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Paracrystallinity in a Coprecipitated Nickel/Alumina Catalyst

Analysis of the lineshapes of catalyst diffraction peaks can provide valuable information about crystallite sizes and structural distortions. Hosemann *et al.* (*1*) for example, have used this information to support a detailed theory of the structure of iron/alumina catalysts used for ammonia synthesis. In this Note, a similar analysis is applied to a nickel/alumina coprecipitated catalyst, and it is suggested that the two catalysts have related structures.

Diffraction line broadening can arise from a multiplicity of causes, e.g., crystallite size, strain, and paracrystallinity. A separation of the different causes is possible, but experimentally difficult, since it requires careful measurement of the variation of the diffraction peak widths as a function of momentum transfer, $Q = 4\pi \sin \theta/\lambda$. This is made possible only by collecting precise measurements over a wide variation of Q. Paracrystallinity is a structural distortion in which the overall dimensions of a crystal remain unchanged, but where the individual vectors between adjacent unit cells can vary in magnitude and direction subject to the constraint that the cells are uniquely defined and the lattice is consequently not amorphous. For a one-dimensional paracrystal the location of an individual cell is determined by the intercell vectors between the cell and its nearest neighbours (*2*). Since these vectors vary about their mean, the lattice has appreciable short-range order, but in contrast long-range correlations disappear. In three dimensions a physical example of a paracrystal is a lattice which contains a high concentration of randomly distributed defects each of which produces a local microstrain (*1*). The location of a single cell is then determined by the superposition of the microstrains caused by all the neighbouring defects.

Hosemann and co-workers (*1, 3*) have studied the ammonia and low-pressure methanol synthesis catalysts. They have reported X-ray measurements of high-order diffraction peaks, which required *4 weeks* of counting to obtain the necessary statistical accuracy to distinguish the different models (*1*). In this Note we report the application of time-of-flight neutron diffraction, using the Harwell electron linear accelerator (LINAC) to the analysis of a coprecipitated nickel/alumina catalyst. The X-ray diffraction line broadening of nickel in these catalysts has always been found to be different from that expected from hydrogen chemisorption measurements of surface area (*4*). Phase analysis and temperature-programmed reduction have shown that the oxide form of such catalysts contains metastable oxide phases with nickel/aluminium ratios between those of nickel oxide and nickel aluminate (*4*). These metastable phases are present because of the nonequilibrium nature of materials prepared by coprecipitation and low-temperature calcination. They are very different from materials which might be produced by the intimate mixing of nickel oxide and nickel aluminate. This model of the oxide form, in which nickel and aluminium ions are both present in a close-packed oxide lattice, provided the first clue that the nickel formed by reduction of the oxide form might be paracrystalline.

Neutron diffraction is an attractive tool for this problem, because of the absence of fluorescence and the form factor which diminish the intensity of diffracted X rays at high values of Q. Using neutrons from a

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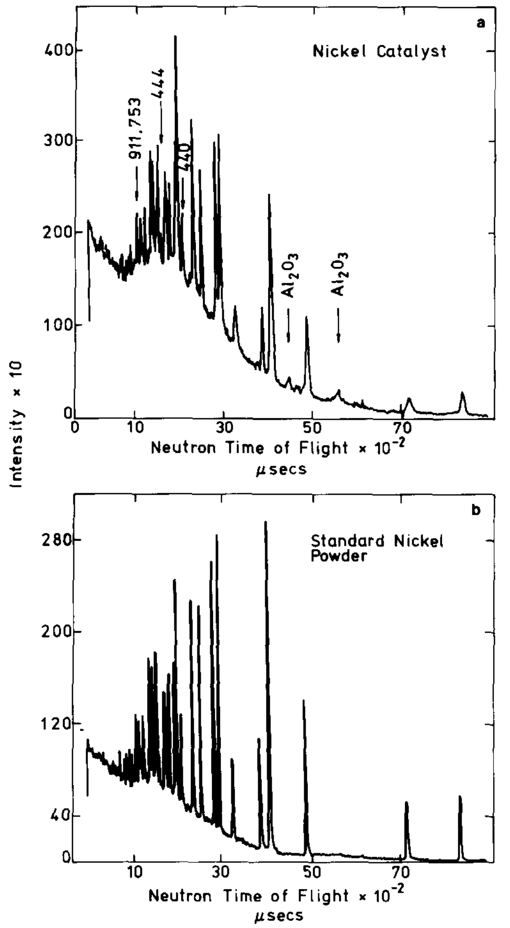

FIG. 1. Time-of-flight diffraction patterns, from (a) coprecipitated nickel/alumina catalyst and (b) sintered nickel powder.

