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NOVEL APPLICATIONS OF ORGANOMETALS: MAGNETIC, ETC. PROPERTIES OF IRON DISPERSIONS (I) IN ZEOLITES AND (II) IN AMORPHOUS GLASS-LIKE CARBONS *

L.N. MULAY, D.W. COLLINS **, A.W. THOMPSON *** and P.L. WALKER, JR.

Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802 (U.S.A.)

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Summary

The first part describes a novel technique for dispersing ultrafine species of iron oxide of controlled particle size (radii < 150 Å) within the cage structure of a zeolite matrix, with the aid of organometals such as ferrocene and iron pentacarbonyl. The particle size and magnetic ordering within the iron clusters are elucidated via ^{57}Fe Mössbauer spectrocopy and via their superparamagnetic behavior displayed by magnetization curves obtained as a function of the magnetic field and temperature. The second part of the paper describes the magnetic properties of iron species (Fe_3C, Fe_3O_4, etc.) dispersed in amorphous glass-like carbons. These are obtained by the polymerization of furfuryl alcohol-containing ferrocene derivatives and by the subsequent pyrolysis of the polyfurfuryl alcohol. The technological relevance and applications of the materials studied in Parts I and II of the paper are pointed out.

Introduction

Work carried out by Mulay with E.G. Rochow in the mid-fifties on molecular motion in ferrocene [1—3] led in later years to investigations of the electronic structure and molecular orbital descriptions of such organometallics using diamagnetic anisotropy [4,5] and Mössbauer spectroscopic [6,7] techniques and to studies of broad-line NMR spectra [8,9] of various organometallics. Several aspects of such research on organometals and coordination complexes have now appeared in books by Mulay and Boudreaux [10]. During the course of recent

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* Dedicated to Professor Eugene G. Rochow on the occasion of his 70th birthday.

** Present address: Allied Chemical Corporation, Morristown, N.J. (U.S.A.).

*** Present address: University of Wisconsin, Milwaukee, Wisconsin (U.S.A.).

research on magnetic phenomena and magnetic materials, some novel materials applications of ferrocene were explored. In this paper we report on two such applications.

Part I. Magnetic and Mössbauer studies on iron dispersions in zeolites

I A. Introduction and experimental

Our interest in this area stems from the extensive studies we reported on the dispersions of iron species (ions, atoms, etc.) in various vitreous silicates [11,12]. One of our objectives in studying supermagnetic systems has been to devise novel synthetic methods for controlling the particle size of the magnetic species by "stuffing" them inside some cage structures. Such systems are useful as supported catalysts.

Some work has been reported on the dispersion of nickel [13,14] (metallic or ions) and on the dispersion of iron [15—18] in zeolite matrices. However, there are difficulties [19] in introducing iron species (atoms or ions) which appear to break down the zeolite structure.

In the following sections we report a synopsis of studies undertaken since 1966 on introducing iron via organometals such as $Fe(CO)_5$, ferrocene, $[(C_5H_5)_2Fe]$ and covalent compounds like $FeCl_3$. The Linde Molecular Sieve 13 X (hereafter abbreviated M.S.) was chosen because it offers a large internal (700—800 m^2/g) and a small external (1—3 m^2/g) area with a relatively uniform pore diam ~10 Å, which is large enough for these compounds to slip through.

Exploratory experiments were carried out using $Fe(CO)_5$, the only liquid iron carbonyl known. Addition to the molecular sieve described before was rather crude at first, but the initial results were promising enough to continue research in this area. Subsequently, in an attempt to control the experimental conditions more closely, an experiment was devised such that an "aerosol" of iron pentacarbonyl was sprayed onto the M.S., which was constantly agitated. This was found to be quite successful when the magnetic measurements were made, as discussed below. A spray atomizer was used to produce the aerosol, and a vibrating plate, on which a crucible containing the M.S. powder was placed, was used to provide the agitation. Other methods of adding the iron pentacarbonyl included attempts to adsorb vapors of $Fe(CO)_5$ into the sieve and attempts to adsorb a solution of $Fe(CO)_5$ in ether. The addition of ferrocene in the form of its solution in benzene has been successful. Anhydrous $FeCl_3$ dissolved in anhydrous ether was also sprayed onto the M.S. $FeCl_3$ is also known to be covalent and was expected to be stable under vacuum. This experiment also was successful. Finally, samples of each addition product were heat-treated in air at 500°C and at 900°C for 5 min and for 30 min in order to (a) convert the addition product to Fe_2O_3 and (b) to cause a growth of their particles.

