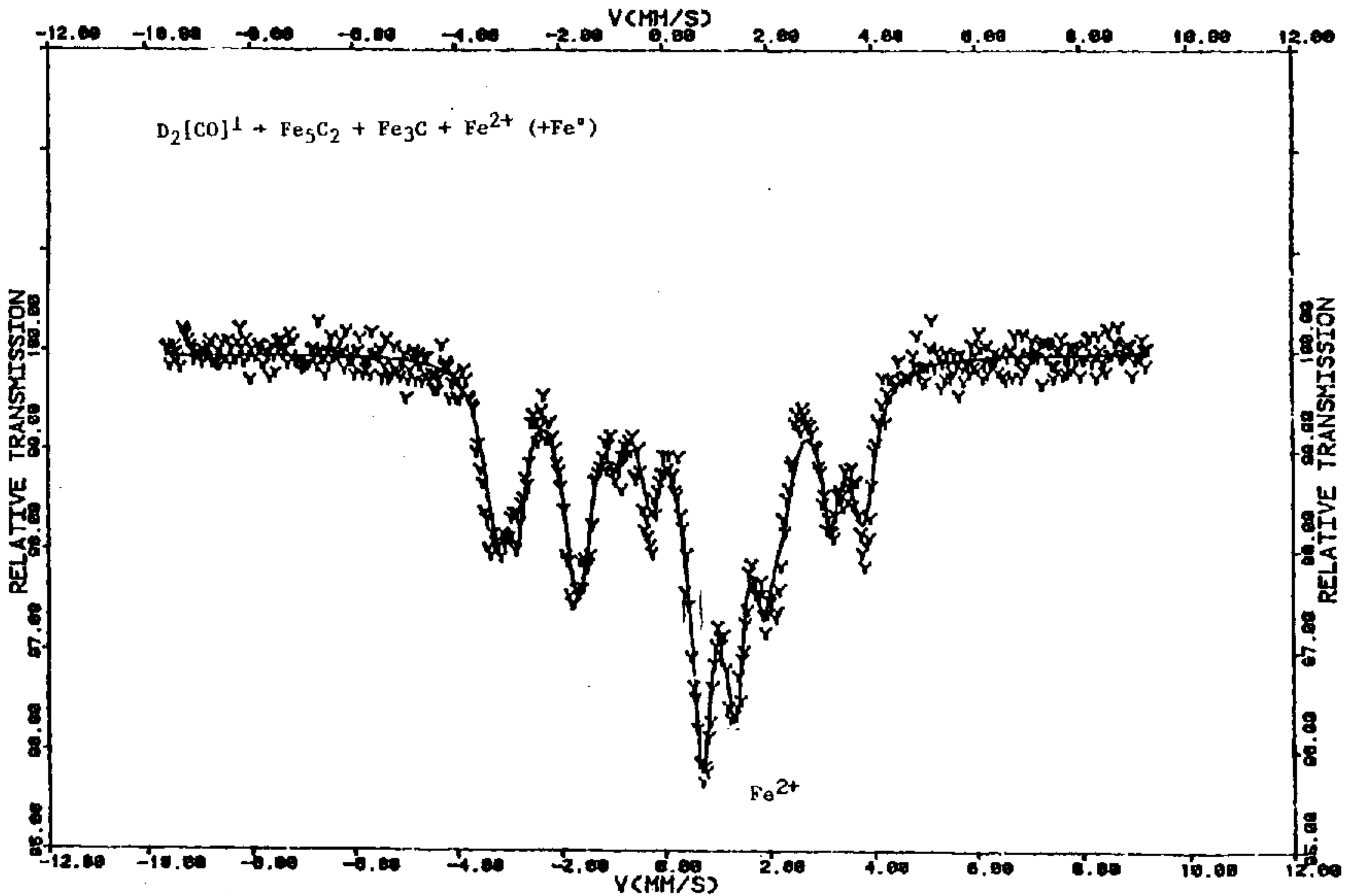


Figure 14. (~48%) Fe-Mn CO (30 cc/min) at 250°C for 24 hrs.

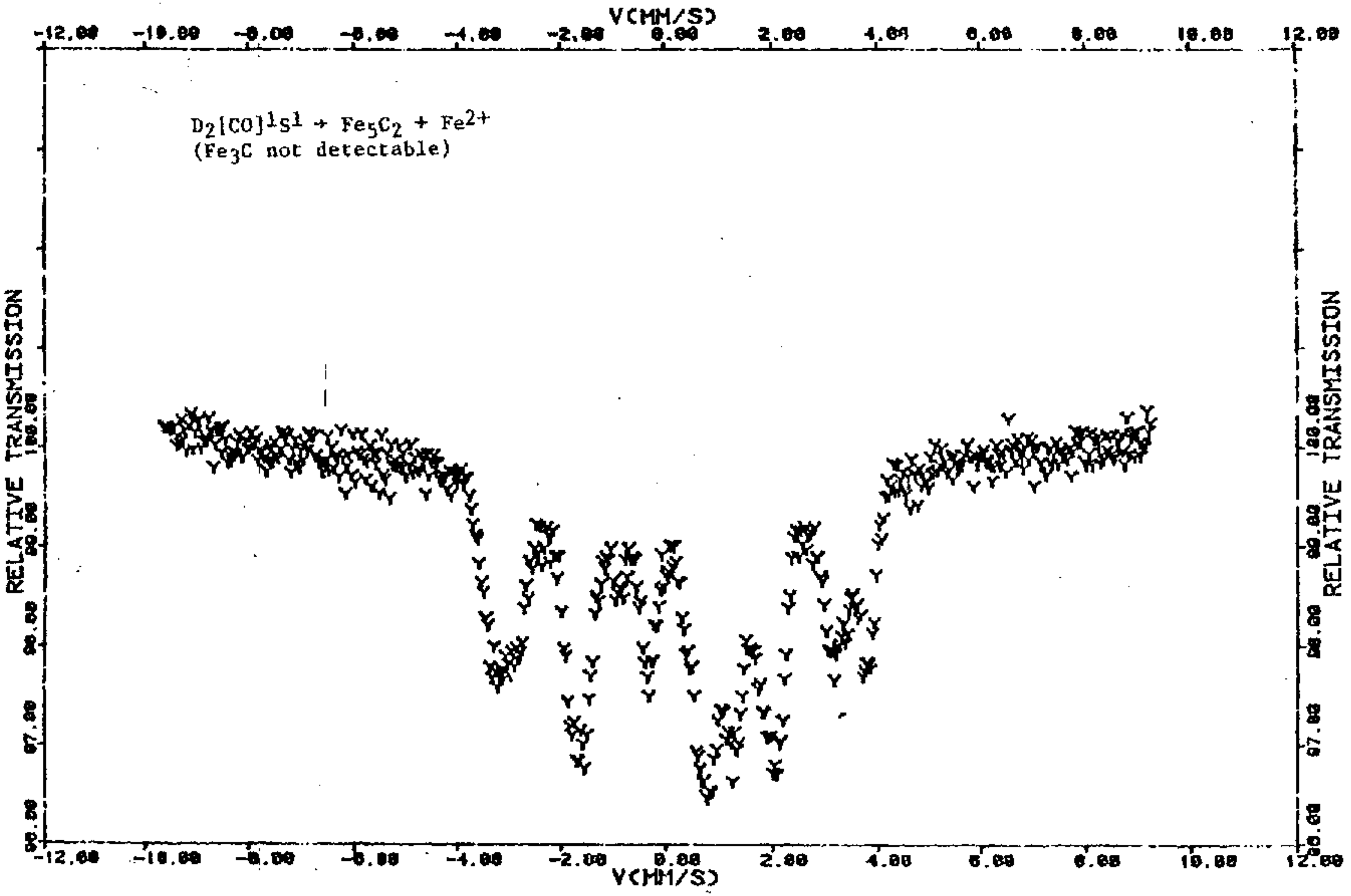


Figure 15. (~48%) Fe-Mn Syngas CO/H_2 = 1:1 (60 cc/min total) at 290°C for 24 hrs. (This sample was first treated by CO at 250°C for 24 hrs.)