LINAC, we obtain an additional advantage from its high intensity of short-wavelength neutrons. The use of the Harwell LINAC in diffraction studies is described elsewhere (*5*).

Five cubic centimeters of a 75 wt% Ni/alumina catalyst which had been reduced in hydrogen at 450°C and used for steam reforming was placed in an aluminium foil container, and investigated with the Harwell backscattering spectrometer (*5*). The resolution correction to the diffraction peak widths was measured from the pattern obtained from a sample of well-sintered nickel powder.

Figure 1 shows diffraction patterns from the Ni/alumina catalyst and the sintered nickel. Diffraction peaks from planes of high order such as the coincident 911 and 753 can be clearly seen. Differences between the patterns of the catalyst and the standard nickel arise partly from the alumina present in the catalyst. This leads to a number of additional peaks, and a higher background intensity due to incoherent scattering from the associated hydrogen, mainly present as hydroxyl groups.

Crystallite size, strain, and paracrystallinity effects can be distinguished from one another by the momentum transfer variation of the contributions they make to line broadening, ΔQ.

For (a) crystallite size effects

$$\Delta Q = \text{constant},$$

TABLE 1

Structural Parameters of Two Paracrystalline Catalysts

	Host metal	a_0 (Å)	Dopant	a_0 (Å)	g_{111}	$\bar{L}_{111}$ (Å)	g_{100}[a]	g_{110}[a]
Nickel/alumina steam reforming catalyst (this work)	Ni, fcc	3.52	$NiAl_2O_4$	8.05	0.012	256 ± 13	0.015	0.0057
Ammonia synthesis catalyst (Ref. (*1*)).	α-Fe, bcc	2.87	$FeAl_2O_4$	8.15	0.0085 ±0.0005	250 ± 60	0.0116 ±0.0006	0.0073 ±0.0002

[a] The values of g in the 110 and 100 directions have been determined by assuming that the paracrystals of the nickel are cubic.

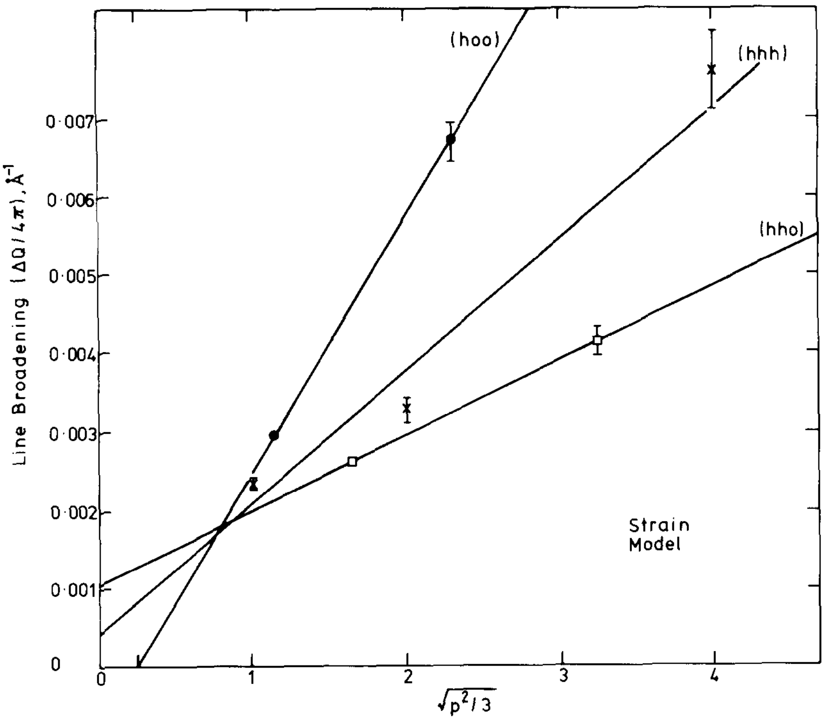

FIG. 2. Line broadening plotted against p; a test for strain contributions.