Analysis of the molecular sieve-$Fe(CO)_5$ addition product indicated 11.8 weight percent Fe (expressed as Fe_2O_3). In the M.S.-$FeCl_3$ addition product, 5.6 weight percent Fe (expressed as Fe_2O_3) was present. The magnetic measurements were made employing the well-known Faraday method, as described by Mulay [20]. A standard spectrometer was used to obtain the Mössbauer spectra for ^{57}Fe relative to sodium nitroprusside (National Bureau of Standards) as a standard.

X-ray diffraction established that M.S. showed indeed the faujasite pattern observed previously (ASTM Powder Pattern No. 12-246) and that the M.S. structure was unaltered by the addition of $Fe(CO)_5$ or by $FeCl_3$. Aging the M.S.-$Fe(CO)_5$ addition product at 500° C immediately gave particles of α-Fe_2O_3 large enough to be detected by X-ray diffration; an increase in the growth of the particles was observed with an increase in the treatment time. At 900°C, the M.S. was transformed into a different structure, and again, a growth of α-Fe_2O_3 was observed with time of heat treatment. In the case of the M.S.-$FeCl_3$ addition product, the presence of α-Fe_2O_3 was noted at 900° C only. No other iron species were found to be present in either case.

An electron microscopic study was made in an attempt to check whether or not there was any appreciable accumulation of magnetic material on the exterior surface of the molecular sieve. However, an RCA electron microscope, with magnification to 15,800 was not able to disclose either the presence or absence of any nonzeolitic material on the exterior surfaces of the M.S.

I B. Magnetic properties and discussion

We calculated the per gram saturation magnetization (σ_s) by plotting the per gram magnetization (σ) versus the reciprocal magnetic field ($1/H$) and extrapolating to $1/H = 0$. The magnetizations are expressed in units of gauss cm^3/g. Following the procedure given by Van der Giessen [21], the magnetic moment (μ in Bohr magnetons) was then obtained from a best fit to a plot of σ/σ_s versus $\mu H/kT$. The particle size (r) in Å was calculated from equation 1, where

$$r = \left[\frac{\mu}{\sigma_s \rho} \times 10^{24}\right]^{1/3}; \qquad (1)$$

σ is the density of bulk α-Fe_2O_3. The average Weiss constant (θ) in K was determined by plotting the reciprocal of the magnetic susceptibility (χ) as a function of temperature. These values are listed in Table 1. ("h.t." refers to the heat treatment conditions).

The calculated values of σ (uncorrected for diamagnetic contributions) of the samples as a function of the H/T ratio are shown in Fig. 1. For the sake of clarity, the data for the "500° C-5 minute" heat treatment has been omitted; it follows very closely the behavior of the "500° C-30 minute" sample. Clearly, the approximate superposition of the data for this relatively "dilute" system conforms to the operational definition of superparamagnetism and suggests the presence of this phenomenon. The minor hysteresis that appears can be attrib-

TABLE 1

MAGNETIC PARAMETERS FOR THE M.S.-$Fe(CO)_5$ SYSTEM

	Sample	θ	σ_S	μ	r
A.	Addition product	−122	0.45	140	85
B.	h.t. 500° C-5 min	−31	0.40	190	95
C.	h.t. 500° C-30 min	−189	0.43	900	160
D.	h.t. 900° C-5 min	−140	1.62	800	100
E.	h.t. 900° C-30 min	−174	0.62	900	140