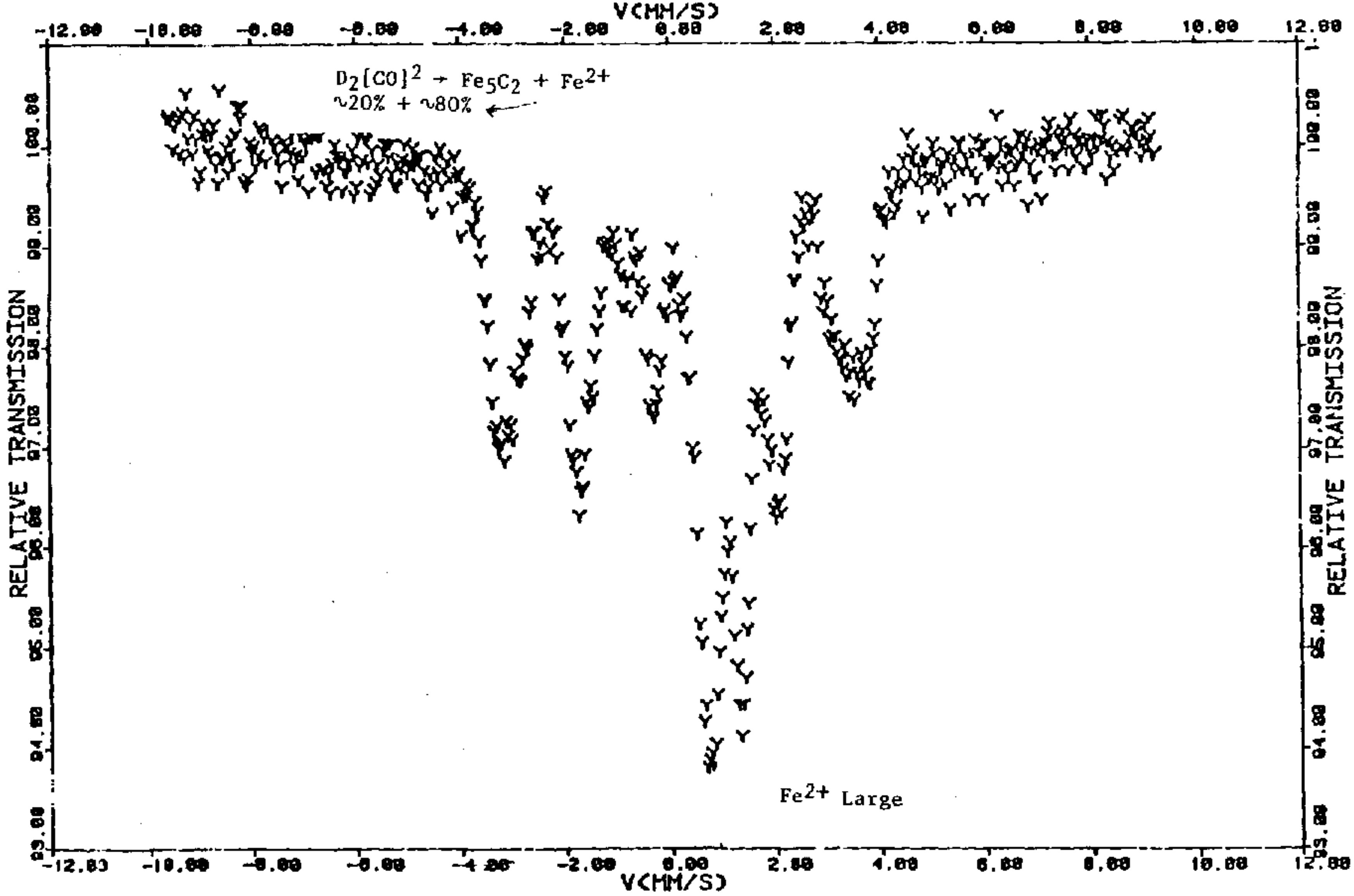


Figure 16. (~48%) Fe-Mn CO (30 cc/min) at 250°C for 24 hrs. (This Sample was first reduced by H_2 (30 cc/min) at 250°C for 24 hrs.)

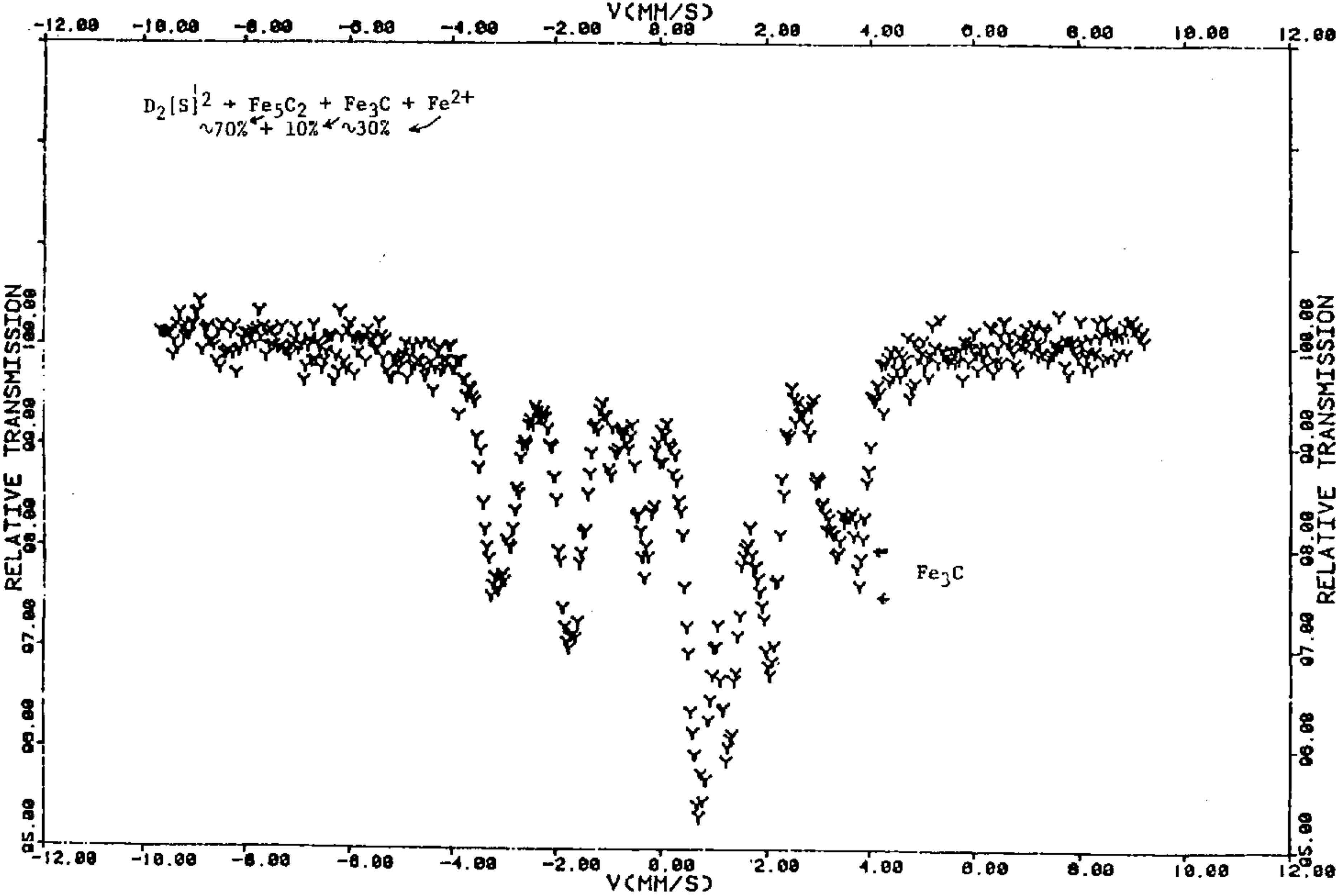


Figure 17. (48%) Fe-Mn Syngas CO/H_2 = 1:1 (60 cc/min total) at 290°C for 24 hrs. (This sample was reduced by H_2 and treated by CO at 250°C for 24 hrs consequently.)

