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A Microdiffraction Study of Gold–Ruthenium Catalyst Particles

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A dedicated scanning transmission electron microscopy (STEM) instrument has been used to obtain microdiffraction patterns from metal particles of diameters in the range 1–3 nm. From about 200 good, clear patterns from particles in gold–ruthenium catalysts on magnesium oxide and silica supports, most could be identified as coming from MgO, Au, or Ru in their known structural forms. About 30 patterns could clearly not be attributed to any known structure. For these patterns, agreement could be found with the assumption of either two-dimensional hexagonal rafts of atoms with periodicities of about 0.25 nm or a faulted body-centered cubic structure with unit cell edge about 0.295 nm. Each of these possibilities involves an interatomic distance 5 to 10% smaller than the bulk of Ru–Ru value. Evidence from high-resolution electron microscopy tends to support the BCC structure. No clear evidence could be found for any association of Au and Ru atoms.

INTRODUCTION

The techniques of electron microscopy, microanalysis, and microdiffraction have been applied extensively for the study of the small metal particles and their oxide supports in supported metal catalyst systems and models of such systems (*1*). For very small particles, with diameters in the range 1–5 nm, difficulties arise because of the limited spatial resolution of the analytical techniques and because the effect of the support introduces complications for the interpretation of the high-resolution images. Recently, encouraging results have been obtained by use of the newer, ultra-high-resolution electron microscopes with which it has been possible to observe the structures of metal atom clusters of 0.5–1 nm diameter on some oxide crystal supports (*2*). For the microanalysis and microdiffraction from very small particles, the dedicated STEM instruments, using field emission guns, have proved effective (*3, 4*). In particular by using a STEM instrument with a special two-dimensional detector system, one finds it possible to obtain diffraction patterns from particles of diameter 1–2 nm on a routine basis (*5, 6*). In the present paper we report the application of this instrument to the study of particles in a bimetallic catalyst system for which the structure of the very small particles has been questioned.

Datye and Schwank (*7*) have reported studies of gold–ruthenium bimetallic catalysts in relation to their activity for reactions such as ethane hydrogenolysis and CO hydrogenolysis. On a magnesium oxide support the activity of Ru appears to be suppressed relative to that on a SiO_2 support, but the activity on MgO increases as Au is added to the Ru. In bulk and for large particle sizes, it is known that Au and Ru have a wide miscibility gap. Electron microscopy and microanalysis results confirm that for particle sizes of 5 nm or greater, the Au and Ru particles are separate and distinct. The influence of the Au on the Ru activity is considered to be dependent on the form of the smaller particles and for these it has been postulated, on the basis of spectroscopic evidence (*8*), that bimetallic clusters of Ru–Au exist. The available evidence from electron microscopy and microanalysis is not inconsistent with this conclusion but is not sufficient to provide clear evidence on the nature of the small parti-

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cles. In a more recent paper (*9*), the results of a microdiffraction study made using a TEM/STEM instrument for which the incident beam diameter is about 20 nm are reported. Evidence was found for the epitaxial orientation of Au and Ru crystallites on the MgO surface, but no evidence was found for any intermetallic compound of different structure.

EXPERIMENTAL

The samples used in this study were kindly supplied by Drs. Datye and Schwank (*7*). Those studied most extensively were on magnesia supports and were labeled RM064 and RM089, where the final two digits indicate the atomic percentage of Ru relative to the total metal content. Samples having smaller amounts of Ru and samples of various composition on a silica support were examined briefly. The samples were prepared by impregnation or co-impregnation of MgO using aqueous solutions of $RuCl_3 \cdot H_2O$ and $HAuCl_4 \cdot 3H_2O$ to give a total metal content of 5% by weight. After drying at room temperature for 16 h and at 300°C for 2 h, the samples were reduced in flowing hydrogen for 2 h at 300°C and then for 2 h at 400°C (*8*).

