MAGNETIC AND/OR MÖSSBAUER SPECTROSCOPIC CHARACTERIZATION OF FINE DISPERSIONS OF TRANSITION METAL CATALYSTS

Part I: Magnetic Characterization of Superparamagnetic Nickel in Presence of a Ferrimagnetic Component


Material Sciences and Engineering Department (136 MRL Building)
The Pennsylvania State University
University Park, Pennsylvania 16802, U.S.A.

1. Introduction

Magnetic properties of catalyst-type materials, such as metal dispersions or oxides are fascinating indeed and have attracted considerable attention during recent years. One of us (LNIM) previously reported on the magnetic properties of dispersions of $\alpha$-Fe$_2$O$_3$ in zeolites$^3-4$ and of Fe$^{3+}$ ions in silicates$^5$ and in glassy carbons$^6$. In addition to transition-metal oxides, the very fine dispersions of $3d$ metals such as Fe, Co, and Ni on various non-magnetic substrates (e.g., SiO$_2$, Al$_2$O$_3$) are technologically very significant because of their widespread use as industrial catalysts for heterogeneous catalysis. Significant fractions of such dispersions display "superparamagnetic properties", which permit their characterization in terms of their particles' profiles (particle shape, size, and their distribution) with respect to very small particles ($< 100 \text{ Å}$), which otherwise elude detailed characterization by standard methods (X-ray line broadening, etc.). Furthermore, the magnetic technique allows an in-situ investigation of chemisorption. However, most of the magnetic studies so far have been on materials containing relatively low amounts (usually below 10%) of the metal which is dispersed on substrates to yield, so to speak, ideal "single phase" superparamagnetic (catalytically active) systems. Studies of this nature have been reported by Carter et al.$^6$ and reviewed by Selwood$^7$ and Whyte$^8$. While such studies have undoubtedly enhanced our understanding of the mechanism chemisorption of electron

*Enquiries should be addressed to this author.
†Permanent address: Chemical Engineering Department; University of Natal, Durban, S. Africa.
donor and acceptor type molecules, very few attempts have been made to thoroughly characterize commercial catalysts containing large amounts of metal (up to 70% with multiphase components) and at temperature employed in actual industrial-type reactors, such as the methanation. Therefore, it seemed desirable to select and to characterize these very types of catalysts with special reference to the following considerations.

Supported metal catalysts containing large amounts of metals have generally different metal dispersions consisting of particles of different size and phases. When such catalysts are heated at high temperatures, crystallite growth occurs via a complicated mechanism which produces a rather undefined metal dispersion. Under these conditions, an exact determination of particle size distribution is very difficult. However, in the case of transition metals, which are used as methanation catalysts, it is possible to delineate and to characterize such dispersions by their magnetic properties. Three major types of magnetic structures, which normally coexist in support metals such as iron, cobalt and nickel catalysts at temperatures significantly lower than their Curie points, are discussed below.

The so-called single-domain or "superparamagnetic" structures, characteristic of very small particles, give magnetization curves which are adequately described by the Langevin equation [Mulay, Bean et al]. Their changes in magnetization are described by spin rotation as in normal paramagnetism. The magnetization is strongly particle size dependent and can be used for the assessment of average particle size of an assembly. True superparamagnetism is characteristic of a collection of very small single domain particles in which thermal energy is dominant during the magnetization process; thus no hysteresis is observed when magnetization ($M$) is plotted as a function of $H/T$, that is, the coercive force ($H_C$) and remanence ($\sigma_r$) are zero.

Secondly, we consider the single-domain anisotropic particles, which can have contributions to their magnetic energy arising from their shapes and crystal structures. These "single-domain anisotropic" particles are thermally stable in the magnetic sense and are characterized by significant hysteresis during magnetization, thus giving measurable values for $H_C$ and $\sigma_r$. Stoner and Wohlfarth and Néel first suggested that the contributions to $H_C$ are small due to the elongated shape of single-domain anisotropic particles far outweighing any contributions from the anisotropy of crystallite alignment within the particles.