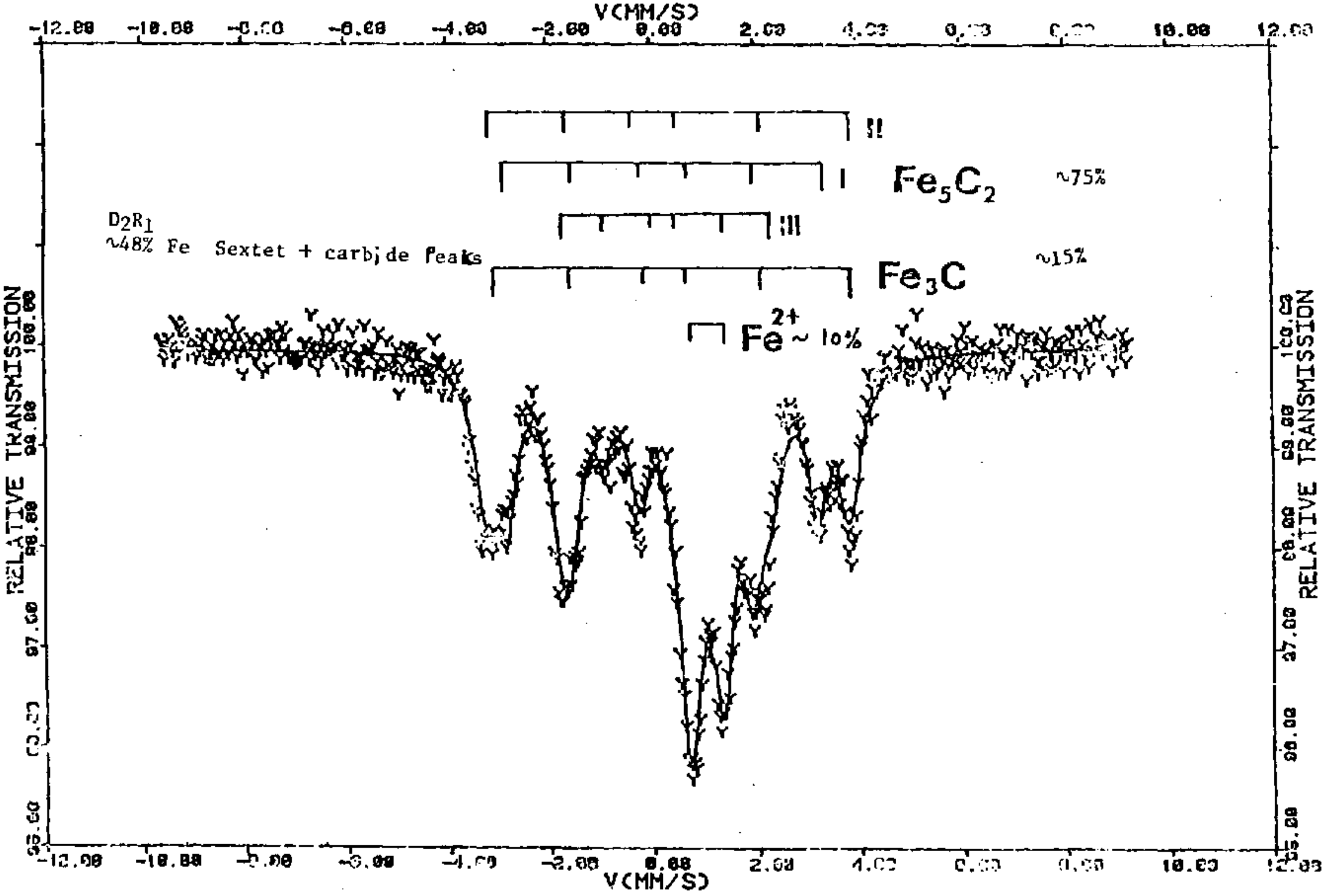


Figure 18. 48% Fe-Mn carbided with CO as before.

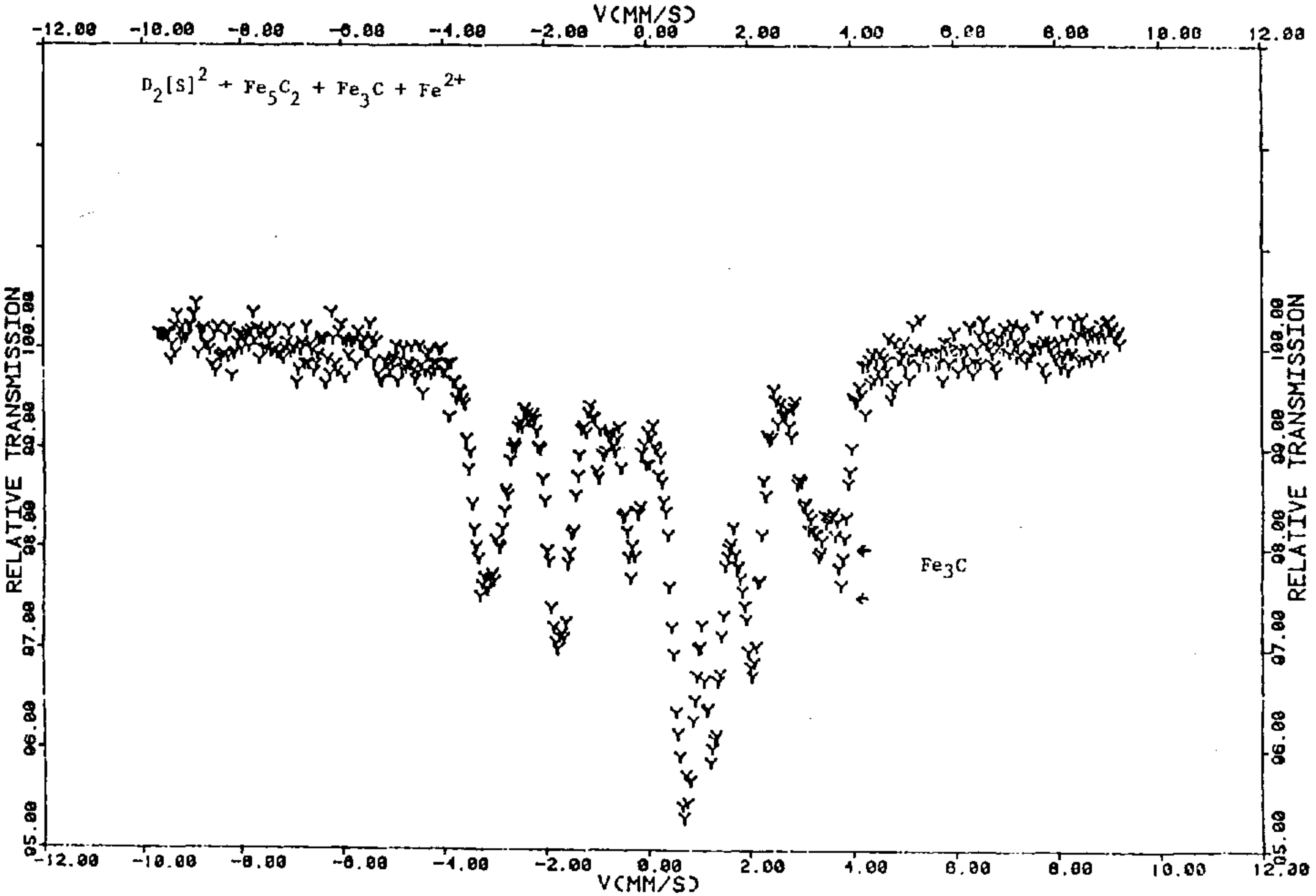


Figure 19. (48%) Fe-Mn Syngas CO/H_2 = 1:1 (10 cc/min) at 290°C for 24 hrs. (This sample was reduced by H_2 and treated by CO at 250°C for 24 hrs consequently.)

