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MOSSBAUER SPECTROSCOPIC STUDIES OF Ni CATALYSTS: PARTICLE SIZE DETERMINATION AND EFFECT OF HYDROGEN CHEMISORPTION

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Résumé.- Les propriétés magnétiques de microcristaux de Ni supportés en silica ont été étudiées au moyen de la spectroscopie Mössbauer. La granulométrie est estimée d'après les variations du spectre à 78 K avec le champ magnétique appliqué. On a trouvé que le moment magnétique des particules et la constante d'énergie anisotrope décroissent au cours de l'adsorption d'hydrogène.

Abstract.—The magnetic properties of silica supported Ni microcrystals have been studied by use of Mössbauer spectroscopy. From the field dependence of the spectra at 78 K the particle size is estimated. It is found that both the magnetic moment of the particles and the anisotropy energy constant decrease when hydrogen is chemisorbed.

Nickel catalysts are widely used in the chemical industry, especially for reactions involving hydrogen. Therefore, chemisorption of hydrogen and its effect on the magnetic properties of Ni particles have attracted much attention, and it has been shown that the magnetic moment of Ni particles decreases upon hydrogen chemisorption. This has been explained by a filling of the 3d band by the electrons of the chemisorbed hydrogen /1/.

In the present work we have used Mössbauer spectroscopy to study the magnetic properties of $^{57}$Co doped small Ni particles supported on silica. The measurements were carried out with applied magnetic fields, H, up to 12.4 kG, in the temperature range 4.2-700 K, and with the sample in hydrogen or in vacuum (10^{-7} torr). In the latter case chemisorbed hydrogen was removed by evacuation at 675 K for 2 hours.

Figure 1 shows spectra obtained in vacuum at 78 K. In the absence of an applied field the spectrum consists of a sharp line arising from Fe in metallic Ni and a "shoulder" with an isomer shift of about 1 mm/s, probably arising from Fe$^{2+}$ in a non-reduced phase. For H > 0, the spectra become magnetically split. These results show that $^{57}$Co is mainly present in small Ni particles in which fast superparamagnetic relaxation occurs. For such particles the magnetic splitting of the spectra is approximately proportional to the Langevin function, $L(\mu H/kT) = \coth (\mu H/kT) - kT/\mu H$, where the magnetic moment $\mu$ of the particles is given by the product of the magnetization $M_s$ and the volume $V$. For $\mu H/kT > 1$,

![Mössbauer spectra of $^{57}$Co doped Ni particles in vacuum at 78 K in various applied magnetic fields](image-url)
a plot of the magnetic splitting of the Mössbauer spectra versus $T/H$ should give a straight line with slope $-k/y$. Figure 2 shows such a plot for the spectra obtained at 78 K. Assuming that $M_s$ is equal to the bulk value we find an average particle diameter of 4 nm. This result is in good agreement with chemisorption and x-ray diffraction measurements.

![Fig. 2: Magnetic splitting $\Delta_{16}$ and $\Delta_{25}$ of lines 1 and 6 and lines 2 and 5 for the spectra obtained at 78 K, plotted as a function of $T/H$.](image)

When the particles were exposed to hydrogen a smaller increase in the magnetic splitting with increasing magnetic field was found, especially at low fields. For example, at 4 kG the spectra can be approximated by broad single lines with line widths given by $r_{vac} = 3.8$ mm/s and $r_{H_2} = 3.0$ mm/s. The difference indicates that $y$ decreases when hydrogen is chemisorbed, in accordance with magnetization measurements /1/.

Figure 3 shows some spectra obtained at 78 K, 25 K, 16 K, and 4.2 K in vacuum and after chemisorption of hydrogen at 300 K. At 4.2 K the spectra are magnetically split (the Fe$^{2+}$ component gives rise to a very broad component in hydrogen and to a somewhat narrower component in vacuum). At 16 K and 25 K the spectra of the Ni particles consist of both a paramagnetic component and a ferromagnetic component, indicating a typical superparamagnetic behaviour. It is remarkable that the area ratio of the ferromagnetic and the paramagnetic components decreases drastically, when hydrogen is chemisorbed. An analysis of the results on the basis of Brown's expression for superparamagnetic relaxation in the low temperature limit /3/ gives the anisotropy energy constants: $K_{vac} = (6 \pm 2) \times 10^4$ J/m$^3$ and $K_{H_2} = (3 \pm 1) \times 10^4$ J/m$^3$. A different approach to the determination of $K$ is based on the influence of collective magnetic excitations, which for $KV/kT >> 1$ gives rise to a reduction in the observed hyperfine field by a factor of about $1 - kT/2KV$ relative to the bulk value /4,5/. The hyperfine field of $^{57}$Fe in bulk Ni at 4.2 K is 283 ± 1 kG /6/. A computer analysis of the present spectra gave $H_{hf}(H_2) = 275 \pm 1$ kG and $H_{hf}(vac) = 277 \pm 1$ kG at 4.2 K. Assuming that the hyperfine field is independent of chemisorption, we find: $K_{vac} = (4 \pm 1) \times 10^4$ J/m$^3$ and $K_{H_2} = (3 \pm 1) \times 10^4$ J/m$^3$. Thus, the two methods give similar results indicating that $K$ decreases when hydrogen is chemisorbed.

The results can be explained by a large surface anisotropy energy constant /7/ which decreases when hydrogen is chemisorbed. Such a behaviour has also been observed in small iron particles /8/, and the results are in accordance with recent FMR measurements /9,10/.

The observed correlation between the superparamagnetic relaxation time and chemisorption may become a valuable tool in the study of chemisorption and catalysis. Because of the strong dependence of the relaxation time on the anisotropy energy constant the effect may be extremely sensitive to small changes occurring at the surface.
References

/3/ Brown, Jr., W.F., Phys. Rev. 130 (1963) 1677
/9/ Blum, J.K. and Göpel, W., Thin Solid Films 42 (1977) 7
/10/ Blum, J.K. and Göpel, W., J. Magnetism and Magnetic Materials 6 (1977) 186