Microdiffraction patterns were obtained by use of an HB5, dedicated STEM instrument, from VG Microscopes, Ltd., modified by the addition of a special two-dimensional recording system (*5, 6*). The microdiffraction pattern is formed on a fluorescent screen and viewed by use of a low-light-level TV camera with an intermediate image intensifier. The output from the TV camera can be viewed and photographed directly or can be recorded on videotape for later frame-by-frame viewing. Provision is also made for the digital recording of diffraction patterns at TV rates (*10*).

The minimum diameter of the beam on the specimen with this instrument is less than 0.3 nm (*11*). To achieve this, it is necessary to use a large-diameter objective aperture so that the incident beam has a convergence of approximately 10^{-2} rad, comparable to the angular separations of diffraction spots from metallic crystals (see Fig. 1). Then, the diffraction spots are made up of large, overlapping disks and are difficult to interpret. For the study of crystals in the size range 1.5–2 nm, it is more convenient to use a smaller objective aperture (10 μm) giving a beam convergence angle of about 2×10^{-3} rad. Then the beam diameter at the specimen level is about 1.5 nm. The diffraction spots from simple metal crystals are then well separated and distinct, although of appreciable diameter.

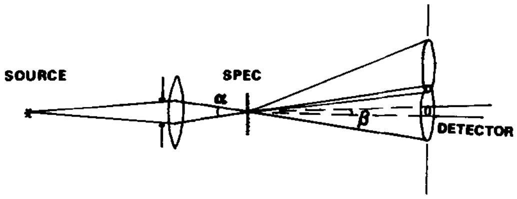

FIG. 1. Diagram of the formation of a convergent beam microdiffraction. The beam diameter at the specimen is inversely proportional to the angular aperture of the incident beam, α, and so to the diffraction spot diameter.

It has been shown that fine structure can arise within the diffraction spots under these conditions for a number of reasons (*12*). Any crystal edge or other discontinuity in the sample may introduce a splitting of the spots. Any variation in thickness or scattering power of the metal crystal or in its support may give rise to distortions of the spots, and these effects are difficult to predict or to take into account. As a result, the accuracy with which crystal planar spacings and angles can be deduced is much poorer than that for the more usual selected-area electron diffraction patterns obtained from large specimen areas.

Other factors limiting the accuracy with which the diffraction patterns can be measured include distortions arising either within the electron optical column or in the recording system. The postspecimen electron lenses in the microscope column may produce pin-cushion distortion which becomes anisotropic if the alignment is poor.

Correction can be made for the effects of such distortions to some extent by use of reference patterns such as those from principal orientations of the crystals of the MgO supporting film. However, considerable care is required because the distortions can vary with the specimen height, the aperture position and the alignment of the microscope lenses.

RECORDING METHODS

There were two ways in which it could be determined that these patterns came from particles in the 1- to 3-nm size range. First, a STEM image could be obtained when the incident beam was scanned over the sample. The incident beam could be stopped at any point in the image where a small particle appeared and the diffraction pattern could be recorded from that point. The difficulty in this procedure is that with an incident beam diameter of 1.5 nm, the image resolution is not better than 1.5 nm so that the small particles are not well resolved. It is possible to obtain images of better resolution (e.g., 0.5 nm) by using a larger objective aperture. Then the small particles can be located and their positions identified in the 1.5-nm resolution image before the microdiffraction pattern is recorded. This procedure served for a number of cases but becomes cumbersome and tedious when larger numbers of patterns must be obtained. It is complicated by changes of the diffraction pattern resulting from drift of the specimen or from motions of the particles under electron irradiation. In many cases the substrate material, whether silica or magnesia, is damaged by the incident electron beam. As the substrate changes, it causes motion of any small particle sitting on, or embedded in, it.

