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DISPERSIONS: CORRELATIONS WITH THEIR METHANATION AND CHEMISORPTION
ACTIVITIES

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AMORPHOUS MAGNETISM II

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MAGNETIC CHARACTERIZATION OF SEMI-AMORPHOUS NICKEL ON ALUMINA
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ABSTRACT

Commercial samples of semiamorphous nickel supported on alumina, typically used as methanation catalysts have been characterized by using magnetization (σ) versus field (up to 20 KOe) and temperature (77-600 K) type curves and by electron microscopy. Hysteresis curves yielded coercive force (H_c) remanence (I_r) and saturation magnetizations (σ_s), following heat treatment of the catalysts between 400-700°C. These parameters are interpreted in terms of the following properties of constituent particles: (a) superparamagnetic (b) single-domain anisotropic and (c) multi-domain. Needlelike "b" and "c" type particles are formed when a sample A with 43 wt % of Ni is heated to about 600 and above 650°C respectively. Another sample B with a higher loading of Ni (67 wt %) consisted of a larger fraction of "a" type particles which on heat treatment increased H_c and σ (sat) as expected, but was more thermally resistant to the formation of "c" type particles. Unlike sample A, B did not show a significant decrease in the methanation activity upon the formation of "c" type particles. The methanation reaction $CO + 3H_2 \rightarrow CH_4 + H_2O$ was followed using standard gas chromatographic techniques. The distribution of the superparamagnetic particles in the presence of multi-domain particles in various heat treated samples has been calculated and shown to correlate well with their hydrogen chemisorption activities.

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INTRODUCTION

Magnetic properties of amorphous materials, including metal dispersions on oxides are fascinating indeed and have attracted considerable attention during recent years. One of us (LNM) previously reported on the magnetic properties of dispersion of α - Fe_2O_3 in zeolites¹ and of Fe^{3+} ions in silicates^{2,3} and glassy carbons.⁴ Among dispersed magnetic systems the very fine dispersions of 3d metals such as Fe, Co, and Ni on various (diamagnetic) substrates (e.g. SiO_2 , Al_2O_3) are technologically most significant because of their widespread use as industrial catalysts in tonnage quantities. Significant fractions of such dispersions display superparamagnetic properties and are considered to be in part amorphous.

Correlations between the (superpara)magnetic properties of the 3d transition metal dispersions and chemisorption have been well recognized and widely investigated over the past three decades.⁵⁻¹¹ Most of the work has been on materials containing very low amounts (usually below 5%) of the metal which was dispersed on substrates to yield, so to speak ideal, "single phase" superparamagnetic systems.^{12,13} While such studies have undoubtedly enhanced our understanding of the mechanism of chemisorption of electron donor and acceptor type molecules, very few attempts have been made to thoroughly characterize commercial catalysts containing large amounts of metal (up to 70%) and to correlate their magnetic properties with catalytic and chemisorptive activities.

In this paper we present typical results on two commercial grade nickel on alumina dispersions containing 43 and 67% Ni with special reference to (i) the delineation of the properties of their magnetic components (superparamagnetic,^{12,13} single-domain anisotropic¹⁴ and multi-domain ferromagnetic), (ii) the change in magnetic properties upon heat treatment to elevated temperatures and (iii) correlation of such changes with corresponding changes in catalytic activity for the reaction: $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$ as well as correlations with their hydrogen chemisorptive properties.

EXPERIMENTAL

Two nickel on Al_2O_3 dispersions A and B with the physical characteristics shown in Table I were investigated.

Magnetization (σ) measurements were performed on a vibrating sample magnetometer (made by Princeton Applied Research Labs., Princeton, N.J.) as a function of the field (up to 20 k Oe) and over a range of temperature (77-600 K) to yield especially values for saturation magnetization per gram (σ sat) of nickel in the catalyst, the coercive force (H_c) and the remanence (I_r). Special quartz sample holders were designed to accommodate in vacuum the as received

Table I: Characteristics of the As Received Ni Samples

	A	B
Nickel, wt %	43	67
Pellet size, in	1/8	3/16
BET surface area, m ² /g	51	117
Average crystallite size (Ni), Å	185	74

samples, and those after reaction and/or heat treatment as described below.