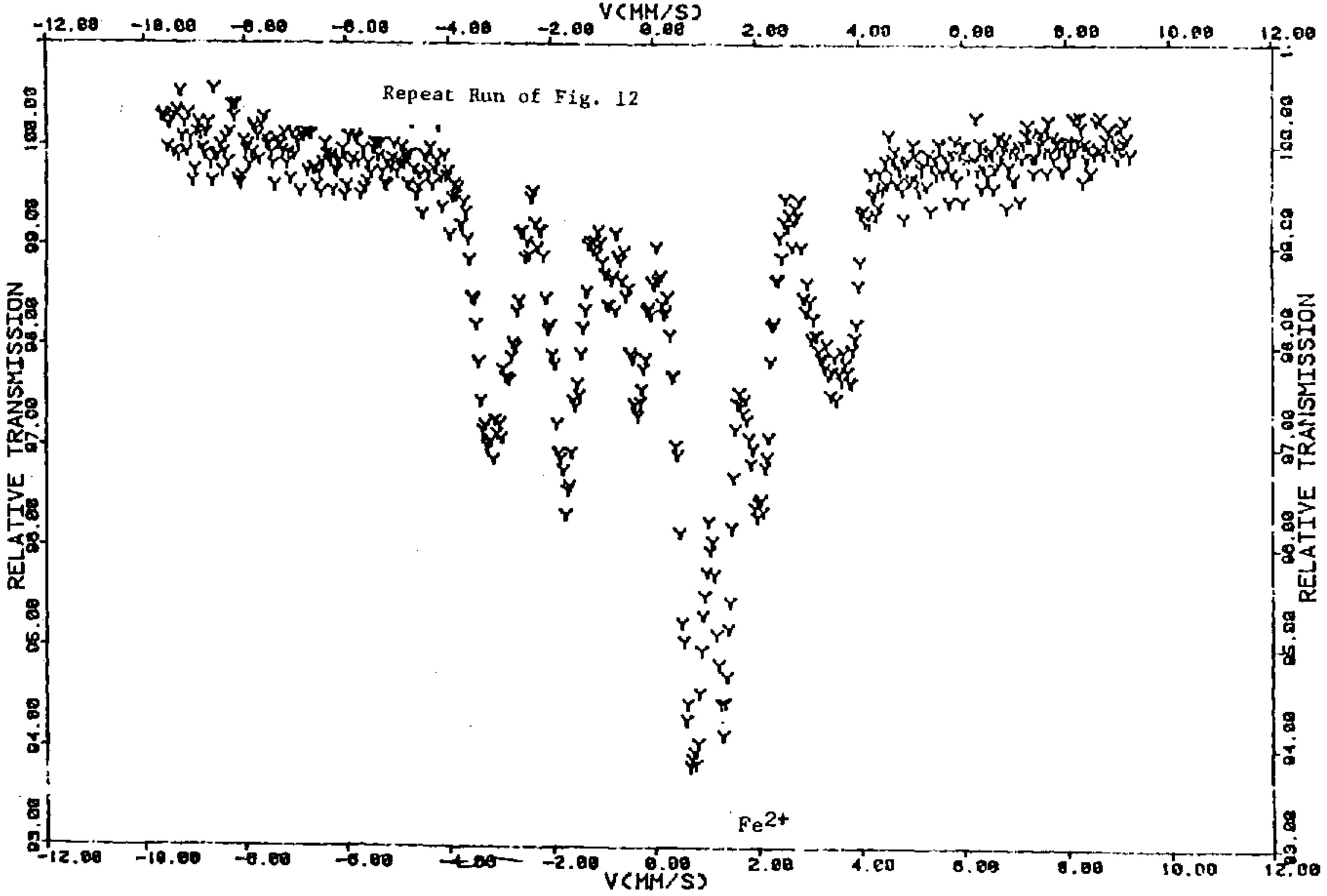


Figure 20. (~48%) Fe-Mn CO (30 cc/min) at 250°C for 24 hrs. (This sample was first reduced by H_2 (30 cc/min) at 250°C for 24 hrs.)

