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# MAGNETIC CHARACTERIZATION OF SEMI-AMORPHOUS NICKEL CATALYSTS AND THEIR METHANATION ACTIVITY

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## ABSTRACT

Commercial catalysts (A) and (B) containing 43 and 67% wt. Ni supported on alumina have been successfully characterized by using magnetization ($\sigma$) versus H (to 20 k Oe) and T (77 – 600°K) type curves and by electron microscopy. Hysteresis curves yielded coercive force, remanence and $\sigma$(saturation) 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 is heated to about 600° and above 650°C respectively. The formation of 'c' type particles coincides with a decrease in the catalytic activity of A for the reaction $CO + 3H_2 \rightarrow CH_4 + H_2O$. B consisted of a larger fraction of 'a' type particles which on heat treatment increased $H_c$ and $\sigma$(sat) as expected, but was more thermally resistant to the formation of 'c' type particles. Unlike A, catalyst B did not show a significant decrease in catalytic activity upon the formation of 'c' type particles.

## 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 (L.N.M.) previously reported on the magnetic properties of dispersion of $\alpha$-$Fe_2O_3$ in zeolites[1] and of $Fe^{3+}$ ions in silicates[2,3] and glassy carbons.[4] Amongst dispersed magnetic systems the very fine dispersions of 3d metals such as Fe, Co, and Ni on various (diamagnetic) substrates (eg. $SiO_2$, $Al_2O_3$) 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 activity.

In this paper we present typical results on two commercial grade nickel on alumina catalysts containing 43 and 67% Ni with special reference to (i) the delineation of the properties of their magnetic components (superparamagnetic,[12,13] single-domain anisotropic[14] and multidomain 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:
$CO + 3H_2 \rightarrow CH_4 + 2H_2O$.

## EXPERIMENTAL

Two nickel on $Al_2O_3$ catalysts A and B with the following physical characteristics were investigated. Nickel, wt.% (A) 43, (B) 67; BET surface area, $m^2$/g (A) 51, (B) 117; average crystallite size, Å, as determined by x-ray line broadening, (A) 185, (B) 74.

Magnetization ($\sigma$) measurements were performed on a vibrating sample magnetometer (made by Princeton Applied Research Labs., Princeton, NJ) 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 ($\sigma$ 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 samples, and those after reaction and/or heat treatment as described below.

Heat treatment of the catalyst was conducted by (a) exposure to $H_2$ for 1 hour at selected heat treatment temperatures (HTT) in the range, 400 – 700°C followed by (b) exposure to the synthesis $H_2$/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 ($H_2$) 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 $H_2$ 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 results[13] 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 multidomain particles with zero $H_c$. These two conversions are believed to be characteristic of what occurs during the sintering of nickel supported on alumina. It should be noted that a partial conversion of 'a' to 'c', due to formation of closed multidomain configurations is not ruled out during heat treatment.
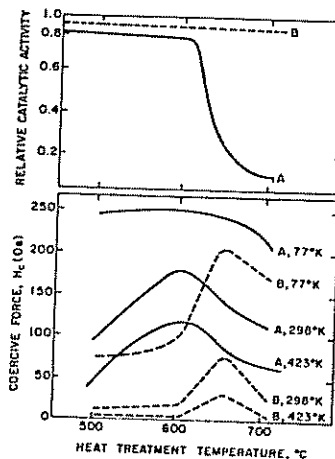


Fig. 1. (Bottom) Coercive force, $H_c$ as a function of the heat treatment temperature (HTT) of the sample. The temperatures of measurement for catalyst A (solid curve) and for B (dashed curve) are shown next to the curves. (TOP) Relative catalytic activity as a function of HTT.

Table I. Effects of Heat Treatment on Catalysts A and B.

| Heat Treatment Temperature, (HTT)°C | Wt. Fraction of Superparamagnetic Particles | | Mean Particle Size, Å (diam) of Super-paramagnetic 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 |

Curves for catalyst A are indicative of the formation of large particles in the multidomain region corresponding to HTT's in the range 600 – 700°C. The relative catalytic activity for 'A' shown at the top of Figure 1 is seen to decrease sharply in this region. The temperature at which the activity of A commences to decrease sharply is seen to coincide with the HTT, at which the maxima in $H_c$ occurs. By contrast there is no such drop in the activity of B at its corresponding maxima in $H_c$. This aspect calls for further investigation. The important point to be noted is that catalyst B shows no loss in catalytic activity even up to a HTT of 700°C. We have estimated the fraction of superparamagnetic particles present in various heat treated samples and their mean diameters, using essentially the approaches and approximations described in the literature[10]. These are outlined in the appendix and the results are given in Table I. It is seen from Table I 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 catalyst 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 700°C indeed represents the least active catalyst. Since the chemisorptive properties of CO and $H_2$ 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.

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 show the formation of needles or chain like clusters up to $T_t$ and their conversion to more regularly shaped particles, resembling those with multidomain properties, above $T_t$. The average crystallite size increased from 185 to 256Å for catalyst A, and from 74 to 160Å 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 multidomain 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.

Further details of studies on the chemisorption of $H_2$ and CO on the supported nickel and the activity of the catalysts will be published separately along with a discussion of other magnetic parameters.

APPENDIX

The weight fractions $x_i$ of the superparamagnetic ("a" type) and hence of the multidomain ("c" type) particles in the various heat treated samples were estimated from the observed curves of the relative magnetization, $\sigma/\sigma_\infty$ versus H/T (at 573°C) by assuming Romanowski's relation[10] for a multi-component system given below.

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

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 multidomain particles show no change and superparamagnetic particles obey the well-known Langevin function. The average moment $\mu_i$ of the "a" type particle is defined by, $\mu_i = I_{sp} \cdot V_i$.

By assuming an overall mean volume $\bar{v}$ for all superparamagnetic particles, as in Selwood[5], a non-linear regression procedure was developed for estimating the weight fraction (x) of the "a" type 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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