The third type of structure, which is characteristic of the 3d metals in their massive or bulk state, consists of relatively large multidomain ferromagnetic particles, which change over to the paramagnetic state above their Curie point. Changes in magnetization with magnetic field below the Curie
temperature are caused by domain wall motion. Their magnetization curves reveal little hysteresis with negligible contributions to $H_c$ and $\sigma_r$, especially when no impurities and strain are present.

Kneller and Luborsky\(^4\) have carried out an elegant theoretical analysis of the contributions of each of the above structures to the coercive force and remanence as a function of the range of particle sizes. They have further substantiated their theory with supporting data obtained for iron-cobalt alloy particles (20-300 Å) dispersed in mercury. Their approach and contributions by Kittel and Galt\(^5\) have advanced our understanding of the particle profile criteria which determine transitions from the (i) superparamagnetic to single-domain anisotropic and from (ii) the single-domain anisotropic to multidomain particles. A schematic curve showing results of these transitions is given in Fig. 1, which is based of reference (15).

![Schematic curve showing results of transitions](image)

**Fig. 1.** Schematic representation based on reference\(^6\) of the dependence of $H_c$ (solid line) and $\sigma_r$ (dotted line) on average particle diameter ($D$) for an assembly of particles consisting of the superparamagnetic (SP), single-domain anisotropic (SD) and the multidomain ferromagnetic (MD) components.

In addition to parameters such as the coercive force and remanence discussed above, information gained from magnetization ($M$) versus field ($H$) (or versus $H/T$) plots is equally useful in the characterization of magnetic particles. For instance, it is possible to obtain the particle size distribution of superparamagnetic particles in the presence of the multidomain ferromagnetic component.\(^9\) This aspect is elucidated in some detail later.

The aspects of magnetic characterization described above provide a novel approach for characterizing the growth and shape of nickel particles during the heat treatment of nickel supported on alumina. In this paper,
we present an analysis of different magnetic structures observed for two commercial samples, containing initially (sample A) 43 and (sample B) 57 wt\% of total nickel, respectively, which were subjected to different heat treatments. In addition, we present particle size distribution of superparamagnetic components in the as-received and heat treated samples in the presence of multidomain ferromagnetic structures, and with special reference to this distribution around 573 K, which is quite close to the reaction temperature for methanation.

2. Experimental Methods

Apparatus:

A vibrating sample magnetometer, manufactured by the Princeton Applied Research Corporation, was used for magnetic measurements. This technique was selected for the present investigation because it involved very large magnitudes of $\sigma$, $\alpha$, and $\sigma_x$ as well as $H_0$. The present investigation did not warrant the use of the more sensitive force-type magnetometers (available in our laboratory), which are otherwise useful for the measurement of weakly dia- and paramagnetic properties. A critique of various measuring techniques including the Lewis' magnetometer is given by Mulay and the progress in magnetic instrumentation and applications relevant to this work has been appropriately reviewed bimonthly by Mulay and Mulay since 1962.

Magnetic fields up to KOe were generated with an electromagnet made by Varian Associates, in conjunction with 12-inch poles tapered to 6-inch. Fields up to 20 KOe have been employed by most workers (cf. 6-9 and references therein) at cryogenic temperatures for studies on fine particles and such were employed in the present studies; furthermore, the special "hill climbing", computations used in the analysis of magnetization curves (described later) allowed so to speak the necessary "extrapolations" to ultra "high fields", thus obviating the need for setting up more sophisticated equipment.

The fields were measured with a separate gaussmeter probe inserted between the poles and located very close to the vibrating sample. Magnetization measurements were recorded digitally over a wide range of magnetic fields. The magnetic field could be reversed easily to yield coercive forces as small as 10 Oe. A low temperature cryostat was used for measurements in the region 77-300 K, whereas for high temperature measurements (up to 973 K), a furnace with non inductive windings of platinum was used. This furnace was surrounded by a water jacket to prevent damage to the detection coils of the magnetometer. The catalyst sample ($\sim 100$ mg) was sealed in the lower section of a partitioned quartz tube, which in turn was attached to the lower end of a brass tube coupled to the transducer of the magneto-
meter. This arrangement permitted the sample tube to vibrate freely in the pole gap of the magnet.