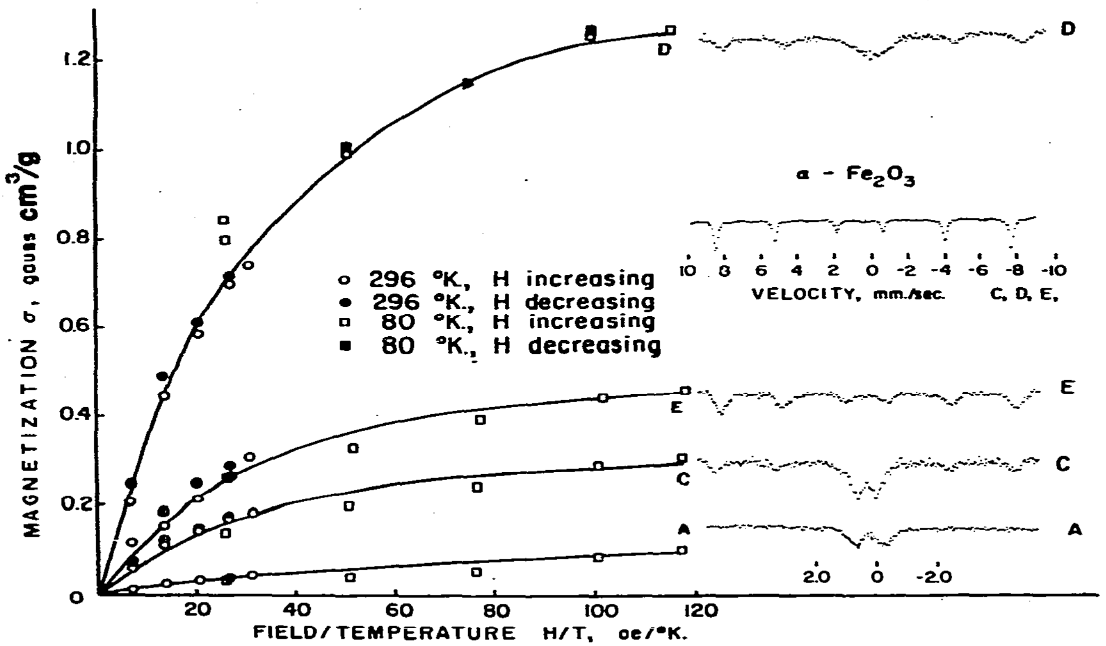


Fig. 1. Magnetization as a function of H/T and the Mössbauer Spectra (~25° C) for the heat-treated samples in M.S.-$Fe(CO)_5$ system (see Table 1).

uted to the ferrimagnetic behavior of the fine particle antiferromagnets as proposed by Néel [22] and discussed below.

The observed Mössbauer spectra as a function of the heat treatment parameters are shown in Fig. 1 and a spectrum for α-Fe_2O_3 is also included for comparison.