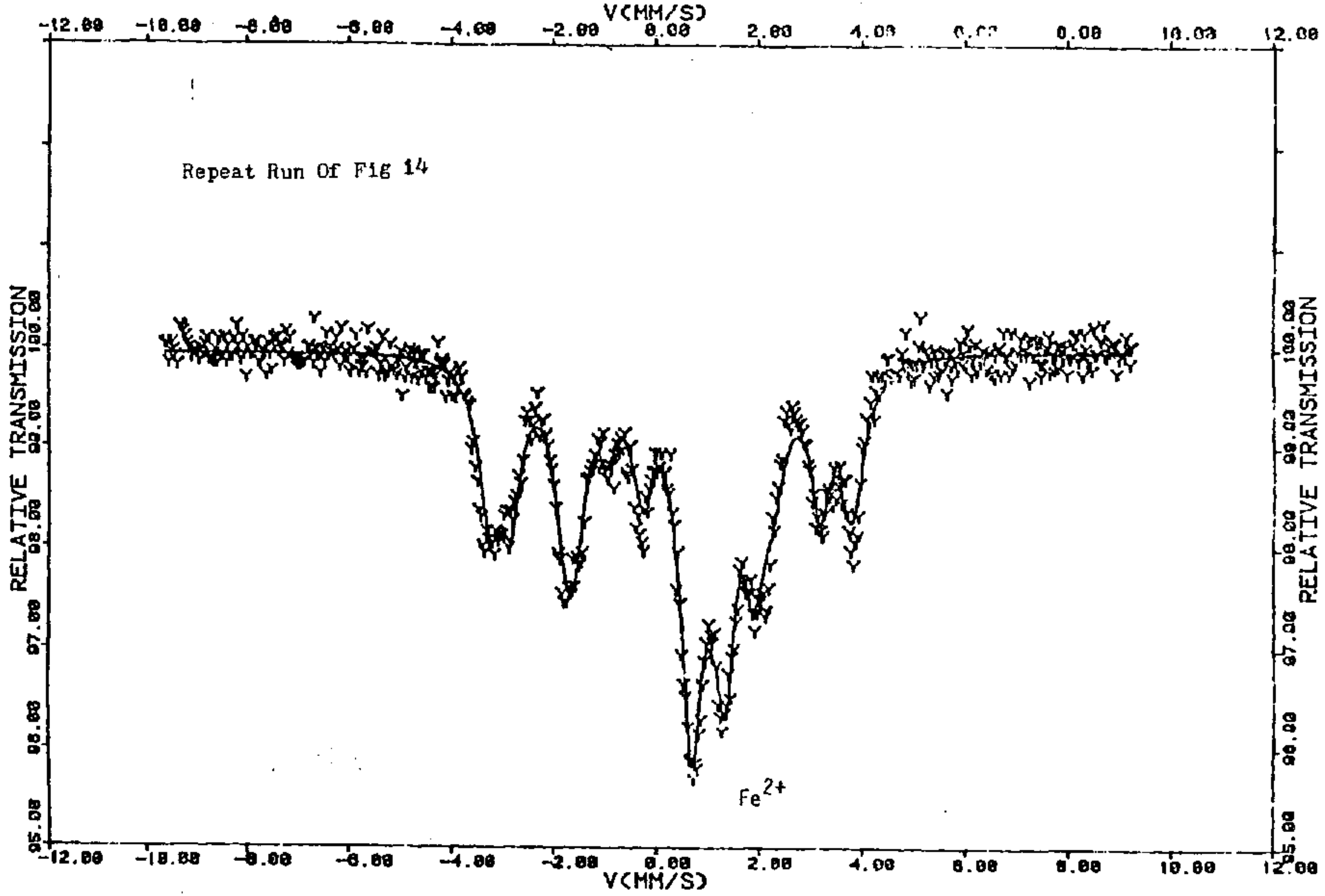


Figure 21. (~48%) Fe-Mn CO (30 cc/min) at 250°C for 24 hrs.

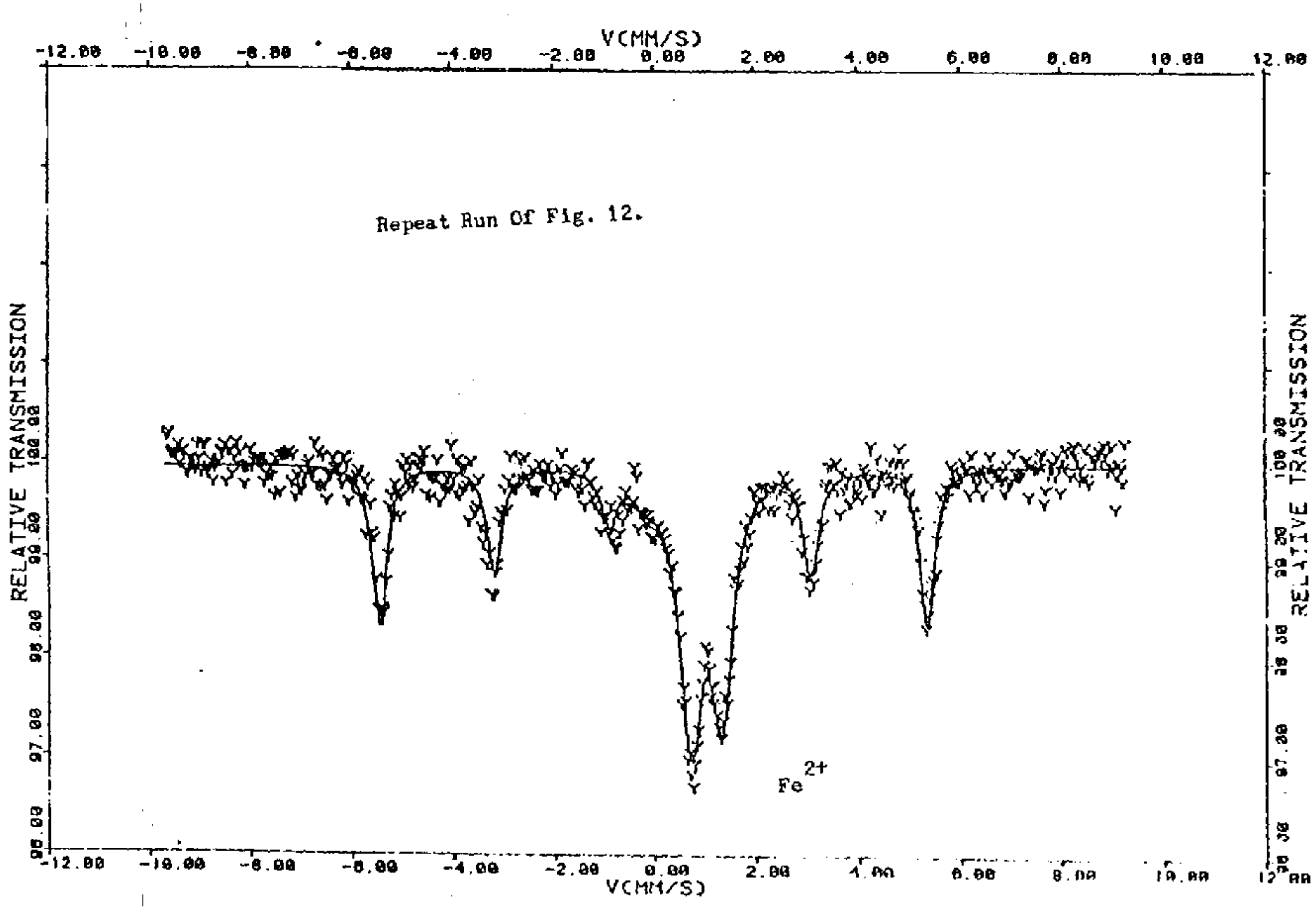


Figure 22. MnFe (-48%) reduced at 250°C, 24 hrs, H_2 = 30 cc/min, Fe° = H.F. = 333.8 KOe; Fe^{2+} = I.S. = 1.0 mm/sec Q.S. = 0.67 mm/sec; Fe^{3+}:I.S. = 0.5 mm/secQ.S. = 1.2 mm/sec.

