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High-Resolution Electron Microscopy of Metal-Intercalated "Graphimets"

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Samples of some commercially available catalysts (known as "Graphimets"), in the form of graphite which had been intercalated with chlorides of Fe, Co, Cu, Ni, and Pt and subsequently reduced at low temperatures, have been examined by high-resolution electron microscopy and other techniques. The observations revealed that the intercalated element was present primarily as small islands of either metal or metal oxide on the surfaces of thin graphite flakes which appeared to have separated as a consequence of the manufacturing procedure. The direct resolution of lattice fringes in electron micrographs of the small (10–100 Å) particles, together with subsequent optical diffraction, provided a means of microdiffraction analysis which enabled identification of the phases present. The very high reaction rate measured for graphite gasification in the case of the Fe Graphimet, which will be described in detail elsewhere, was in keeping with the small particle size and the correspondingly large surface area. Finally, the potential of electron microscopy at the lattice resolution level for resolving a number of outstanding questions concerning the role of small metal particles in catalysis is briefly discussed.

1. INTRODUCTION

The properties and structure of graphite, when intercalated with various metal-based complexes, have been the subjects of considerable study during recent years (*1–4*) with much of the attention centring around their striking electronic and catalytic properties (*5*). The graphite–transition-metal systems are of particular interest because of their potential as hydrogenation catalysts. Measurements of catalytic activity, as mentioned later in this paper and described elsewhere (*6, 7*), provided the stimulus for an examination of the fine structure of several allegedly "metal-intercalated Graphimets" to be undertaken using the technique of high-resolution electron microscopy.

Although graphite cannot be directly intercalated with transition metals, intercalation is claimed to be possible by the reduction of intercalated salts of these metals. A wide range of commercially produced metallic intercalates is available from the Ventron Corporation under the general name "Graphimets" (*8*). A detailed description of the preparation procedure is included in a U.S. patent disclosure by Lalancette (*9*). In brief, the process involves heating a mixture of purified graphite powder and metal chloride in flowing chlorine for some days at about 500°C. Reduction is accomplished by treating the graphite–metal-chloride with lithium biphenyl at −50°C under a helium atmosphere. After washing with tetrahydrofuran, acetone, and water, the "Graphimets" are vacuum dried at 140°C. This process is said "to produce the metal substantially in atomic dispersion between the planes of the graphite." On the basis of the total metal content of Graphimets "the distance between each metal atom is calculated to be on the order of 5 Å" (*8*).

In view of the exceptional catalytic activity of these materials it was of considerable interest to carry out electron microscope observations for comparison with earlier studies of metal-chloride intercalates by Evans and Thomas (*2*). Preliminary ac-

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counts of the initial results of this study have been presented previously at conferences (*10, 11*).

EXPERIMENTAL METHODS

The very finely divided Graphimet powders (~200 mesh) were prepared for electron microscopy by simply spreading a small quantity of a particular type on a glass slide, adding a small drop of methanol, and then placing a specimen grid previously coated with a holey carbon film on top of a fairly sparsely populated region of the suspension. The Graphimet flakes adhered very well to the carbon film, with projections over the holes allowing the material to be examined without interference from the support film.

Specimens were normally screened in a Siemens 102 electron microscope, which was also used for some stereomicroscopy, and then examined in detail in the Cambridge University 600-kV high-resolution electron microscope (HREM) (*12, 13*). The latter microscope had previously demonstrated that it could provide directly interpretable resolutions approaching 2 Å, as well as being able to resolve lattice fringed to spacings as fine as 1 Å (*14*), and would thus be ideal for a high-resolution examination of these materials.

Observations were primarily at an accelerating voltage of 500 kV with axial, bright field illumination and magnifications in the range 200,000–350,000 times although, for correction of image astigmatism, magnifications of 750,000 times or more were commonly used. Image contrast, in the case of the thinnest flakes, was generally low, necessitating the recording of through-focus series in order to obtain im-

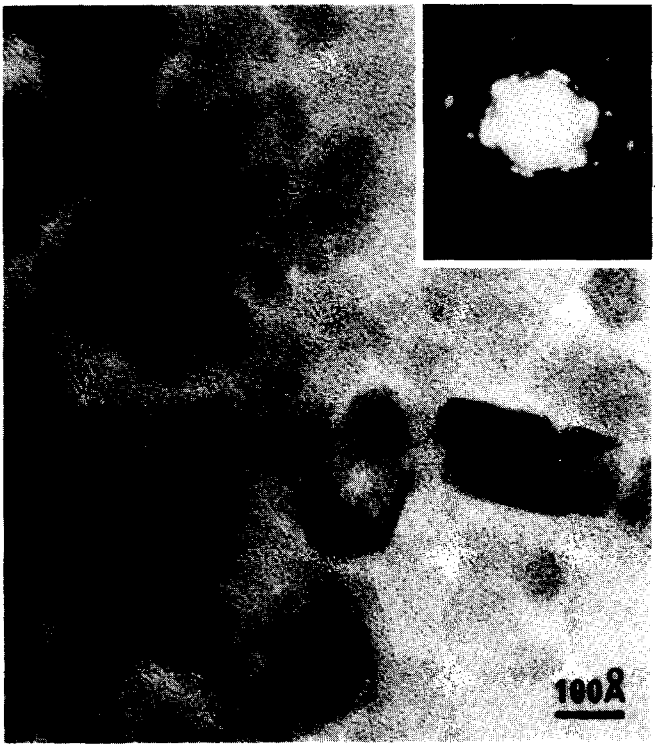

FIG. 1. Typical region of the Graphimet Fe-5, showing the general morphology of Fe_3O_4 particles, together with the corresponding electron diffraction pattern (inset). The major ring spacings of the latter can be indexed as corresponding to Fe_3O_4 by reference to rings arising from the graphite support.