Plots of saturation magnetization (σ_s) as a function of the calculated particle size (r) (not shown here) displayed an increase in σ_s up to ~100 Å and a subsequent decrease. This behavior suggests a growth of fine antiferromagnetic particles. Below a critical size, greater spin uncompensation is assumed to increase with increasing particle size; Néel [22] has suggested that the number of uncompensated spins (p) in a fine particle antiferromagnet increases as $\sqrt{N}$, where N is the total number of spins. In effect, the system appears to behave as a ferrimagnet up to a critical particle size. At a critical size, represented by the maximum in the curve, antiferromagnetic single domains are beginning to form; the magnetic data for this point, which represents the highest degree of ferrimagnetic character that the system achieves, exhibits minor hysteresis behavior even at 77 K. Above the critical size, there is greater spin compensation occurring in the direction of a bulk antiferromagnet. This is supported by the Mössbauer spectra in which hyperfine splitting, indicative of the presence of long range magnetic order, first appears at the critical size. Thereafter, the long range magnetic ordering increases at the expense of the superparamagnetic particles. Similar particle size-dependent Mössbauer spectra have been reported by several workers and have been reviewed by us [23]. Hence, for our M.S.-Fe_2O_3 system, it would appear that the critical particle size at room temperature is ~100 Å, the radius at which hyperfine splitting in the Mössbauer spectrum first appears. Although we cannot discuss here all of our quantitative results on the Mössbauer spectra for the M.S.-$Fe(CO)_5$ and the M.S.-$FeCl_3$ systems, it should be noted that we have used Néel's well known relaxation equation [22] [$1/\tau = f_0 \exp(-KV/kT)$], Van der Woude and Dekker's [24] approach and an anisotropy constant of $K = 3 \times 10^4$ erg/cm^3 given by Naik and Desai [25] to obtain a critical radius of ~110 Å corresponding to volume V, for our superparamagnetic system. This result is likely to be foruitous; nevertheless, it indicates a possibility that should be investigated in greater detail. Interestingly, Creer [26] has also suggested from static magnetic studies that 100 Å is the critical size for α-Fe_2O_3.

The concept of the growth of fine antiferromagnetic particles is also supported by the increase in the Weiss constant (θ), which is a measure of the exchange interactions, in the direction of bulk α-Fe_2O_3.

Thus the dispersion of iron species in zeolites shows not only superparamagnetic behavior but also provides a new way for studying the magnetic ordering within superparamagnetic clusters.

Part II. Dispersions of iron in amorphous glass-like carbons

II A. Introduction and experimental

In the preceding Part we reported studies on the superparamagnetic behavior of dispersions of iron species in zeolites obtained by using organometals such as ferrocene and iron pentacarbonyl. During a search for novel methods for dispersing iron, we noticed the possibility of dispersing Fe species in a diamagnetic carbon host lattice. The technological relevance of this work lies in obtaining carbon compositions with desirable pore structures, which, in turn modify a number of their physical properties. A number of amorphous glass-like carbons containing iron were supplied to us by Professor P.L. Walker, Jr. A schematic of their synthesis is shown in Scheme 1.