Heat treatment of the catalyst was conducted by (a) exposure to H₂ for 1 hour at selected heat treatment temperatures (HTT) in the range 400-700°C followed by (b) exposure to the synthesis H₂/CO mixture for an additional 1 hour at HTT.

Catalytic activities were measured in terms of the methanation reaction which was carried out by passing a mixture of 17 mole percent of carbon monoxide (CO) in hydrogen (H₂) at atmospheric pressure through a vertical reactor packed with a known weight of catalyst pellets. These pellets were crushed to give fine powders (100-170 mesh) and low residence times (0.003-0.019 secs) were used so that activities could be measured unaffected by diffusion effects.¹⁵ Methane content in the product stream was monitored using a Hewlett Packard chromatograph with a column of 100-120 mesh fraction of Carbosieve B, obtained from Supelco, Inc. The column was operated at 50°C. Methane production at 300°C, after reduction of the catalyst for 1 hour in H₂ and reaction for 1 hour, was used as the basis for comparison of activities of catalysts taken to different HTT.

RESULTS AND DISCUSSION

Typical plots of the coercive force (H_c) measured at three temperatures (T_m = 77°, 298°, 423°K) as a function of the HTT for catalysts A and B are shown in Fig. 1. Maxima in H_c are observed around HTT's of 600°C and 650°C respectively for catalysts A and B. A comparison of these curves with Kneller and Luborsky's results¹³ suggests that the maxima are probably due to two competing processes: first, conversion of "a" superparamagnetic to "b" single-domain anisotropic particles producing an increase in H_c and then a conversion of such "b" particles to "c" type multi-domain particles with zero H_c. These two conversions are believed to be characteristic of what occurs

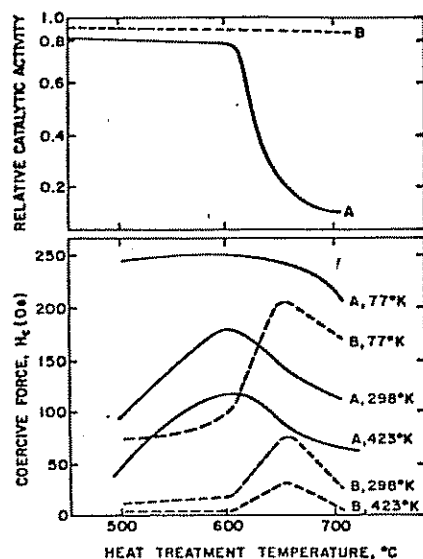


FIG. 1 Rel. activity (top) and H_c (bottom) vs HTT $^{\circ}$ C. Magnetic measuring temperature in $^{\circ}$ K.

during the sintering of nickel supported on alumina. However, a partial conversion of "a" to "c" due to formation of closed multi-domain configurations is not ruled out during heat treatment.

Curves for catalyst A indicate the formation of large particles in the multi-domain region corresponding to a HTT range, 600-700 $^{\circ}$ C. The relative activity for "A" (Fig. 1) decreases sharply in this region. The temperature at which the activity of A commences to decrease sharply coincides with the HTT, at which the maxima in H_c occurs. By contrast the activity of B does not drop at its corresponding maxima in H_c . This aspect is being investigated. It should be noted here that B shows no loss in activity even up to a HTT of 700 $^{\circ}$ C. We have estimated in Table II the fraction of superparamagnetic particles in various heat treated samples and their mean diameters, using essentially the approaches and approximations described in the appendix.¹⁰ Table II shows that for catalyst B (despite its high concentration of nickel), the size of the superparamagnetic particles remains nearly constant and the fraction of such particles decreases less over the range of HTT's as compared to A.

Thus the magnetic technique provides a better characterization of the particles in terms of the critical sizes of superparamagnetic particles as well as their abundance than the gross estimates of crystallite sizes often reported in the catalysis literature. The small fraction (0.12) of superparamagnetic particles of A at HTT of

Table II. Weight Fraction of Superparamagnetic Particles in Heat Treated Samples A and B

Heat Treatment Temperature (HTT) ^o C	Wt. Fraction of Superparamagnetic Particles		Mean Particle Size, Å (diam) of Superparamagnetic Fraction	
	A	B	A	B
As received	0.36	0.58	25	24
500	0.27	0.48	29	25
600	0.21	0.40	54	28
700	0.12	0.26	37	26

700^oC indeed represents the least active catalyst. Since the chemisorptive properties of CO and H₂ have been shown to be dependent on the d-band characteristics of such particles^{5,6} the magnetic technique may be said to provide additional characterization of the particles at the microscopic level. This aspect is discussed later.