Fig. 2. Quartz tube assembly showing the sealed in position of the catalyst pellet sample. X and Y represent the pick-up coils of the magnetometer. A platinum-wire wound furnace (not shown) slips over the quartz sample chamber to provide uniform temperature over the catalyst sample.

The quartz tube assembly is shown in Fig. 2. It was designed so that the catalyst sample could be supported firmly in the tube. This set-up prevented undue vibration of the sample itself within the tube and consequently prevented the generation of spurious signals in the magnetometer. Furthermore, the assembly allowed the insertion of a copper-constantan thermocouple tip close to the sample for an accurate measurement of temperature. The magnetometer was calibrated with a standard spherical sample of nickel, for which the saturation magnetization (\(M_s\)) is 484 gauss, which gives the per-gram magnetization, \(\sigma_s = 53.4 \text{ emu/g} \). [Tebble and Craik\textsuperscript{18}].

\*These authors and authors of papers in the J. Catalysis, etc. use "emu/g" or "gauss-cm\(^3\)/g" to designate the magnetization (\(\sigma\), \(\sigma_s\)) and the remanence (\(\sigma_r\)). They also use the Oersted (or Gauss) for the magnetic field (\(H\)). Conversion to S.I. units is done using the following: Magnetization of 1 Gauss = 10\(^3\) Am\(^{-1}\); A field (\(H\)) of 1 Oersted (or 1 Gauss) = 79.6 Am\(^{-1}\). For a discussion of magnetic units see Mulay\textsuperscript{19}, Jackson\textsuperscript{18} and Bleaney and Bleaney\textsuperscript{10}. 
The as-received and heat treated samples were reduced in $H_2$ and sealed under vacuum in quartz tubes prior to magnetic measurements. Reduction was for 8 hours in flowing ultrapure $H_2$ at 623°K followed by outgassing for 6 hours at 623°K to a final vacuum of $10^{-6}$ Torr. The sample was then cooled to room temperature in vacuum. Sealing of the sample tube under vacuum was carried out while the sample was surrounded by liquid nitrogen so as to prevent its sintering during sealing.

3. Results and Discussion

3.1. General Characteristics of the Catalysts

Some important physical characteristics of the as-received catalysts are listed in Table 1. Heat treatment of the catalysts was carried out by (a) exposure to flowing ultrapure $H_2$ at 1 atm for 1 hour at selected heat treatment temperature (HIT), followed by (b) exposure to a $H_2/CO$ synthesis mixture containing 1 mole % CO for an additional 1 hour at the HIT. The above procedures failed to cause complete reduction, which was reflected in the thermomagnetic analysis, described in a later section. This situation is not surprising in the light of reports by Martin et al. who found that reduction is less than 100% complete even at 923°K.

3.2. X-Ray Diffraction Studies

Average nickel crystallite sizes for the as-received and heat treated samples were estimated from the observed X-ray line broadening for the (111) diffraction peak using the classical Debye-Scherrer equation. Strictly speaking, diffraction peak broadening is produced by a combination of crystallite size broadening, strain broadening, and defect broadening; but it is being assumed here that crystallite broadening is predominant so as to be consistent with the conventional approach used in the catalysis literature. Apparently the nickel is of such small crystallite size that the (220) and (311) diffraction peaks were too weak to use for estimating crystallite size. The (200) diffraction peak was comparable in line width to the (111) peak for all heat
treatment temperatures, and thus gave similar crystallite sizes. Result based on the broadening of the (111) diffraction peak are given in Table 1 and 2. It is seen that the average crystallite size for the as-receive