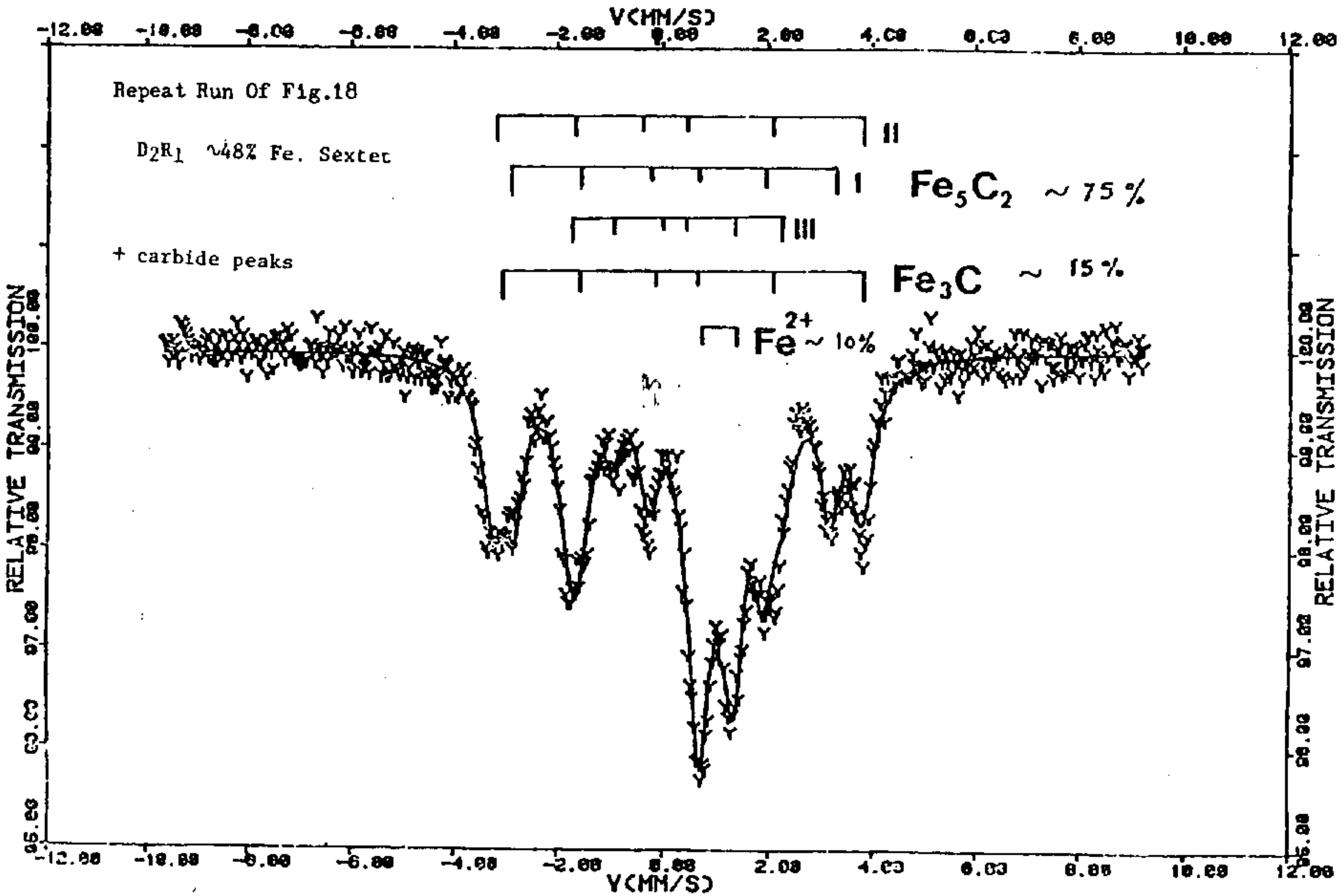
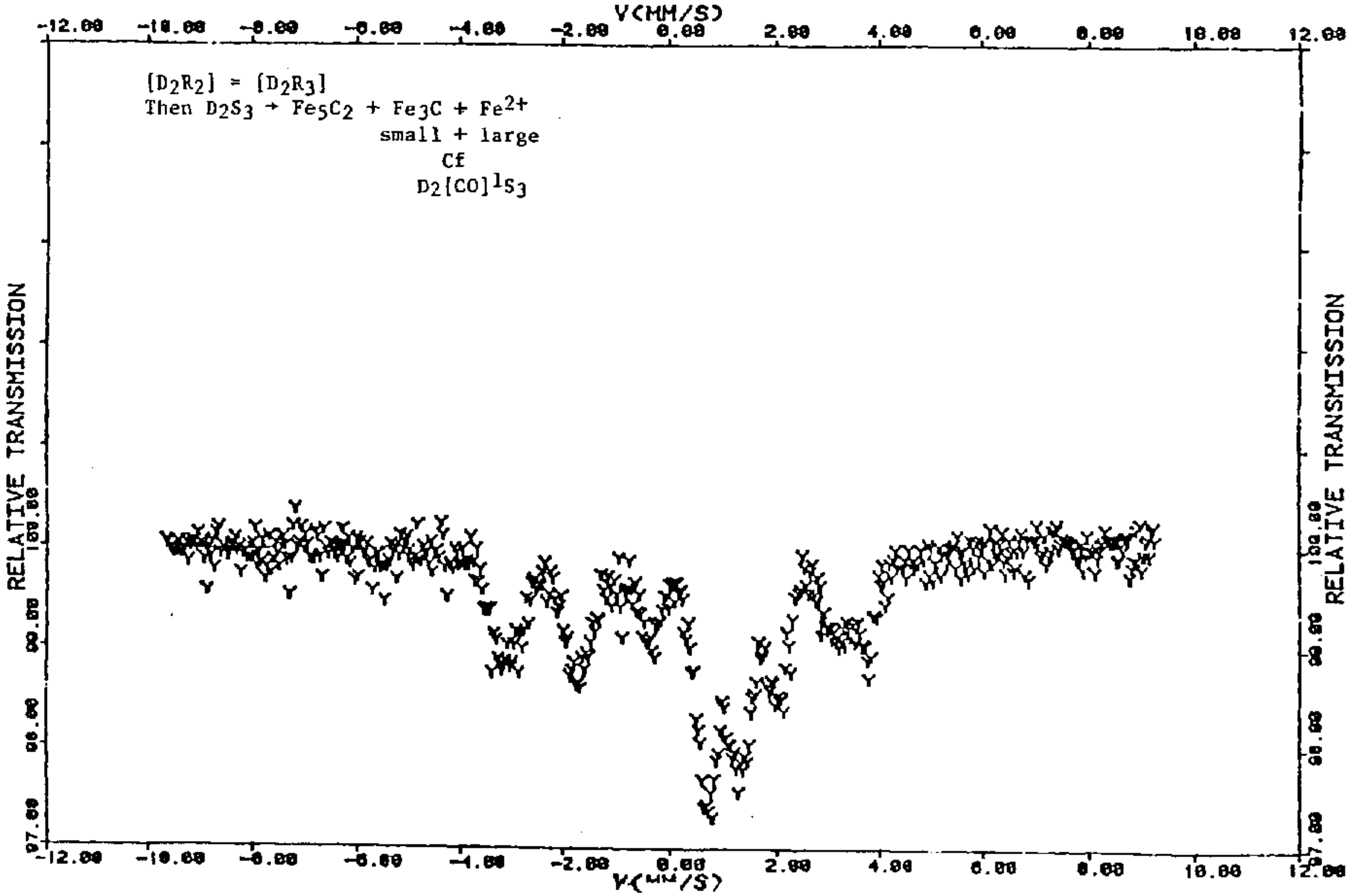


Figure 23. 48% Fe-Mn, carbided as before.



$[D_2R_2] = [D_2R_3]$
Then $D_2S_3 \rightarrow Fe_5C_2 + Fe_3C + Fe^{2+}$
small + large
Cf
$D_2[CO]^1S_3$

Figure 24. (-48%) Fe-Mn Syngas CO/H_2 = 1:1 (60 cc/min total) at 290°C for 24 hrs. (This sample was first reduced by H_2 at 250°C for 24 hrs.)

IEEE TRANSACTIONS ON MAGNETICS, VOL. MAG-19, NO. 5, SEPTEMBER 1983 2001

MAGNETIC AND MÖSSBAUER CHARACTERIZATION OF TRANSITION METAL CATALYSTS SUPPORTED ON ALUMINOSILICATES

M. Oskooie-Tabrizi, C. Lo, and L. N. Mulay*

ABSTRACT

Decomposition of $Fe_3(CO)_{12}$ on a series of mordenites was studied by magnetic measurements and Mössbauer spectroscopy. Particle size determination for these Fischer-Tropsch catalysts indicated that the best dispersion can be obtained when the number of acid sites in mordenite is maximum. Thermomagnetic measurements and Mössbauer spectroscopy suggested that some iron clusters are inside the pores of mordenites. The change in the Mössbauer isomer shift for Fe/mordenites elucidated the nature of metal-support interactions.