A second procedure is to locate an area of thin supporting material with a relatively high density of small metal particles and then to turn off the imaging scan and record the diffraction patterns on videotape as the beam is moved manually over the chosen area. The videotape can then be played back and the diffraction patterns on individual frames can be selected and photographed. In this way large numbers of patterns can be recorded and the time taken to record each is the time for one TV frame. The patterns are not affected greatly by specimen movements; in fact, it is often possible to record the changes of the patterns as the particles rotate and, in some cases, change their structure. It is usually possible to distinguish clearly the patterns given by the small particles from those given by a crystalline support, since for the latter the patterns tend to persist during relatively large movements of the beam and the diffraction spots do not have the same fine structure (*12*). The method is limited by the difficulty of correlating diffraction patterns with particle sizes or forms seen in images.

RESULTS

A total of about 500 patterns were recorded, either by photographing directly the TV display screen or by recording the patterns on videotape and then photographing selected frames from the videotape. A large group of these pictures was discarded when it was found that excessive distortion made it difficult to interpret them. An intermittent fault in the TV display system varied the scan ratios at times. An additional large group of patterns was discarded because they contained no useful spots which could not be attributed to MgO or else contained spots which were excessively blurred.

Of the 200 or so good, well-defined patterns, most could be attributed to Ru, Au, or MgO within the uncertainties associated with the limited accuracy of measurement. After long periods of exposure to air, patterns attributable to RuO_2 were found in some cases. About 30 patterns which could clearly not be accounted for by these structures and also could not be attributed to any other known oxide or other compound of Au or Ru were obtained. It was concluded that these patterns arose from an unknown

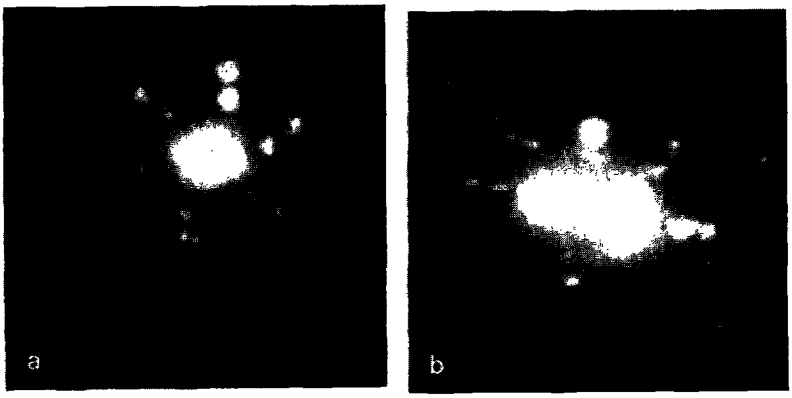

FIG. 2. Convergent beam microdiffraction patterns from the unknown structure (inner six spots) and from MgO in [111] orientation (strong hexagon of (220)-type spots).

structure. Since the lattice spacings of this structure are not very different from those of Ru, Au, and MgO, it is possible that many more of the patterns recorded actually came from this structure but were not sufficiently complete or distinct to make the identification reliable.

The accuracy with which diffraction patterns could be measured was limited by the large and irregular form of the diffraction spots and by the various distortions mentioned earlier. When the pattern from the metal particle was recorded with that of the crystalline MgO substrate, as in Fig. 2, or when neighboring particles gave patterns which were recognizably those of known structures (as in Fig. 3), the lattice plane spacings could be deduced with an accuracy of better than 5% and interplanar angles determined to within about 5°.

Some of the MgO substrate material consisted of large crystals and was resistant to radiation damage. Other parts appeared to be almost amorphous and highly sensitive to irradiation by the incident beam.

The most characteristic unidentified patterns were close to being hexagonal with planar spacings, d_{100}, of about 2.1 Å (Figs. 2b and 4). The inner spots were most intense and intensities decreased rapidly with radius. They may be compared with [001] patterns for Ru having $d_{100} = 0.234$ nm and the second ring of spots, the (110) type, stronger than the (100) because of the close-packed hexagonal structure. In the [111] orientation, Au gives hexagonal patterns with weak (100)-type spots with $d = 0.249$ nm (Fig. 5) if the small crystals are faulted, twinned, or very thin.