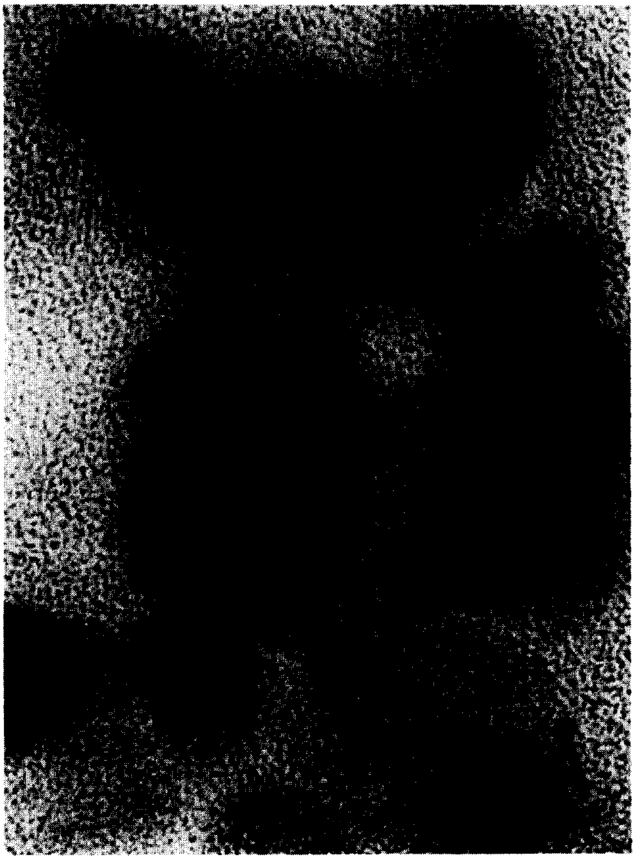

FIG. 2. High-magnification image of the Graphimet Fe-5. The presence of fringes within the particles corresponds to the resolution of lattice planes; the fringe spacing identifies the particles as consisting of Fe_3O_4.

ages close to the correct objective lens defocus. Selected area electron diffraction patterns from crystal regions as small as 2000 Å could be obtained with either an appropriately sized diffraction aperture or a small focused spot. Use of the ±30° specimen tilt cartridge of the HREM also permitted the recording of stereo images, if required, with tilt angles typically of 5.0°; hence providing the possibility of localising the relative positions of any morphological features of particular interest. The direct resolution of crystal lattice planes both in the graphite sheets, and in the particles themselves, provided a direct calibration of image magnification. It was relatively common to observe at least one set of the 2.1-Å lattice fringes arising from the (1.00) graphite reflections, and often the second, or even third, set was also seen. An optical bench, equipped with a 10-mW He–Ne laser, was used for analysis of the recorded micrographs since an accurate measurement of lattice spacings of unidentified materials could then be provided. Some X-ray diffraction analysis was carried out on the Ni Graphimet sample.

RESULTS

Electron Microscope Observations

The examination of specimens in the electron microscope generally revealed the presence of small, approximately circular, regions in dark contrast, as illustrated for the Graphimet Fe-5 (5% iron) in Fig. 1. In

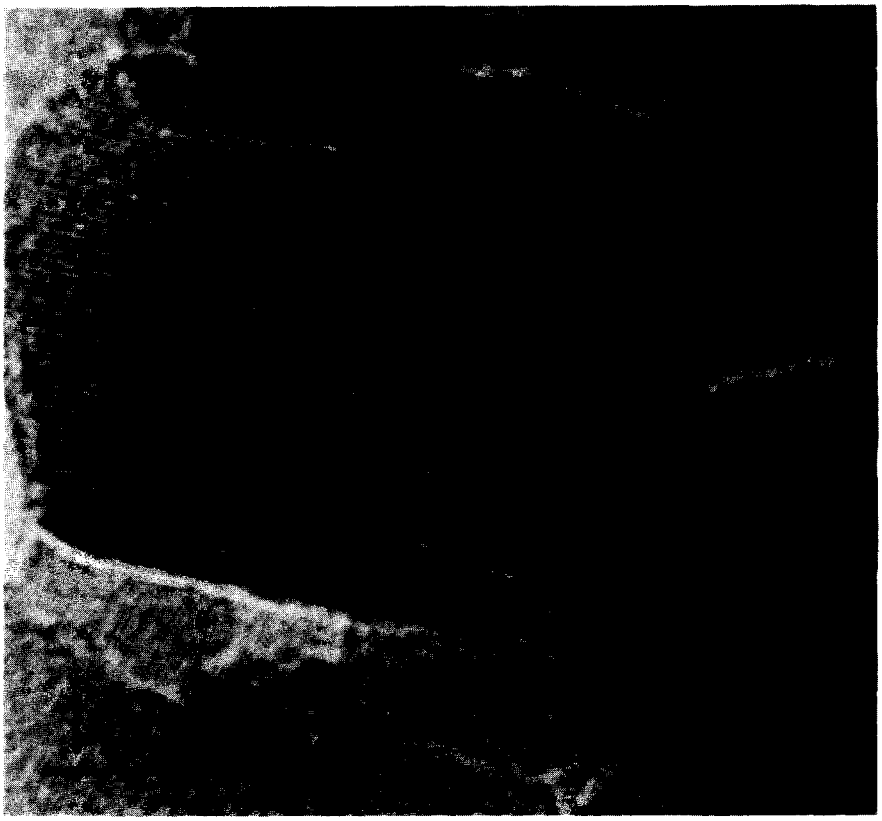

FIG. 3. Two small particles of Fe_3O_4 oriented with their (111) lattice planes (4.9 Å) parallel to the electron beam.

these Fe samples the apparent particles usually occurred in clusters with electron diffraction patterns, such as that shown in the inset to Fig. 1, which typically revealed the superposition of several graphite flakes. In this particular case it seems that there are two principal flakes rotated by about 15° relative to each other. The ring pattern, which could be indexed as having the spacings of Fe_3O_4, was shown later to arise from the actual particles.