Table 2

<table>
<thead>
<tr>
<th>HITT, °K</th>
<th>Catalyst A</th>
<th>Catalyst B</th>
</tr>
</thead>
<tbody>
<tr>
<td>723</td>
<td>193</td>
<td>111</td>
</tr>
<tr>
<td>773</td>
<td>233</td>
<td>133</td>
</tr>
<tr>
<td>873</td>
<td>239</td>
<td>140</td>
</tr>
<tr>
<td>923</td>
<td>255</td>
<td>160</td>
</tr>
<tr>
<td>973</td>
<td>233</td>
<td>133</td>
</tr>
</tbody>
</table>

catalyst B is only 40% of that for catalyst A. This is presumably due, at least in part, to a relatively smaller loading of nickel per unit BET area to catalyst B. For both catalysts, average crystallite size increases progressively with increasing HITT. However, for a given HITT, the relative increase in crystallite size is more pronounced for catalyst B than for catalyst A. For example, the average crystallite size for catalyst B heat treated at 973°K is twice as much as that for the as-received sample, whereas the corresponding increase for catalyst A is only 60%.

With regard to our discussion on needle shaped particles, it should be stressed that their presence was unequivocally confirmed in catalysts A and B subjected to HITT of 73 and 92°K respectively by the significantly large magnitude of $I_{||}$ and $\sigma_{r}$ (especially at low measuring temperatures); these measurements are described later.

3.3. Thermomagnetic Analysis

Plots of relative magnetization, $\sigma/\sigma_{0}$ (total), as a function of temperature over the range 77 to 700°K are shown in Fig. 3 for the as-received catalysts A and B along with the thermomagnetic curves for an "ideal" superparamagnetic dispersion of nickel and for bulk nickel. Unfortunately, Michel et al. did not define the scale for their magnetization axis and as such no quantitative interpretation can be derived from their curve. The significance which can be attached to this curve is that the magnetization of an ideal superparamagnetic system, as expected, decreases asymptotically with temperature, because there is no magnetic interaction between the single-domain superparamagnetic particles. Furthermore, this situation, in contrast to the ferromagnetic case, prevents the possibility of any co-operative effects between domains and, consequently, forbids the onset of any phase transition, thus eliminating the appearance of a Curie temperature. For these reasons the ideal superparamagnetic behaviour is said to be analogous to the 'magnetically dilute' paramagnetic situation in which no interactions take place.
Fig. 3. Relative magnetization ($\sigma/\sigma_0^{(bulk)}$) as a function of temperature. Here $\sigma_0^{(bulk)}$ refers to the true saturation magnetization of bulk nickel at 0°K. The magnetization for nickel dispersions studied by Michel et al. is shown on the right which is in arbitrary units.

between neighbouring species. The only difference lies in the fact that superparamagnetic particle may consist of several thousand paramagnetic species (atoms or ions). This gives rise to very large magnetic moments (of several thousand Bohr magnetons per particle) in the superparamagnetic system. In comparison to the curve of Michel et al., the curve at the top in Fig. 3 represents the characteristic ferromagnetic multidomain behaviour of bulk nickel.

Figure 3 shows that catalysts A and B have a behavior intermediate between that of bulk nickel and ideal superparamagnetic dispersion. That is, the Curie temperatures ($T_C$) for samples A and B are not as sharp as for bulk nickel for which $T_C=631°K$. This fact is attributed to the presence of a substantial fraction of superparamagnetic particles in A and B. The fact that the relative magnetization, $\sigma/\sigma_0^{(bulk)}$, for these samples does not reach the maximum value of unity can be attributed to the possibility that part of the nickel remains bound to the substrate as nickel aluminate (involving the Ni$^{2+}$ type of paramagnetic ions), indicating incomplete reduction and equally importantly, because a large number of spins remain uncompensated on the surface of the superparamagnetic particles present in the system. Superparamagnetic particles are indeed difficult to saturate even at a field of 20 KOe and 70°K. It should be noted that these uncompensated spins and, so to speak, the holes in the d-band of nickel are believed to be responsible for the chemisorption of molecules and subsequent catalyzed reactions.
3.4. Effect of Heat Treatment Temperature on $H_C$ and $\sigma_r$.

Figures 4 and 5 show typical plots of $H_C$ and $\sigma_r$ as a function of HTT and measuring temperature, $T_m$. Maxima in the plots suggest that a growth in particle size with increasing HTT has occurred. In the following paragraphs we outline some generalizations concerning both catalysts A and B, and in the last paragraph we point out differences in their magnetic behavior which characterize the changes in their particle profiles with HTT.