Several structures which could possibly give diffraction patterns having the geometry of those observed were found. In each case the structure was formed by introducing distortions to close-packed metal structure types and allowing for the presence of two types of atoms, Au and Ru, on the assumption that some compound of the two metals must be present to produce the distorted structure. One was monoclinic space group C2/m with $a = 0.53$ nm, $b = 0.25$ nm, $c = 0.63$ nm, and $\beta = 127°$. Another was monoclinic with $a = 0.421$ nm, $b = 0.245$ nm, $c = 0.448$ nm, and $\beta = 122°$. In each case an ordered array of Au and Ru atoms would give spot intensities in poor agreement with those observed and weak spots of relatively large spacing (0.3 to 0.5 nm) in some orientations which were not observed. A disordered arrangement of atoms may be possible, but it is difficult to see how disorder (a statistical concept) could exist in a crystal less than 2 nm in diameter or without allowing the structures to revert to a high-symmetry form. A further factor

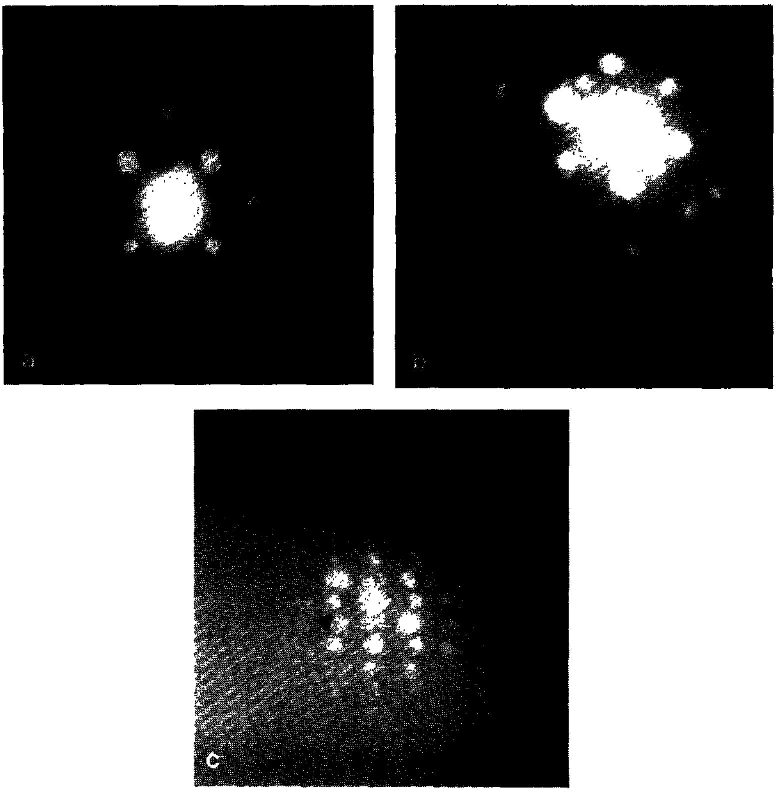

FIG. 3. Microdiffraction patterns from crystals, 15–20 Å diameter of (a) Au [100], (b) Ru [100], and (c) Au [100] plus unknown structure.

was that each of the postulated structures involved the very short metal–metal distance of 0.25 nm (as compared to 0.27 nm in bulk Ru and 0.287 nm in bulk Au).

It is known that interatomic distances in surface layers of metals may be expanded or contracted by more than 10% (*13*) and so unusual interatomic distances may be ex-

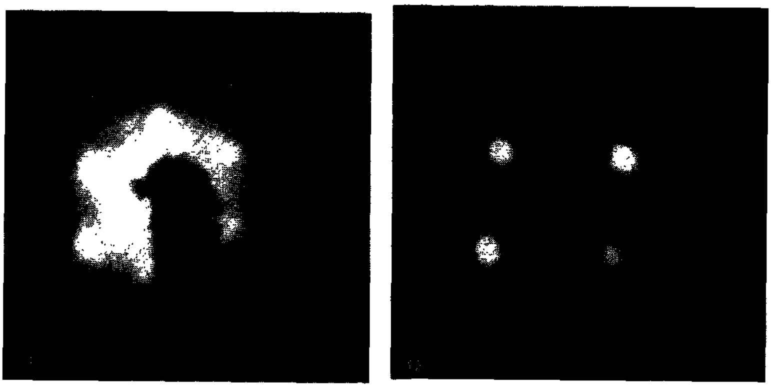

FIG. 4. Microdiffraction pattern from unknown structure (a) close to hexagonal orientation and (b) tilted away from hexagonal orientation (larger scale than that in Figs. 2 and 3).