At higher magnifications, such as that in Fig. 2, it sometimes appeared that the particles in these clusters overlapped, suggesting that they might be present on the surfaces of several graphite flakes. This was later confirmed by stereomicroscopy, as discussed further below. At even higher magnification, lattice fringes on a cross-grating pattern were often clearly visible and could be indexed as having spacings corresponding to those of Fe_3O_4, as evidenced, for example, by the 4.9-Å spacings in Fig. 3 and the striking 2.53-Å (311) fringes in Fig. 4. The corresponding optical diffraction pattern is also provided in the latter case. The relative appearance of the oxide particles and the graphite, together with the particle size and number, lead to a very rough estimate of 5 wt% Fe which was that specified for Graphimet Fe-5.

The structure of Graphimet Co-5 (i.e., 5% cobalt) was found to be generally similar to the corresponding iron Graphimet, as illustrated in Fig. 5. Selected area electron diffraction patterns from large clusters and optical diffraction from lattice and cross-grating images both confirmed that the particles were Co_3O_4. An interesting example is shown in Fig. 6. The graphite basal

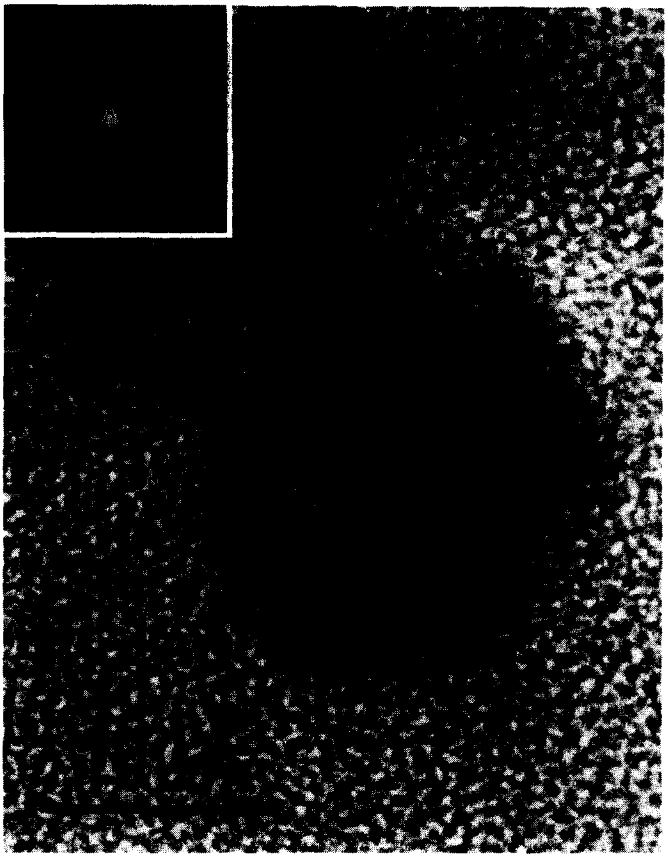

FIG. 4. High-resolution image of the 2.53-Å (311) lattice fringes (here running almost horizontal) from a particle of Fe_3O_4 together with the optical diffraction pattern (inset)—the faint pair spots at right angles in the latter correspond to the 2.97-Å (220) lattice planes which are barely discernable in the image (running perpendicular to the (311) fringes).

planes are viewed side-on showing the 3.4-Å (00.2) lattice fringes together with the perpendicular set of 2.1-Å (1.00) fringes, as well as one of the Co_3O_4 particles nearby. Normally the contrast of these particles seemed lower than for those of Fe_3O_4 suggesting that they could be somewhat thinner although this may have been due to their respective orientations relative to the electron beam. There also appeared to be a tendency for them to congregate along the edges of overlapping graphite flakes.

The appearance of the Graphimet Cu-5 resembled that of the other Graphimets. Most of the cross-grating lattice fringe patterns observed, such as those shown in Fig. 7, could be indexed as corresponding to Cu_2O in both spacing and angle. Note, however, that not all spacings observed were assignable to this oxide; some CuO, or other copper compounds, were possibly also present in small quantities.

Similar particle "islands" were observed during high-resolution examination of a sample of Graphimet Ni-10. As for the Co Graphimet the contrast of the islands was usually lower than that for the Fe Graphimet, although with the expected higher number density of particles. Visual inspection of micrographs and optical diffraction analysis revealed the presence of numerous areas exhibiting the interlayer 3.4-Å graphite spacing which again provided a convenient calibration. Almost all of the "islands"