![Catalyst A graph](image)

Fig 4. $H_C$ (solid lines) and $\sigma_r$ (dashed lines) as a function of heat treatment temperature for catalyst A. The measuring temperature is indicated on each curve.

A feature common to catalysts A and B is that over the entire range of HTT of the catalysts (773-973 K) the $H_C$ and $\sigma_r$ values are practically zero at $T_m=573^\circ$K. However, at $T_m=423^\circ$K and below, significant values for $H_C$ and $\sigma_r$ are observed, which can be attributed to the formation of single-domain anisotropic (that is 'needle shaped') particles. This behavior suggests that the 'blocking temperature', $T_B$, for the two catalysts is somewhere* between 423 and 573 K. This observation is consistent with Kneller and

---

*Extrapolation of plots of $H_C$ versus $T_m$ to $H_C = 0$ indicates that $T_B \sim 500^\circ$K for the types of systems considered here. The dependence of $T_B$ on particle volume in the case of Ni$_2$SiO$_4$ and Ni$_2$Al$_2$O$_4$ sputtered films is discussed in detail by Gittleman and coworkers."
Fig. 5. $H_c$ (solid lines) and $\sigma_f$ (dashed lines) as a function of heat treatment temperature (HIT) for catalyst $B$. The measuring temperature is indicated on each curve. Note that $H_c$ and $\sigma_f$ plots with practically zero values at a measuring temperature of 573°K are seen to overlap over the entire HIT range.

Luborsky's theory and their observations for cobalt particles dispersed in mercury, as summarized in Fig. 1. The maxima in $\sigma_f$ and $H_c$ are attributed to the formation of single-domain anisotropic (needle shaped) particles. Furthermore, the maxima in $H_c$ observed at specific HITTs suggest that these maxima result from shape anisotropies and not from crystalline anisotropies of such needle shaped particles. From published results of Kittel and Galt, the critical particle diameter for crystal anisotropy to become significant for nickel (fcc) at 300°K is about 438Å with a maximum $H_c$ of only 135 Oe, whereas a maximum $H_c$ of 3150 Oe can occur for needle shaped particles having a much lower diameter of about 70Å. Since many of the isolated particles on the catalysts have diameters much less than those required for significant crystal anisotropy as determined from hydrogen chemisorption discussed later (see ref. 24), and also because the observed coercive forces are quite large, it appears that the anisotropy contributions to $H_c$ are mainly due to the presence of elongated (needle shaped) particles. Electron microscopy did reveal the presence of such particles in catalysts $A$ and $B$ when subjected to HIT of 873 and 923°K respectively.
A comparison of the curves in Fig. 4 and 5 with Fig. 1 based on Kneller and Luborsky's results suggests that the maxima are probably due to the following competing mechanisms (i) and (ii), which occur during the heat treatment of the catalysts:

(i) Conversion of superparamagnetic particles to single-domain anisotropic particles occurs by some migration and growth process on the catalyst surface at and below the characteristic HTT at which maximum coercivity and remanence occur.

(ii) Conversion of single-domain anisotropic particles to multidomain particles occurs via a migration and growth process above the characteristic HTT.

However, a partial conversion of superparamagnetic particles directly to multidomain particles, especially at higher temperatures, cannot be ruled out. These considerations complicate the modeling of the sintering process. Perhaps a more elaborate analysis is required than that put forward by Ruckenstein and Pulvermacher and by Flynn and Wanke.

Catalysts $A$ and $B$ show maximum values of $H_C = 250$ Oe and 200 Oe, respectively, and of $\sigma_r \approx 14$ gauss at $T_m = 77^\circ K$. The fact that $A$ showed the maximum in $H_C$ at a lower HTT than $B$ suggests that $B$ is more resistant, in the thermal sense, to the formation of needle shaped particles and/or to their conversion to multidomain particles.

3.5. Magnetization Versus $H/T$ Curves.

Curves for the relative magnetization $\sigma/\sigma_r$ as a function of $H/T$ were obtained for the as-received and heat treated nickel catalysts $A$ and $B$, using fields up to 20 KOe and over a range of $T_m$, generally between 300 and 600$^\circ$K.