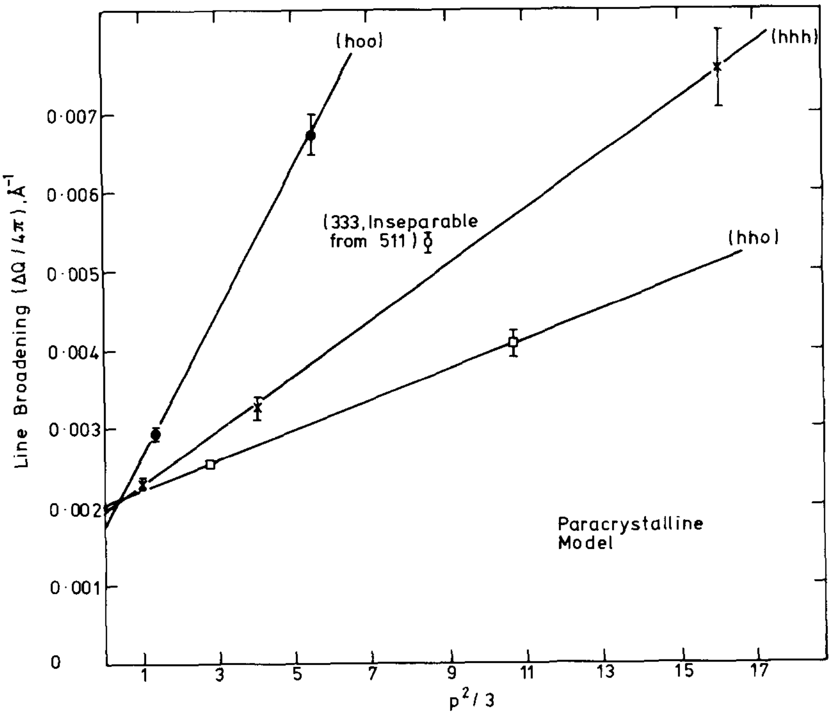

FIG. 3. Line broadening plotted against p^2; a test for paracrystallinity contributions.

(b) strain

$$\Delta Q = kp + \text{constant},$$

(c) paracrystallinity

$$\Delta Q = kp^2 + \text{constant},$$

where $p^2 = h^2 + k^2 + l^2$ for any specific line. Due to crystallite anisotropy it is necessary to study this relationship for diffraction from a single set of parallel lines. For nickel, the 111, 222, and 444 peaks are free from accidental overlap and are the most accessible group to study. Figures 2 and 3 show the line broadenings of these peaks plotted against $(p^2/3)^{1/2}$ and $p^2/3$, respectively. The broadenings were determined by fitting a theoretical resolution function to the data (*6*) and subtracting in quadrature the instrumental resolution contribution. In both figures values for (h00) and (hh0) reflections lie on different straight lines showing the crystal anisotropy. For the (hhh) reflections the points fall clearly on the line $\Delta Q = kp^2 + c$, demonstrating the presence of paracrystallinity in the coprecipitated nickel/alumina catalyst.

The full paracrystallinity expression linking momentum transfer broadening with p^2 is

$$\Delta Q = \frac{2\pi}{\bar{d}_h}\left[\frac{1}{N_h} + (\pi g_h p_h)^2\right],$$

where $\bar{d}_h$ is the mean separation between neighbouring atoms perpendicular to the lattice planes h. $g_h^2\,\bar{d}_h^2$ which equals $(\overline{d_h^2} - \bar{d}_h^2)$ is the variance of $\bar{d}_h$, and $\bar{L}_h = N_h\bar{d}_h$ is the dimension of the paracrystal perpendicular to the lattice planes h. As before $p_h^2 = h^2 + k^2 + l^2$. The linear addition of the two contributions to the line broadening assumes that they are both good approximations to Cauchy profiles (*7*). Consequently from the slope and intercept of Fig. 3, it is possible to obtain values for $\bar{L}_{111}$ and g_{111}. These are found to be 256 Å and 0.012, respectively. The values of $\bar{L}_{111}$ and g_{111} are similar to those found by Hosemann *et al.* (*1*) for the ammonia synthesis catalyst, and Table 1 lists these and other relevant structural parameters.

It is likely that there is a common mechanism for the structural perturbation in each catalyst involving solution of a spinel phase in the host metal. Since the ratio of the volume of a nickel atom in bulk nickel to that of an oxygen anion in nickel aluminate is 1.5 : 1, the substitution seems likely to involve one $(AlO_2)^-$ group for three nickel atoms. A quantitative assessment of whether the experimental g values are consistent with one defect geometry rather than another must await the measurement of the proportion of alumina dissolved in the nickel.

It has now been shown that paracrystalline distortions are present in three different catalysts, the coprecipitated Cu–ZnO/Al_2O_3 low-pressure methanol synthesis catalyst (*3*) the coprecipitated Ni/Al_2O_3 catalyst of this work, and the Fe/Al_2O_3 ammonia synthesis catalyst prepared by the fusion technique (*1*). Work now in progress at Harwell is attempting to explain in more detail the effects of paracrystallinity upon the structural changes arising from thermal treatments of these three catalysts.

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C. J. WRIGHT
C. G. WINDSOR

Materials Physics Division
A.E.R.E., Harwell
Oxfordshire OX11 ORA
England

D. C. PUXLEY

British Gas
London Research Station
Michael Road
London SW6 2AD
England

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