FIG. 5. Microdiffraction pattern from faulted Au crystal in [111] orientation showing weaker net of "forbidden" reflections.

pected in particles of diameter 2 nm or less in which the atoms are almost all on the surface. However, if such interatomic distances occur, alternative, more satisfactory explanations of the patterns are possible, namely that the patterns come from relatively simple, but spatially limited, structures.

A two-dimensional hexagonal net of atoms of spacing 0.245 nm, perpendicular to the incident beam, will give a hexagonal net of diffraction spots with *d* spacing 0.212 nm with intensities falling off uniformly with angle, as observed. Tilting of the incident beam will give little or no change of relative intensities. However two, four, or all of the inner circle of spots will show spacings of less than 0.212 nm. A variety of such patterns was observed. Other patterns could be explained by postulating similar two-dimensional nets of atoms with somewhat larger periodicities, up to the 0.27 nm of bulk Ru or beyond. The superposition of two or more hexagonal nets to give a three-dimensional structure, if in close-packed stacking, would weaken the (100) spots and strengthen the (110) spots. This was not often observed (but see Fig. 5).

An alternative explanation for the near-hexagonal patterns is that they arise from a body-centered cubic (BCC) structure with $a = 0.295$ nm or more containing one or more faults on (110)-type planes and viewed in a [111] direction. For such a BCC structure, the pattern in the [111] direction shows a hexagonal net of (110)-type spots with spacing 0.21 nm. The presence of faults would mean that tilts away from this orientation would distort the hexagonal net, making one or two of the planar spacings either greater (up to 0.24 nm) or less than 0.21 nm with the intensity decreasing with the deviation from the 0.21-nm value.

For comparison, it may be noted that if the BCC structure were Ru with the bulk interatomic distance of 0.27 nm, the (110) spacing would be 0.221 nm or 5% greater, and for BCC Au it would be 0.235 nm. Hence it would be necessary to postulate a decrease in the Ru–Ru distance of up to 5% to account for the observations on the basis of a faulted BCC Ru structure.

The hexagonal spot patterns corresponding to periodicities of the order of 0.21 nm were observed for Ru–Au on MgO samples containing 64% Ru but not for samples with 10 or 100% Ru. They were also observed for Ru–Au on silica with 48% Ru.

DISCUSSIONS AND CONCLUSIONS

The possibility that two-dimensional rafts of metal atoms occur in some bimetallic catalysts has been suggested on the basis of EXAFS and other data (*14*). Electron microscopy images of Ru–Cu and Os–Cu catalysis have been interpreted as implying the presence of two-dimensional rafts (*15*) on the basis that some small crystals give low contrast. While the variation of contrast could well arise from a variation of diffraction conditions rather than from variations of thickness, the low contrast of many small particles in the cited micrographs and in our own STEM images is not inconsistent with a two-dimensional structure.

The possible occurrence of a body-centered cubic Ru structure has been suggested by some high-resolution electron microscopy results from another type of sample (D. J. Smith, private communication). The explanation of our results in terms of such a structure may be favored in that it involves a 5%, rather than a 10%, decrease in the Ru–Ru distance. Further evidence in favor of this interpretation was provided by the STEM images obtained with the HB5 (Fig. 6a) and by high-resolution electron micrographs of the samples obtained by Dr. N. Long using the JEM 4000 EX microscope (resolution 1.6 Å) (Fig. 6b). The resolution obtained appeared to be affected to some extent by movement of the specimen crystals or the supporting film under electron irradiation, but crossed fringes of 0.2-nm spacing were frequently visible. While the small crystals of diameter 1–2 nm on the MgO supports gave low contrast which could be consistent with a two-dimensional structure, no evidence for two-dimensional structures could be found. Thus the small crystal images invariably appeared almost circular, whereas two-dimensional particles tilted with respect to the beam could appear elongated. Also the lattice fringes seen in the small particles were commonly in one or two directions only, whereas a two-dimensional raft would invariably give a two-dimensional net of points or lines in the image.