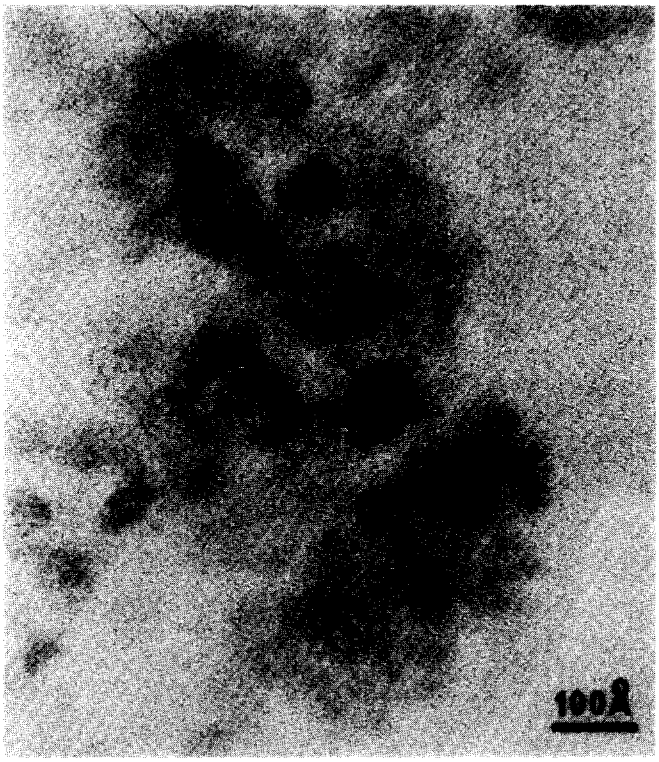

FIG. 5. Typical region of the Graphimet Co-5, showing clusters of Co_3O_4 particles supported by graphite.

showed a spacing of 2.03 Å, frequently with a 70° cross-grating pattern, which corresponded to the Ni (111) lattice, as illustrated in Fig. 8a. Figure 8b shows an interesting moiré pattern probably arising from particles on both surfaces, plus lattice fringes from each particle. Note that a few of the particles showed lattice spacings of 2.52 Å, which corresponds to that of NiO, and X-ray diffraction analysis also revealed a few faint lines corresponding to NiO. These observations indicated that a small amount of nickel was present as oxide.

Stereopairs of images of Ni Graphimet, such as those shown in Figs. 9a and b, were also recorded and subsequently examined in a stereoscopic viewer. These results confirmed the earlier impression that the graphite occurred as overlapping flakes with the metal clusters present on the surfaces. This is illustrated in the sketch in Fig. 9c. Surprisingly, some of the Ni particles seem to project out from the surface and are not coplanar as might be anticipated. This arrangement increases the exposed surface area of Ni available for catalytic activity.

The islands observed in Graphimet Pt-1 were very much smaller and less numerous than in the other samples examined, in keeping with the relatively low volume fraction of Pt (approximately one-fifth to one-tenth that of the particles in the other samples). A representative micrograph of the particle size and distribution is shown in Fig. 10: typical particles are only 10–20 Å in diameter. The tendency of the particles to cluster along crevices between two overlapping flakes, or at surface steps, was again apparent, as indicated by arrows, although there did not appear to be any preferred orientation of the Pt lattice planes relative to that of the graphite. Also note that only graphite reflections were ob-

FIG. 6. High-resolution image showing lattice planes in a particle of Co_3O_4 (top right) together with 2.1- and 3.4-Å lattice fringes elsewhere arising from the graphite support.

served in the selected area electron diffraction pattern. Many particles were approximately oriented with respect to the electron beam direction and exhibited the 2.27-Å (111) spacing of metallic Pt (see Fig. 11): some also showed the 70° cross-grating pattern. No larger spacings indicative of oxide were observed.

Mössbauer and Electron Energy Loss Spectroscopy

Other analytical techniques were also utilised to provide some comparison with the high-resolution results. For example, Mössbauer spectroscopy of a bulk sample confirmed that most, if not all, of the iron in Graphimet Fe-5 was present as Fe_3O_4. The spectrum was relatively noisy because of the small amount of sample available, and the possible presence of a small amount of iron in another form could not be excluded. Electron energy loss spectroscopy was carried out on several samples using the HB-5 STEM in the Cavendish Laboratory (*15*); representative spectra for the Fe Graphimet and Ni Graphimet are shown in Figs. 12a and b, respectively. These results also confirmed that the particles were composed of iron oxide in the Fe Graphimet and of metallic nickel in the Ni Graphimet.

Structure of Graphite

High-resolution observations of the graphitic structure in the Graphimets obtained during the course of this work are also of

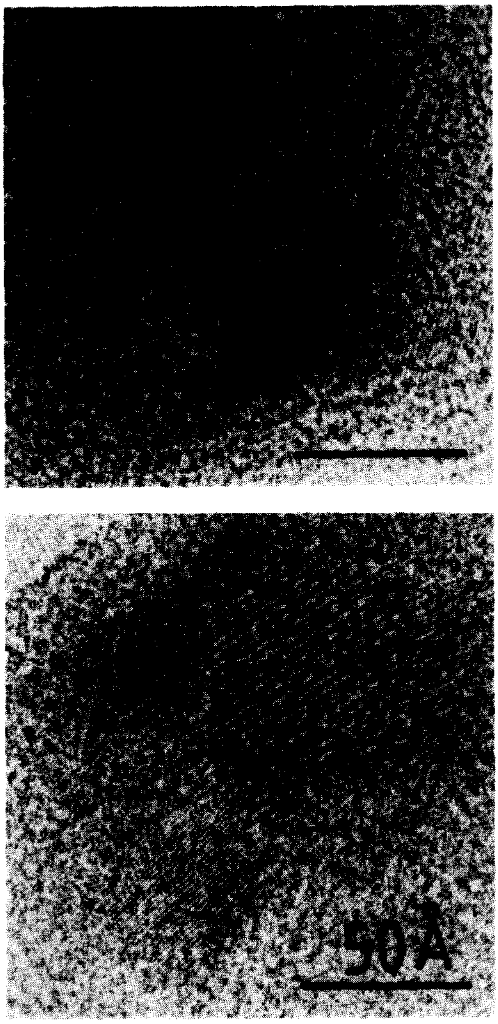

FIG. 7. High-resolution images of small particles in the Cu Graphimet. The lattice plane separations and angles observed correspond to those expected of Cu_2O.

considerable interest. A good example of the "interlayer" structure showing the 3.4-Å basal planes is illustrated in Fig. 13. This type of structure was much more common and well developed in Ni Graphimets than any of the others examined. Generally, the 2.1-Å (1.00) lattice spacings of graphite appear quite uniform in the micrographs, yielding sharp optical diffraction patterns. In contrast, the 3.4-Å (00.2) fringes are frequently seen to be distorted, exhibiting radial streaking in the optical diffraction pattern, as shown in Fig. 14.