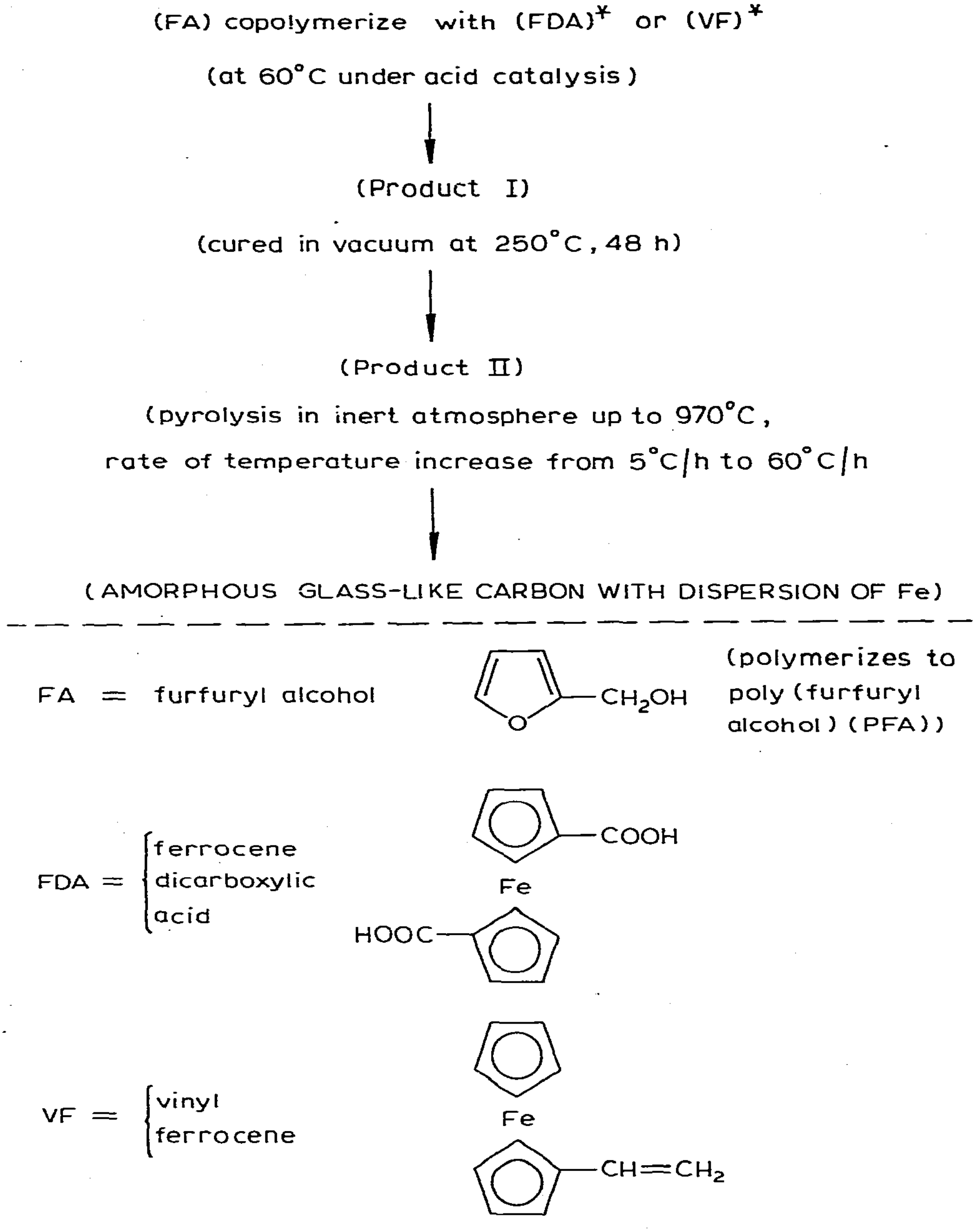
The particular samples studied are given in Table 2. In this table, M indicates magnetization measurements, and S indicates susceptibility measurements.

The vibrating sample magnetometer technique was selected because of its ability to furnish rather quickly the magnetization as a function of the field and temperature, especially for samples with large magnetic moments. A

TABLE 2

SAMPLES STUDIED AND TYPE OF MEASUREMENTS

Sample	Preparation temperature			
	500° C	625° C	700° C	970° C
PFA	M	M	M	M
PFA + 1% FDA	M	M	M	M
PFA + 3% FDA	—	M,S	M	M,S
PFA + 1% VF	M	M	—	M
PFA + 10% VF	M,S	M,S	M,S	M,S



* Note: The concentration of FDA varied from 1 to 3% and that of VF from 1 to 10% by weight.

Scheme 1. Details of the synthesis of iron containing glassy polymers and their technologically useful properties are given by, Kammareck et al. [28].

magnetometer of this type, manufactured by the Princeton Applied Research Laboratory, Princeton, N.J., was employed for all magnetization measurements reported here [20]. Several high temperature susceptibility measurements (from room temperature to 750° C) were carried out using an automated Faraday balance described by Butera et al. [27]. The sensitivity of this particular balance was fairly low. This limited the samples to be measured to those with high iron content and to those available in large quantity. The large amount of sample rendered the absolute measurement of the susceptibility to be somewhat ambiguous. Thus, only relative susceptibilities are reported here. However, the Curie points of the materials were accurately established.

II B. Magnetic properties and discussion

Magnetization versus field measurements were made on all samples. The samples that contained iron displayed weak ferromagnetism. For all samples save one, saturation occurred at 5—6 kgauss. The 500°C VF sample saturated at 2—3 kgauss. The saturation magnetization per gram (σ) of Fe for various samples containing iron was measured. Results are shown in Fig. 2a.