INTRODUCTION

For several decades a standard technique for obtaining fine dispersions of transition metals on various high surface area supports such as Alumina (Al_2O_3), Silica (SiO_2), etc. involved their impregnation with salts (usually nitrates) of the transition metals and subsequent decomposition of the salt in the presence of H_2. Collins and Mulay [1] showed that upon decomposition of $Fe(CO)_5$ in Linde 13X (with a pore aperture of 10 Å) a fine dispersion of α-Fe_2O_3 was obtained in the cages. Since then there has been a prolific activity in dispersing various metal carbonyls such as $Fe_3(CO)_{12}$ into more exotic cage structures such as silicalite, ZSM-5, which have a medium pore (5.5 Å) channel type structure [2]. These systems have proved to be promising catalysts for syngas ($CO+H_2$) conversion to gasoline range (C_6-C_{11}) hydrocarbons [3]. In addition, mordenites, which fall under the zeolite category, have also been investigated as potential candidates for syngas conversion [4]. When impregnated with transition metal, carbonyls [$M_x(CO)_y$] and subsequent decarbonylation (removal of CO) give a variety of oxides [α-Fe_2O_3, γ-Fe_2O_3, etc.] in the freshly prepared samples. The oxides in turn could then be reduced to clusters of Fe° (atoms), carbided and used for syngas conversion. The work on ZSM-5 and mordenites have raised interesting questions concerning a possible interaction between the Fe species and the acidic sites in such supports.

The work reported here was undertaken to systematically elucidate such interaction in a wide variety of mordenites with the (SiO_2/Al_2O_3) "ratio" = 12,17,20,60 and having a wide range of acid sites. It was shown by other workers [5] that maximum number of acid sites is present in the mordenite when the ratio is 17.

For this purpose in-situ magnetization measurements as a function of the field (H) and temperature (T) were used as a "macroscopic" probe to find the particle size of superparamagnetic particles. Fe^{57} Mössbauer spectroscopy was used as a microscopic tool for finding the valence state of the Fe species and for identifying the phases present. It was also used to detect their superparamagnetism and any magnetic ordering within large particles.

EXPERIMENTAL

The original mordenites were supplied by the Norton Co., Akron, Ohio. It had the oxide formula per unit cell: $H_xAl_xSi_{48-x}O_{96}$ in which 'x' depended on the SiO_2/Al_2O_3 ratio. The mordenite structure had an elliptical pore of size 6.7 x 7.0 Å.

Mordenite samples in which Fe species (~15%) were introduced by using $Fe_3(CO)_{12}$ were supplied by the Pittsburgh Energy Technology Center. A brief description of sample preparation is given by Rao [6].

Magnetization measurements were carried out with a Vibrating Sample Magnetometer and a Faraday microbalance [7]. Samples were investigated in the range 80-900 K in an applied field of up to 15 KOe. All samples were heated for thermomagnetic measurements at the rate of 5°C per minute.

The Mössbauer spectra were obtained with an Austin Associates constant acceleration spectrometer with a 50 mCi Co^{57} source and a Nuclear Data ND-100 multichannel analyzer. Spectra were recorded and Mössbauer parameters were obtained relative to a standard NBS iron foil.

RESULTS, DISCUSSION AND CONCLUSIONS

From the well known Honda-Owen plots of χ vs 1/H, the ferromagnetic impurity in the mordenites was estimated to be ~300 ppm and as such this contribution was neglected in subsequent measurements with Fe/mordenite samples. It is seen from Fig. 1 that practically all samples showed a superparamagnetic behavior. Sample A (ratio = 60) showed a much higher magnetization than other samples, such as B (ratio = 20), C (ratio = 17), and D (ratio = 12). Sample C,

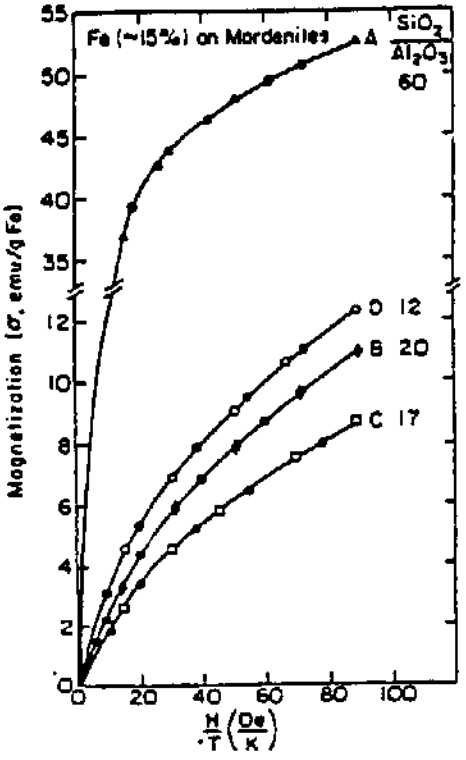


Fig. 1 Magnetization as a function of H/T for Fe on mordenites with varying SiO_2/Al_2O_3 ratio.

Manuscript received February 28, 1983.

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which has the highest number of Bronsted acid sites [5], showed the smallest particle size (∿14 Å). The plot of σ for Fe species as a function of "SiO_2/Al_2O_3" ratio in mordenite is shown in Fig. 2. The arrows indicate a ratio = 17 in this figure.

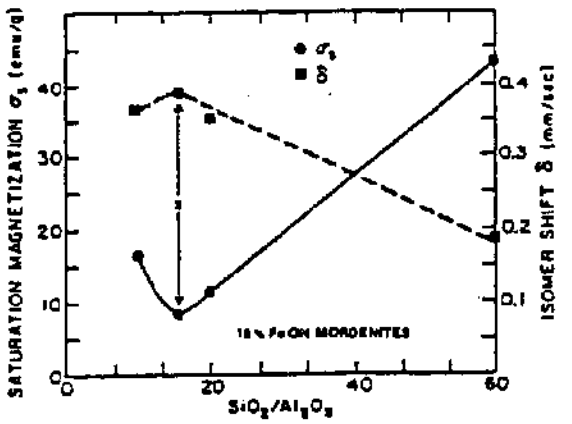

Fig. 2 Saturation magnetization (σ_s) and isomer shift (δ) versus SiO_2/Al_2O_3 ratio. The arrows show the ratio = 17, at which the acidity is highest.

The particle size was calculated from the low and high field approximation of the Langevin function. The average particle size decreased systematically from sample A (∿50 Å), sample B (20 Å), and sample D (18 Å) reaching a minimum value for sample C (14 Å), which has the highest number of acid sites in the mordenite structure.

Thermomagnetic measurements showed a similar trend for all samples. A typical curve is shown in Fig. 3, for sample B (ratio = 20). A maximum is seen around 450°C.a reduction in σ is attributed to thermal randomization. On cooling an irreversible increase in σ is also noticed. This may be ascribed to an agglomeration of clusters from the initial highly dispersed iron oxide phase to a more stable γ-Fe_2O_3 with a larger particle size. For sample A (ratio = 60) σ_s was found to be 73 emu/g of Fe_2O_3 which agrees well with the bulk saturation magnetization for γ-Fe_2O_3 [8]. This σ_s for sample A demonstrates that for the sample with lowest acidity, almost all iron clusters have grown to a larger (bulk) size, whereas σ_s for sample C (ratio = 17) showed 38 emu/g of Fe_2O_3, suggesting that almost 50% of iron species showed superparamagnetism.

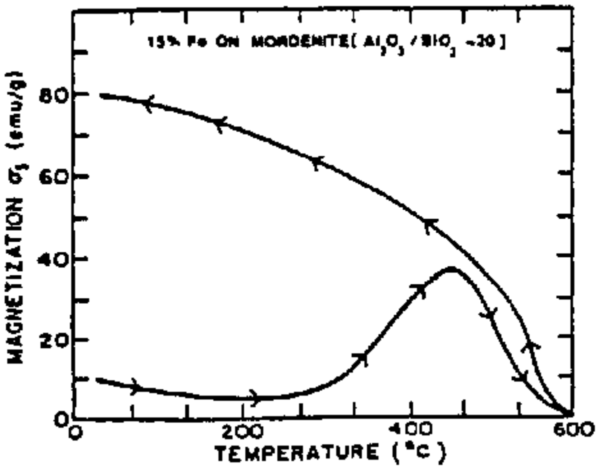

Fig. 3 Thermomagnetic measurements for Fe on mordenite with SiO_2/Al_2O_3 = 20.