This is probably a consequence of the intercalation–dechlorination process, although it may sometimes be due to the presence of some residual intercalated metal atoms.

Catalytic Activity

Samples of the Fe Graphimet were used to catalyse the gasification of bulk graphite by wet hydrogen. The techniques employed are described in detail elsewhere (*6*), as are the results and implications of catalytic rate measurements. However, it appears to be worth summarising here that the Fe Graphimets proved to be extremely active catalysts for the above-mentioned process. Indeed, on a unit-Fe-weight basis, they were over a 1000 times more active than finely divided iron powder (~8 μm diameter). This represents an increase of about the same order of magnitude as the increase in total surface area relative to the powder of the numerous tiny islands of Fe in the Graphimet.

DISCUSSION

The principal objective of this study has been an attempt to characterise the morphology of a series of Graphimets using high-resolution electron microscopy. Our observations have been successful in that it was shown that the intercalation of graphite by metal chloride, with subsequent low-temperature reduction, has primarily resulted in the formation of small metal-containing "islands" ranging from about 10 to 100 Å in diameter. These particles, which appeared from their contrast, and their diameters perpendicular to the beam, to be up to about 100 Å in thickness, apparently occurred on the surfaces of the graphite, often in clusters, or decorating the edges of overlapping flakes. With lattice fringes in the range 2–5 Å being readily obtained in these particles over a wide range of defocus, together with the possibility of cross-

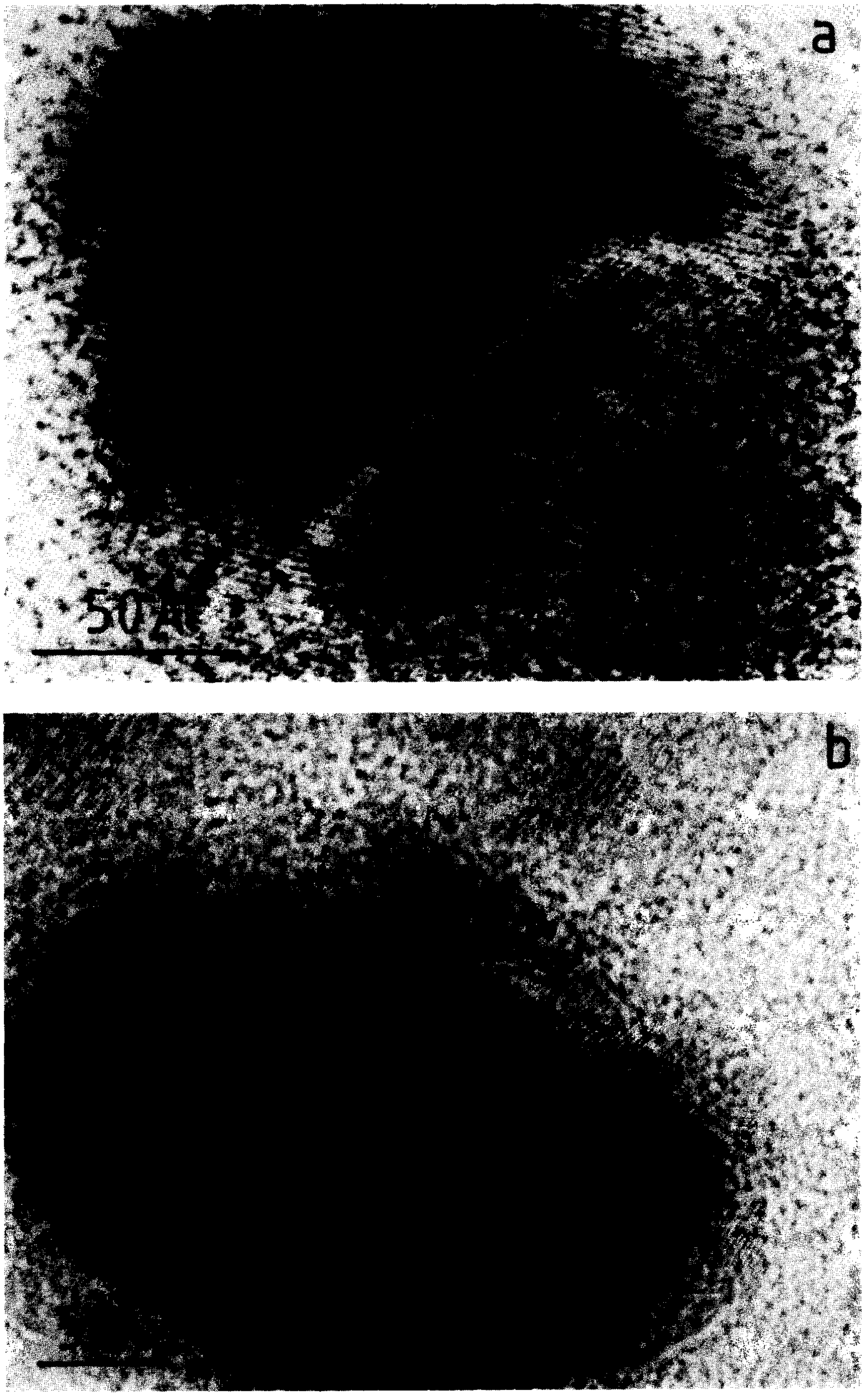

FIG. 8. (a) High-resolution image of small particle in the Ni Graphimet. The 70° cross-grating pattern of 2.03-Å lattice fringes identify the particle as being constituted of metallic Ni. (b) Partially overlapping particles showing 2.03-Å Ni (111) lattice fringes in each, together with coarse spacing moiré fringes in the region of overlap.