On the assumption that the particles are heavily faulted BCC and three-dimensional, not too far from spherical in form, it would be expected that occasionally a diffraction pattern would be obtained with the incident beam almost parallel to the faults on (110) planes. Such a pattern is shown in Fig. 7. Such a pattern could be given by a BCC crystal in a [111] orientation, heavily faulted on (110) planes to give the strong diffuse lines. From the spot positions the lattice plane spacings appear to be contracted by about 5% parallel to the faults and expanded to about 10% perpendicular to the faults.

The high-resolution electron micrographs such as that in Fig. 6b show the lattice fringes appropriate for the metal particles. For some crystals there appears to be an amorphous layer about 0.5 nm thick on the surface. This could well be contamination. No evidence was seen of any crystalline oxide or other product of possible reaction with the substrate.

It was not possible with instruments available at present to use microanalysis techniques to determine the compositions of the individual crystals showing the particular diffraction patterns. The small interatomic distances implied, of 0.25 nm or less, suggest that the small particles were Ru rather than Au. The EXAFS data (*15*) suggest that in particles of average diameter of about 4 nm the Ru–Ru distance is about 0.265 nm, or 1.6% less than the bulk value of 0.2695 nm. The contraction of the Ru–Ru distance could possibly be much greater in the case of smaller particles, 1 to 2 nm in diameter. Evidence from electron microscopy (*16*) suggests that for the surface atoms of Au in small particles there is an expansion of the interplanar spacings by 15–20%.

The available evidence thus suggests that the diffraction patterns not attributable to known structures arise from either two-dimensional structures or, more probably, heavily faulted BCC structures which must be predominantly Ru. The limitations of the accuracy with which interplanar spacings and relative intensities can be determined from the microdiffraction patterns make it difficult to decide whether some of the patterns tentatively attributed to Ru or Au could also be produced by this structure, tilted to particular orientations. It may be estimated that between about 5 and 50% of observed patterns could possibly be produced in this way.

The deductions from the diffraction patterns do not provide any insight into the possible role of Au in influencing the catalytic activity of the Ru or of the difference between the MgO and the SiO_2 as a supporting material. From patterns such as those in Fig. 2 it is evident that, on those parts of the MgO substrate which were crystalline, an epitaxial relationship could exist between the anomalous structure and