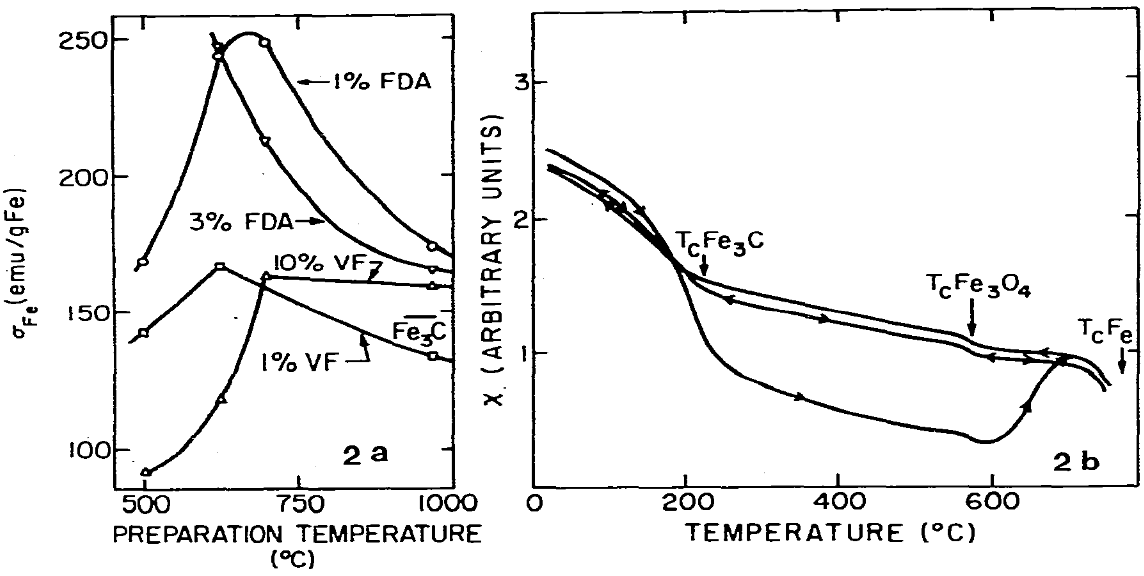
The FDA samples show similar behavior with an approach at the high temperature end to the saturation magnetization of Fe_3C (cementite), which was found in these carbons by a combination of electron microscopy and X-ray diffraction. It is interesting to note that the "dilute" (1% FDA) sample shows relatively higher saturation magnetization than the "concentrated" (3% FDA) sample over a wide range of their preparation temperatures. Thus it may be surmised that the 1% FDA sample has relatively small particles (probably superparamagnetic) of iron species, which are more difficult to saturate. In both cases, the final product obtained by preparing the samples at a higher temperature (~1000° C) turns out to be Fe_3C, which is formed by the conglomeration of such particles, large or small, existing at preceding temperatures of preparation.

While the 1% VF and 10% VF samples show a similar trend over the low temperature region of preparation (500 to 700° C) this trend is reversed over the higher range (700 to 1000° C). This is suggestive of an unusual mode of conglomeration for the VF system, which is quite different than the FDA system.

In any case, it is noteworthy that the 10% VF system also approaches the formation of Fe_3C. The 1% VF samples appear to show the same trend as the FDA sample; however the magnetization at 970° C is below that of Fe_3C. This may be due to incomplete conglomeration of fine particles to form bulk Fe_3C.

Electron micrographs of the 500° C, 10% VF sample show small "cubic" areas of high density material. Micrographs of the samples treated at higher temperatures show the material in these areas to have migrated out. It is apparent that the trend in magnetization reflects this migration. However, this species as of now has not been identified.

Despite the large error involved in measuring diamagnetic magnetization a diamagnetic increase with increasing preparation temperature was observed. This increase in the diamagnetic magnetization is probably due to a decrease in paramagnetic centers (i.e. free radicals) with heat treatment.