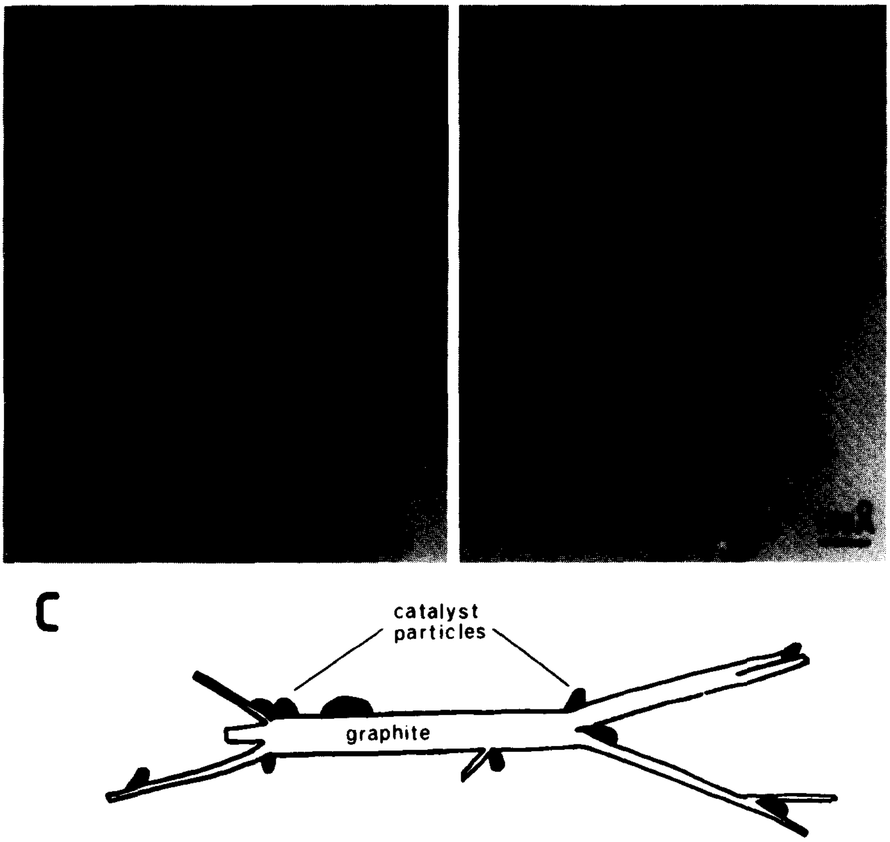

FIG. 9. (a) and (b) Pair of images from the same region of the Ni Graphimet sample, with a 5° tilt between them in order to provide a stereoscopic impression of the particles and the graphite support. (c) Schematic representation of graphite flakes and typical catalyst particle distribution.

calibration using the graphite lattice spacings and the use of the optical diffraction from small areas, it has been shown that accurate values for lattice spacings could be provided. Indeed, direct, unambiguous identification could be made of the metal, or metallic oxide, constituents of the particles. The observed splitting and fragmentation of the graphite probably resulted from the intercalation–reduction distortion. The finely divided metal will be very pyrophoric, and oxidation presumably occurs for Fe, Cu, and Co powders when the respective Graphimet powders are exposed to air after vacuum drying. It should be noted that the metal (oxide) structure observed is in keeping with earlier direct observations of Thomas and co-workers (*1*, *2*) on various chloride intercalates.

It is worth commenting that the ability of recent-generation HREMs to provide lattice information directly in small particles, as demonstrated here and elsewhere [e. g., (*16*, *17*)], should make these instruments ideal for resolving a number of outstanding questions concerning the catalytic behaviour of such particles. For example, it has been suggested [e.g., (*18*)] that the occurrence of atomic packing arrangements different from that of the bulk lattice in the case of small clusters in some metals might lead to more favourable catalytic sites. During the present study, there was little evidence for such alternative stacking: most small particles observed seemed to consist solely of perfect single crystals. Moreover, despite their tendency to cluster together, it did not appear that the small particles were generally in some sort of crystallographic alignment with the graphite support. However, it is possible that definite orientation relationships might exist in other supported catalytic systems: these could be established directly by high-resolution observations similar to those made here.