The shape anisotropy of the particles is believed to be responsible for the increase in H_c up to the transition temperature (T_t), and their disappearance is expected to cause the subsequent decrease in H_c. This conclusion is supported by evidence from electron microscopy, which clearly shows the formation of needles or chainlike clusters up to T_t and their conversion to more regularly shaped particles, resembling those with multi-domain properties, above T_t. The average crystallite size increased from 185 to 256 Å for catalyst A, and from 74 to 160 Å for B over the range of HTT.

Curves for the remanence (I_r) measured at the same temperatures as H_c and as a function of HTT resemble those of H_c and are not shown here. Their unique feature is that the peaks appeared sharper and at somewhat lower values of HTT corresponding to smaller particles than in the corresponding H_c curves as one would expect from the theoretical treatment.¹³ Thus, the parameters H_c and I_r are indeed useful in characterizing the presence of single-domain anisotropic particles, which are formed at least partially during the transition from the essentially superparamagnetic to the essentially multi-domain regions. Furthermore, the HTT at which the single-domain anisotropic particles are formed appears to be characteristic of the "dispersive" state of the metal on the catalyst support.

Another distinction between the two samples was observed in terms of their hydrogen chemisorption, which was studied by standard techniques.⁵ These techniques yield the number of hydrogen atoms chemisorbed on the surface of the catalyst, which in turn corresponds to the number of surface nickel atoms.

From these results the percent degree of dispersion (f) is calculated simply as the fraction $f = (\text{Ni atoms at the surface} + \text{total number of nickel atoms in the bulk per gram of catalyst}) \times 100$. Relevant information is given in Table III, which again shows that the catalyst B has an overall better degree of dispersion (and hence better catalytic activity) than catalyst A over the entire range of HTT.

The degree of dispersion is plotted as a function of the weight fraction of superparamagnetic particles in Fig. 2, for various heat treated samples. The average particle sizes from Table II are also shown next to the data points for the two catalysts. This figure clearly indicates that the dispersion for B is indeed relatively large (7.6 to 10%), as we would expect, for smaller particles (24 to 28 Å) with a better distribution (26 to 58%), thus this type of correlation between the results of a strictly chemisorptive technique and the magnetic technique is helpful in quantitatively characterizing the dispersions of metals such as Ni on diamagnetic supports.

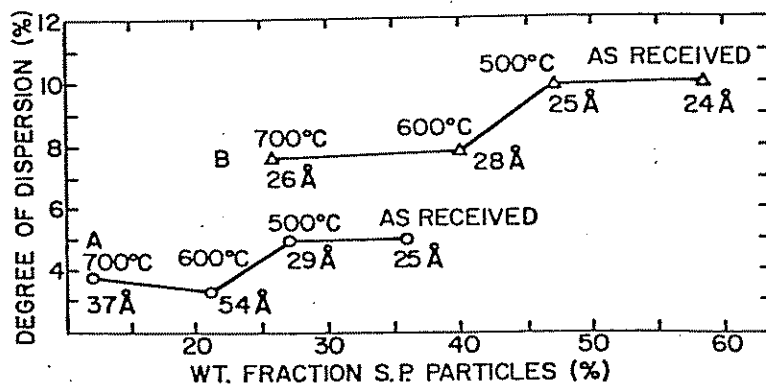


FIG. 2 Plots of the degree of dispersion (f) vs weight fraction of superparamagnetic particles for various heat treated samples.