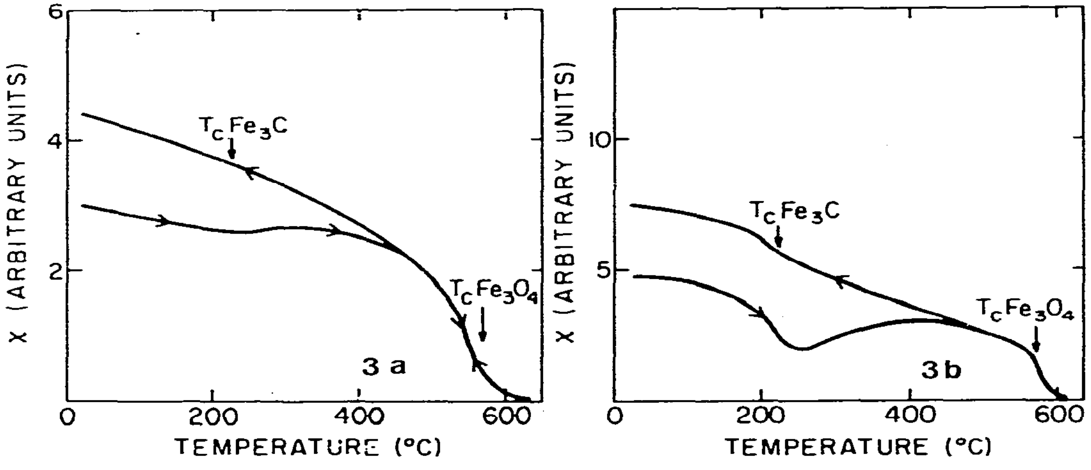
a

b

Fig. 2 (a) Saturation magnetization measured at 19 kgauss and 25°C for various glassy carbon samples as a function of their preparation temperater. (b) Magnetic susceptibility in arbitrary units as a function of temperature for the glass-like carbon prepared with 10% VF (970°C).

II C. Susceptibility measurements

Susceptibility versus temperature measurements were made on several of the samples, temperatures not exceeding the preparation temperatures. Except for the 500°C-10% VF and 625°C-10% VF samples, the samples all displayed similar behavior. The samples were heated and cooled several times as susceptibility



a

b

Fig. 3 (a) and (b). Magnetic susceptibility in arbitrary units as a function of temperature for the glass-like carbon prepared with 10% VF (a 500°C, b 625°C).

measurements were being made. Figure 2b shows the observed behavior. Besides the Curie point for Fe_3C at 222°C, the curve also shows a Curie point at about 565°C, that for magnetite (Fe_3O_4). As the samples were heated above 600°C, there was observed an increase in the susceptibility with a turnover above 700°C indicating the Curie point of metallic iron at 770°C. Cooling back to room temperature, a marked decrease in the amount of Fe_3C is observed. Since Fe_3C is an unstable compound, it must be concluded that the Fe_3C is being decomposed to metallic iron when heated above 600°C. This is interesting, since these samples, in their preparation, have previously been heated, in some cases, to above this temperature. In some way, the preparation method forces the formation of Fe_3C. It has been thought that these glass-like carbons have closed pores, thus being imprevious to gases. This may not be so, since these materials were stored in air for six months or better before susceptibility measurements were made. During this time, air may have entered the pores or some gas produced during the preparation may have escaped.

The susceptibility of the 500°C-10% VF and the 625°C-10% VF samples (Fig. 3) both showed similar behavior, somewhat different from the other samples. The Curie points observed are those for Fe_3C and Fe_3O_4. Unlike the previous samples, the Fe_3C decomposes to Fe_3O_4 instead of iron. Here again, the heat treatments during preparation have forced Fe_3C formation. However, the small cubic areas of high density material revealed by electron microscopy cannot be determined from the data.

Further work along the lines indicated here is being continued in the hope of producing good superparamagnetic systems, which may act as efficient carbon supported iron catalysts.

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