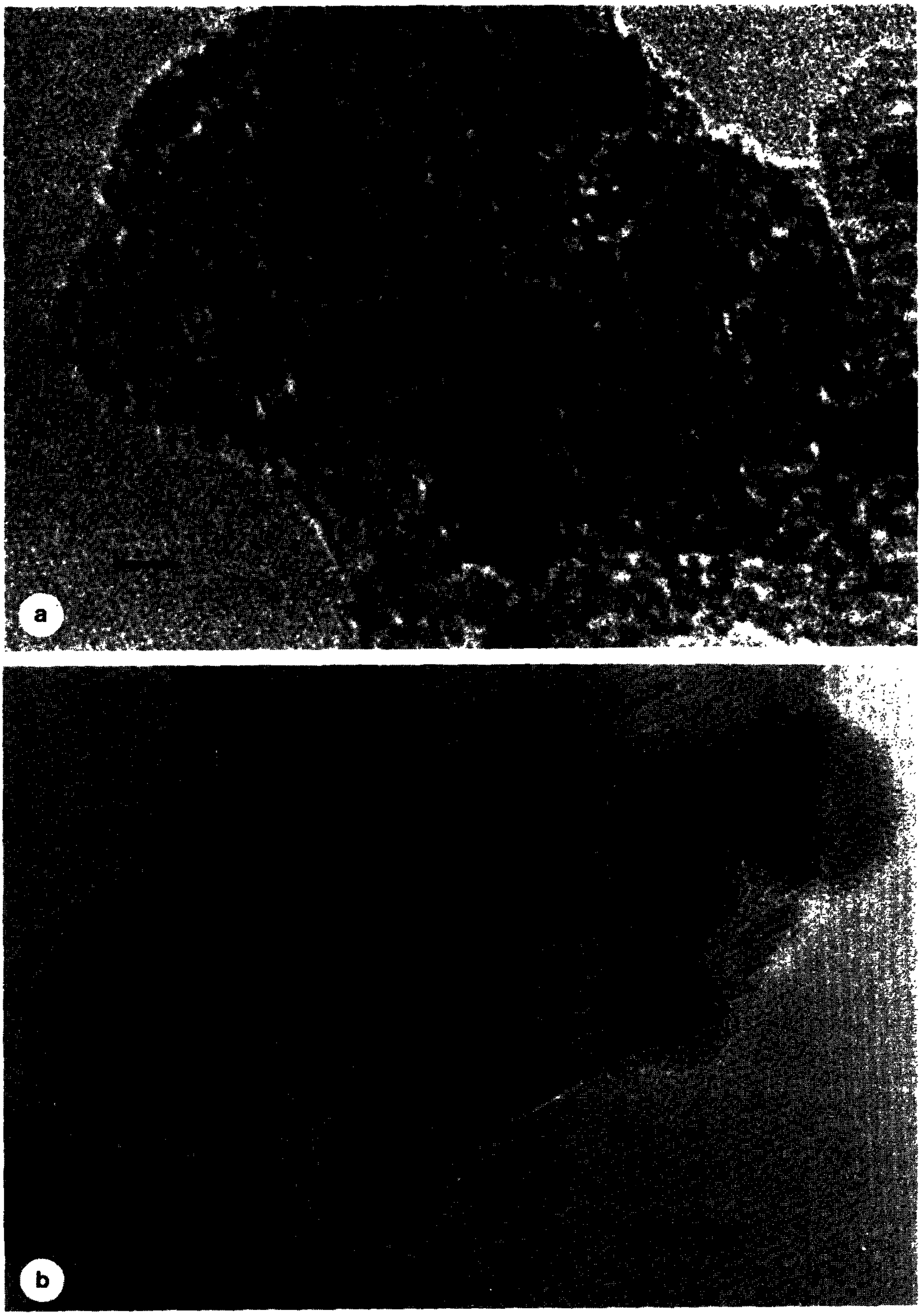

FIG. 6. Electron micrographs of the metal particles on crystalline MgO supports. The scale marker is 50 Å in each case. (a) STEM image of RM064 sample. (b) High-resolution image of RM100 sample obtained with the JEM 4000 EX (Courtesy of Dr. N. J. Long).

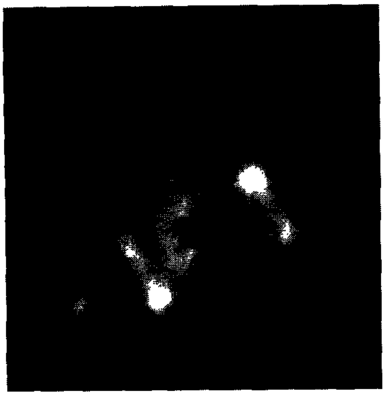

FIG. 7. Pattern from heavily disordered crystal, thought to be Ru with disorder of layer stacking.

the MgO crystal. However, the near-hexagonal spot patterns were also found on the amorphous MgO and SiO_2 substrates. The contraction of the lattice parallel to the faults (or 2D nets) is not present for the samples having 100% Ru and so this contraction may depend in some way on the presence of Au. However, no clear evidence has been found of the formation of any compound or of any close association of the Au and Ru in the small particles.

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