This behavior could be due to highly dispersed particle clusters containing few atoms inside the channels of the mordenite (ratio = 17).

A composite of Mössbauer spectra obtained for samples with Fe on mordenites with various SiO_2/Al_2O_3 ratios at room temperature is shown in Fig. 4. As shown in Fig. 4(A), the spectrum consists of a strong doublet arising from Fe^{3+}, a small doublet from Fe^{2+}, and a weak sextet from larger particles. With decreasing acid sites, the interaction between the iron species and the support also decreases giving rise to an increase in the particle size. Hence, fine dispersion could not be achieved in this case. The small amount of Fe^{2+} possibly due to FeO formation [9] indicated that the charge transfer [10] ($Fe^{2+} \rightarrow Fe^{3+}$) during the decomposition of iron carbonyl was not completed. This is again due to the lower number of acid sites. As the number of acid sites increases, the sextet disappears at a ratio of 20, and the sample shows complete superparamagnetic behavior (Fig. 4(B)). Furthermore, the Fe^{2+} doublet disappears at a ratio of 17 (Fig. 4(C)). The isomer shift (δ) of the strong doublet arising from Fe^{3+} for various Mordenite-Fe catalysts is shown in Fig. 2. It is seen that δ increases as the ratio decreases from 60 to 17. This may be ascribed to the expansion of the s-orbital of Fe arising from the increase of protons (H^+) in mordenite. Thus, the s-electron density at the Fe nucleus is reduced and consequently δ is increased. The room temperature Mössbauer spectra were also obtained for samples heated at 900K. In addition to

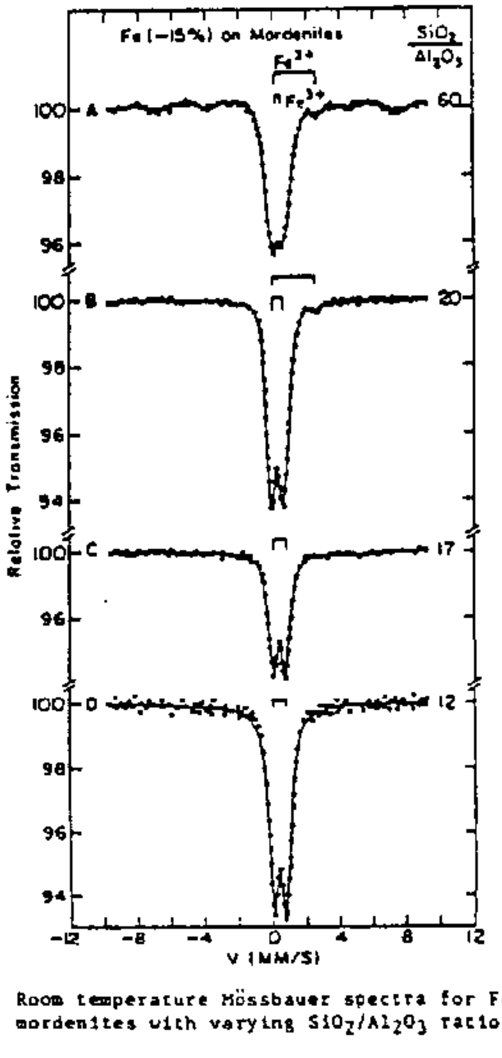

Fig. 4 Room temperature Mössbauer spectra for Fe on mordenites with varying SiO_2/Al_2O_3 ratio.

the sextet for bulk γ-Fe_2O_3, a superparamagnetic doublet was observed at a ratio of 17. These observations further indicated that a strong interaction between the acid sites and the Fe species constrained the growth of such species during sintering.

It is seen from the above results that (i) with increasing acid sites in the mordenite framework, a better dispersion of superparamagnetic clusters of Fe-oxides is obtained. The highest metal dispersion was seen with the Mordenite having the highest acid sites (ratio = 17); that (ii) due to high acidity of the mordenite, some Fe^{3+} ions could penetrate into the pores of mordenites; and (iii) a metal support interaction is observed with increasing acid sites in the mordenite. This is believed to arise from the expansion of s-orbitals of Fe by interaction with protons in mordenite. Further details along with kinetic studies on the syngas reaction will be published separately.

ACKNOWLEDGEMENTS

We thank V.U.S. Rao, B.D. Blaustein and R.R. Schehl of the Pittsburgh Energy Technology Center, DOE, Pittsburgh, Pennsylvania, for their active support and helpful discussions. We are grateful to Prof. Gordon A. Melson and his associates at the Virginia Commonwealth University, Richmond, Virginia, for supplying the Fe/mordenite samples.

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APPENDIX

The structure of a typical sodium-mordenite $[Na_8Al_8Si_{40}O_{96}]\cdot 24H_2O$ viewed along the [001] direction is shown below. It is orthorhombic with unit cell dimensions: a = 18.1, b = 20.5, c = 7.5 Å. The structure depicts the pore structure described under the experimental section. It should be noted that the mordenites, used in the present study were in the "Hydrogen" form. These were obtained by exchanging Na^+ ions with H^+.

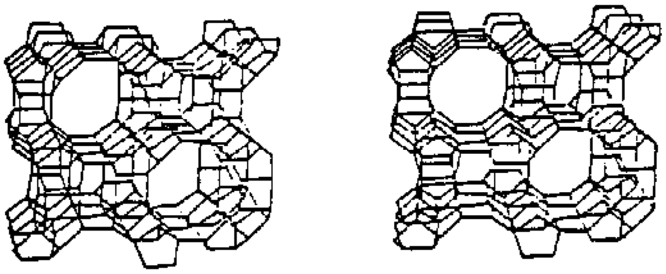

Fig. 5 Structure of a typical mordenite [see C.K. Hersh, "Molecular Sieves," Reinhold Publ., New York (1961); and D.W. Breck, "Zeolite Molecular Sieves," John Wiley and Sons, New York (1974)].

V . CONCLUSIONS

Project: Fe:Mn Catalysts

Synthesis: 10% Fe, 90% Mn and 50% Fe: 50 Mn (PETC: samples from Dr. Diffenbach, (TPO), Tischer, Pennline et al.)

1. Characteristics:
   - a. Mössbauer spectroscopy of 10 Fe: 90 Mn shows slow reduction with H_2:CO, presence of various carbides and relatively slow synthesis gas reaction. Departure from S-F plots (reported by Dr. Tischer, PETC).
   - b. Magnetic measurements show formation of Mn-ferrite as an intermediate.
2. Characterization:
   Mössbauer on 50:50 Fe:Mn → quick reduction. Desired Fe-carbides and catalytic activity (PETC). Less formation of spinel Mn ferrite (from magnetic and Mössbauer data). Mn-ferrite not considered by previous workers.

VI. CONCLUSIONS

Project: Fe/TiO_2

Synthesis: Fe/TiO_2 [2 samples] were supplied by PETC (Dr. V.U.S. Rao)

Characterization: Mössbauer and magnetic measurements show presence of Ilmenite + Fe-Titanate

Results: Mössbauer and magnetic data show SMSI. Ease of reduction of $Fe^{3+} \rightarrow Fe^{\circ}$ depends on many factors (Fe loading, sample preparation, and reduction conditions).

Conclusions: Carefully planned research required(2 arbirary sample -not enough)

Use should be made of existing knowledge of semi-conductor and metallic properties of Ti_nO_{2n-1}. (Ti_2O_3) and Magneli phases. (~20 papers by Mulay et al., P.I. during the past decade)

November 1983

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