Finally, there would appear to be two particular areas where more detailed observations on the present specimens would prove interesting and worthwhile. Firstly, the structure of the graphite support, its probable disruption by the intercalation–reduction reaction, and the presence of any residual intercalates, have admittedly only been given almost cursory attention, since these were not the object of the current study. Secondly, any changes in either particle morphology, or that of the graphite

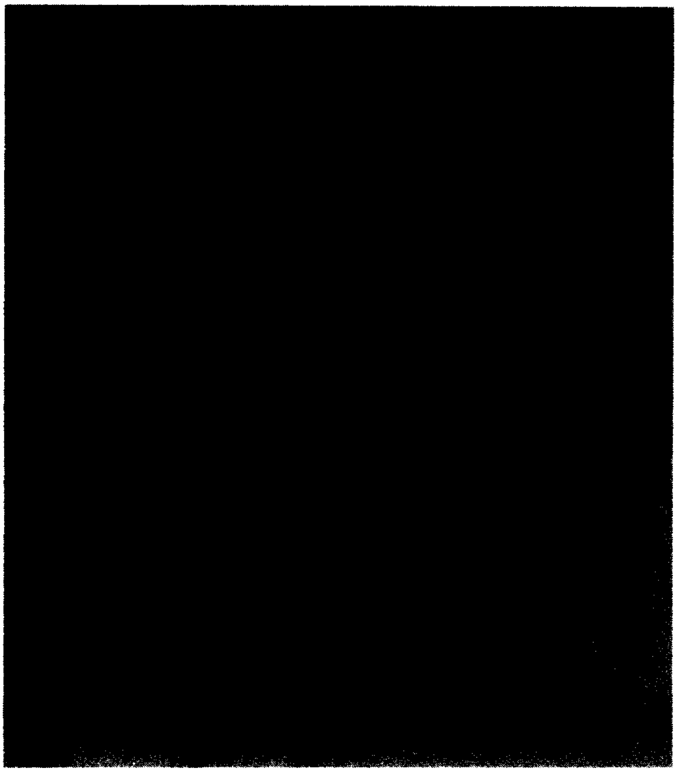

FIG. 10. Typical region of the Graphimet Pt-1. The particle size, and number density, is observed to be much smaller than in the other samples. Arrows indicate regions where the particles appear to be decorating edges of graphite flakes.

FIG. 11. High-resolution image from the Pt Graphimet showing a number of very small particles with lattice fringe spacings corresponding to that of Pt.

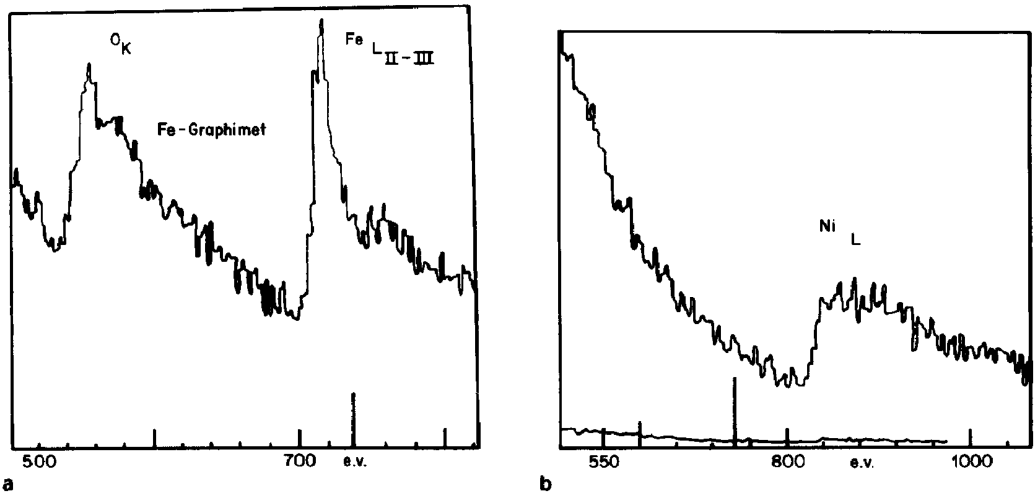

FIG. 12. Electron energy loss spectra from (a) Fe Graphimet and (b) Ni Graphimet. These confirm the presence of iron oxide in (a) and metallic nickel in (b).

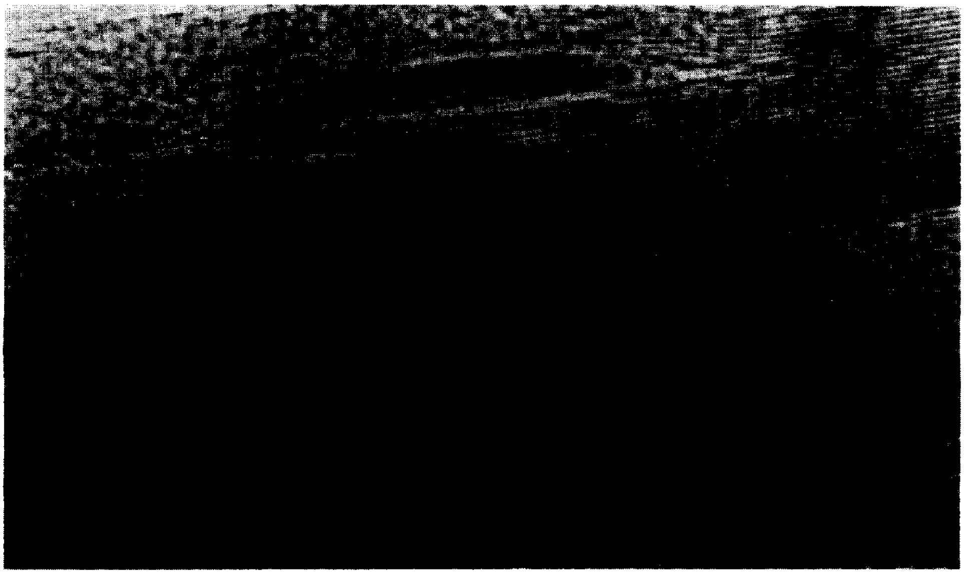

FIG. 13. Graphite basal plane interlayer structure (3.4 Å), from a sample of Ni Graphimet. Apparent terminating planes are indicated by arrows.