Typical magnetization plots for catalyst $B$ are given in Fig. 5a. In the dis-

Fig. 5. (a) Typical magnetization ($\sigma/\sigma_r$ vs $H/T$) curves for catalyst $B$ for the as-received and heat treated samples. A magnetization curve for superparamagnetic particles ($30\mu$ radius at 573$^\circ$K) is shown for comparison.
In section to follow we consider the plots obtained at 573°K only (Fig. 6 and 7).

![Fig. 6](image-url)  
**Fig. 6** Relative magnetization ($\sigma/\sigma_s$) plots as a function of the ratio Field ($H$)/Measuring Temp. ($T$), for catalyst A for the “high field” region. The heat treatment temperature (HTT) of each sample is indicated on the curve.

![Fig. 7](image-url)  
**Fig. 7.** Relative magnetization ($\sigma/\sigma_s$) as a function of the ratio Field ($H$)/Measuring Temp. ($T$), for catalyst B for the “high field” region. The heat treatment temperature (HTT) of each sample is indicated on the curve.

for several reasons. First, this temperature is within the range of temperature over which methanation is usually conducted, and as such any quantitative interpretation derived from the magnetization curves at this temperature would be expected to have a direct technological relevance. Second, at this temperature any single-domain anisotropic particles would be expected to behave essentially as superparamagnetic particles and thus make a minor
contribution to \(\sigma_r\) and \(H_c\). That is, as discussed in an earlier section concerning \(T_B\) and with reference to Figs. 4 and 5, \(\sigma_r\) and \(H_c\) were indeed found to be almost zero \(T_m=573^\circ K\). In addition to these criteria we found that a temperature of \(573^\circ K\) was most suited because it was well below the Curie temperature of nickel \((631^\circ K)\) and thus yielded large values of \(\sigma\) which could easily be measured to the desired accuracy.

The above discussion points to the situation that at \(573^\circ K\) it is sufficient to consider the presence of only two types of particles, namely the superparamagnetic and the multidomain ferromagnetic. In analyzing the magnetization curves we have adopted a new approach in that we estimate the fraction and the mean particle volume for the superparamagnetic component in the presence of the multidomain ferromagnetic particles. It should suffice to point out that the magnetization curves for a two component systems\(^9,27\) show a steep slope in the low field region, resembling the behavior of a ferromagnetic system; at high fields the approach to saturation is rather slow, like that of superparamagnetic particles. Thus, at high fields the total magnetization is composed of a constant saturation magnetization component arising from the ferromagnetic fraction \((1-x_i)\) and another (variable) component which is strongly dependent on the particle size of the superparamagnetic fraction \((x_i)\), which obeys the Langevin equation. Thus, the equation for the high field magnetization is given by

\[
\frac{\sigma}{\sigma_s} = \left(1 - \sum x_i\right) + \sum x_i L_i \frac{I_{sp} \bar{v}_i H}{kT}.
\]

(1)

The expression under the summation sign refers to the superparamagnetic particles; \(L\) denotes the Langevin function, \(\bar{v}_i\) is the mean volume of the particles within the \(x_i\) fraction, and \(I_{sp}\) is the spontaneous magnetization for bulk nickel.\(^{17}\) This equation can be be fitted by a regression routine to experimental data for the evaluation of \(x_i\) and a mean particle volume \(v_i\) as proposed by Selwood and co-workers\(^7,28-30\). The Langevin term\(^7\) for particles with mean volume \(\bar{v}\) is given by:

\[
L = \frac{I_{sp} \bar{v} H}{kT}.
\]

(2)

where the product \(I_{sp} \bar{v}\) represents the saturation magnetic moment of the particle. A value of \(I_{sp}=32.5\) gauss was taken for bulk nickel at \(573^\circ K\).\(^{17}\)