Table III. Results of Hydrogen Chemisorption

HTT ^o C	Sample A		Sample B	
	No. of Ni atoms per g(x 10 ²⁰)	Dispersion f(%)	No. of Ni atoms per g(x 10 ²⁰)	Dispersion f(%)
As re- ceived	2.26	5.12	6.93	10.01
500	2.45	5.54	6.72	9.78
600	1.48	3.36	5.38	7.82
700	1.67	3.78	5.24	7.62

APPENDIX

The weight fractions x_i of the superparamagnetic ("a" type) and hence of the multi-domain ("c" type) particles in the various heat treated samples were estimated from the observed curves of the relative magnetization, σ/σ_∞ versus H/T (at 573^oK). Typical magnetization curves for catalyst B only are shown in Fig. 3.

Romanowski's equation¹⁰ for a two component system was assumed for deriving the weight fractions of the superparamagnetic ("b" type) and ferromagnetic ("c" type) particles:

$$\frac{\sigma}{\sigma_\infty} = \left(1 - \sum_i x_i \right) + \sum_i x_i L \left(\frac{I_{sp} v_i H}{kT} \right)$$

The expressions under the summation signs refer to superparamagnetic particles; L denotes the Langevin function and v_i the mean volumes of the particles within the x_i fraction. This expression is applicable at high fields such that saturation magnetization of multi-domain particles show no change and superparamagnetic particles obey the well known Langevin function. The average moment μ_i of the "a" type particle is defined by, $\mu_i = I_{sp} \cdot v_i$ (a magnetization curve for superparamagnetic particles of 30^oÅ radius, and at 573^oK, assuming the Langevin function is also shown in Fig. 3 for comparison with the observed curves).

By assuming an overall mean volume v for all superparamagnetic particles, as in Selwood⁵, a nonlinear regression procedure was developed for estimating the weight fraction (x) of the "a" type

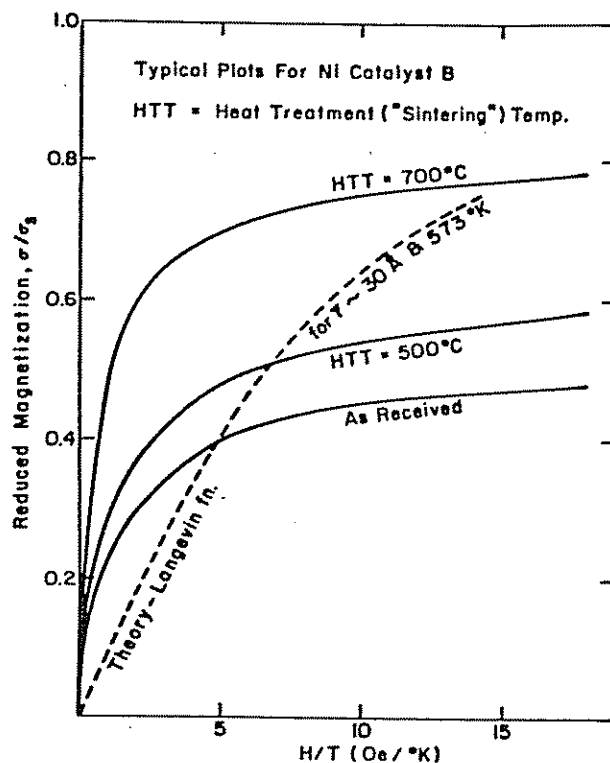


FIG. 3 Typical magnetization (σ/σ_s) vs (H/T) curves for catalyst B for the as received and heat treated samples. A magnetization curve for superparamagnetic particles (30Å radius at 573 K is shown for comparison (see Appendix).

particles, and the mean particle diameter of this fraction based on spherically shaped particles. The regression program used accomplished convergence very easily with a conventional hill climbing subroutine.

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DISCUSSION

E. Siegel: Can you distinguish between the particles that are ferromagnetic and those that are superparamagnetic?

L. N. Mulay: I would say that it is probably the metallic nickel which is superparamagnetic and not the nickel aluminate because from a chemical point of view it is certainly easier for the nickel metal atoms to form a cluster.

R. Hasegawa: In the title of your talk you have the word semi-amorphous. I did not see any indication that you are dealing with an amorphous material here.

L. N. Mulay: By definition, if one supposes the entire system to be superparamagnetic, that system would lack order and could be considered amorphous. Here we have a system that is partially ferromagnetic and I associated that part with the crystalline part of the matrix, so that the superparamagnetic particles would contribute to that semi-amorphous reference I used.