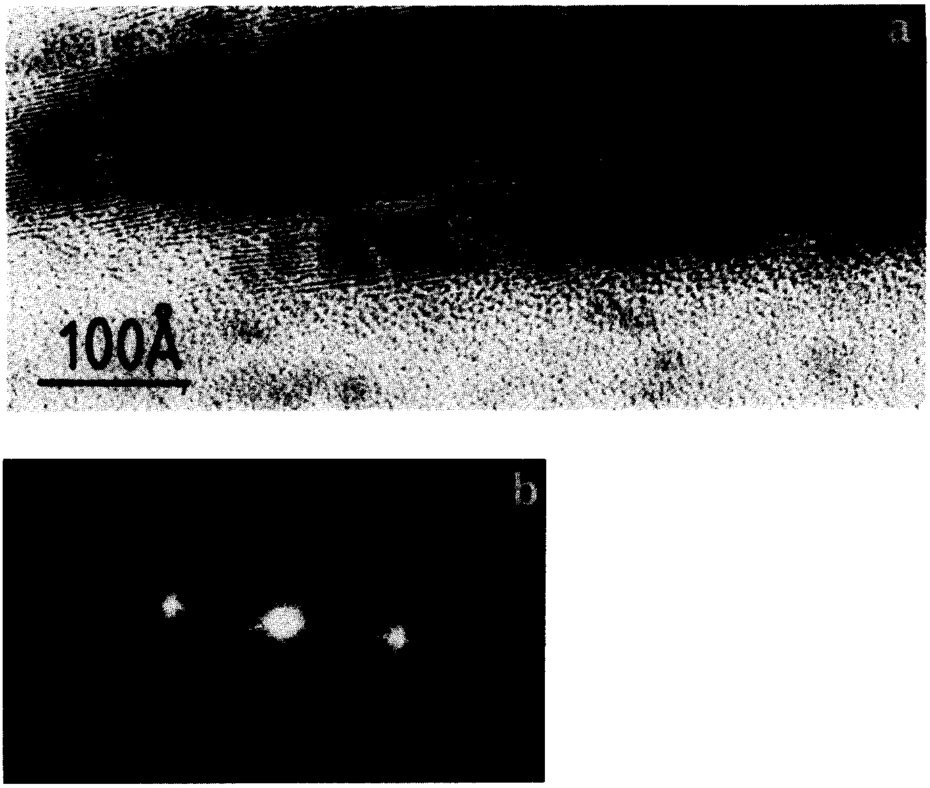

FIG. 14. (a) Region of interlayer structure showing considerable lattice distortion, possibly due to some intercalated metal, confirmed by the optical diffraction pattern (b).

support, following use as catalysts, might provide valuable insight into the catalytic reaction itself. Further observations are in progress and will be reported in due course.

ACKNOWLEDGMENTS

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REFERENCES

1. Thomas, J. M., Millward, G. R., Davies, N. C., and Evans, E. L., *J. Chem. Soc. Dalton Trans.* **23,** 2443 (1976).
2. Evans, E. L., and Thomas, J. M., *J. Solid State Chem.* **14,** 99 (1975).
3. Saunders, K. C., and Fryer, J. R., private communication 1978.
4. Thomas, J. M., Millward, G. R., Schlögl, R. F., and Boehm, H. P., *Mater. Res. Bull.* **15,** 671 (1980).
5. Bach, B., Evans, E. L., Thomas, J. M., and Barden, M., *Chem. Phys. Lett.* **10,** 547 (1971).
6. Fisher, R. M., and Szirmae, A., in preparation.
7. Otto, K., and Shelef, M., *Carbon* **15,** 117 (1977).
8. Alfa Division, Ventron Corporation, Sales Catalogue, p. 451 (1977–1978).
9. Lalancette, J. M., U.S. Patent No. 3,847,963, dated November 12, 1974.
10. Fisher, R. M., Smith, D. J., Freeman, L. A., Pennycook, S. J., and Howie, A., *Carbon Conference* **14,** 318 (1979).
11. Freeman, L. A., Smith, D. J., and Fisher, R. M., *in* "Developments in Electron Microscopy and

Analysis 1979" (T. Mulvey, Ed.), p. 439. Institute of Physics, Bristol/London, 1980.

12. Nixon, W. C., Ahmed, H., Catto, C. J. D., Cleaver, J. R. A., Smith, K. C. A., Timbs, A. E., Turner, P. W., and Ross, P. M. *in* "Electron Microscopy and Analysis 1977" (D. L. Misell, Ed.), p. 13. Institute of Physics, Bristol, 1978.

13. Cosslett, V. E., *Proc. R. Soc. London Ser. A* **370,** 1 (1980).

14. Cosslett, V. E., Camps, R. A., Saxton, W. O., Smith, D. J., Nixon, W. C., Ahmed, H., Catto, C. J. D., Cleaver, J. R., A., Smith, K. C. A., Timbs, A. E., Turner, P., and Ross, P. M., *Nature* **281,** 459 (1979).

15. Pennycock, S. J., Batson, P. E., and Fisher, R. M., *in* "Developments in Electron Microscopy and Analysis 1979" (T. Mulvey, Ed.), p. 337. Institute of Physics, Bristol/London, 1980.

16. Marks, L. D., and Smith, D. J., *J. Cryst. Growth,* **54,** 425 (1981).

17. Smith, D. J., and Marks, L. D., *J. Cryst. Growth,* **54,** 433 (1981).

18. Hamilton, J. F., and Baetzold, R. C., *Science* **205,** 1213 (1979).