The high field results shown in Figs. 6 and 7 were analyzed to estimate the parameters \(\Sigma \bar{x}\) and \(v_i\) as given by Eqs. 1 and 2. For this purpose a computer program for non-linear regression analysis of the data was used, which incorporated a hill climbing procedure. This program easily accomplished convergence, and a very good fit was obtained between the computed values (shown by a solid line in Figs. 6 and 7) and the experimental data points.
The estimates of the fractions of superparamagnetic particles, relative to the total metal present in the two catalysts, and the mean particle sizes within the superparamagnetic fractions obtained by computer analysis are shown in Table 3. The increased transformation to multidomain particles at high

Table 3.
Effect of Heat Treatment on Superparamagnetic Particles
in Catalysts A and B

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Superparamagnetic Particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, K</td>
<td>Wt Fraction</td>
</tr>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>As received</td>
<td>0.36</td>
</tr>
<tr>
<td>773</td>
<td>0.27</td>
</tr>
<tr>
<td>873</td>
<td>0.21</td>
</tr>
<tr>
<td>973</td>
<td>0.12</td>
</tr>
</tbody>
</table>

It is evident. The transformation to multidomain particles is accompanied by a marked overall magnetic structural change characteristic of 3d transition metals. Changes in the mean particle size of the superparamagnetic fraction are less marked for catalyst B, in line with its lower loading of nickel per unit area.

It is noteworthy that the mean particle size of the superparamagnetic particles for both catalysts decreases with increase in IHTT from 873 to 973°K; the decrease is more pronounced for catalyst A. These results suggest that during heat treatment in this temperature range, supported nickel particles undergo redispersion resulting in the formation of smaller particles. Similar observations have been reported by several workers (cf 30). Furthermore, Fiedorow and Wanke31 have recently shown that when alumina supported platinum catalysts are heated in oxygen, significant changes in platinum dispersion occur over a certain IHTT range.

3.6. Chemisorption of Hydrogen;

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 \( f = \frac{N_i \text{ atoms at the surface}}{\text{total number of nickel atoms in the bulk per gram of catalysts}} \times 100 \). Relevant information is given in Table 4, 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 IHTT.
Table 4.
Results of Hydrogen Chemisorption

<table>
<thead>
<tr>
<th>HTT°C</th>
<th>Sample A</th>
<th>Sample B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No. of Ni atoms per g ($\times 10^{20}$)</td>
<td>Dispersion $f$ (%)</td>
</tr>
<tr>
<td>As received</td>
<td>2.26</td>
<td>5.12</td>
</tr>
<tr>
<td>500</td>
<td>2.45</td>
<td>5.54</td>
</tr>
<tr>
<td>600</td>
<td>1.48</td>
<td>3.36</td>
</tr>
<tr>
<td>700</td>
<td>1.67</td>
<td>3.78</td>
</tr>
</tbody>
</table>

The degree of dispersion is plotted as a function of the weight fraction of superparamagnetic particles in Fig. 7a for various heat treated samples. The average particle sizes from Table 3 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.

4. Conclusions

We have shown that commercial Ni-Al$_2$O$_3$ catalysts indeed can be characterized using magnetization ($\sigma$) versus field/temperature type measure-
ments with regard to the particle size distribution of very small catalytically active (superparamagnetic) particles in the presence of large ferromagnetic structures and under conditions close to the reaction temperature normally encountered in methanation. We have also shown that crystallite growth during heat treatment occurs from the (i) superparamagnetic to (needle) shape-anisotropic particles, and (ii) from the shape-anisotropic to very large multidomain structures. These conversions also were followed remarkably well using parameters such as the coercive force and remanence. Thus, several basic concepts and theories developed in the past for the ideal one-phase systems by magneticists have been applied to the characterization of commercial catalysts of technological relevance. Our work suggests the possibility of employing magnetic characterization of quality control in the commercial production of catalysts. Further work correlating the particle size distribution of superparamagnetic particles with their actual methanation reactivity in these commercial catalysts as well as their \( H_2 \) chemisorption activities will be published separately.

References


[23] Gittlemen, J. I., Abeles, B., and B ozowski, S., Phys. Rev. (B) 9(9), (1974) 3891 (N workers have used an AC mutual inductance bridge (10a), not requiring an external field for their (apparently) ideal superparamagnetic system).