Micron and Microscopica Acta, Vol. 18, No. 3, pp. 165–169, 1987.
Printed in Great Britain.

0730–6260/87 $3.00 + 0.00
© 1987 Pergamon Journals Ltd.

STEM AND MICRODIFFRACTION STUDIES OF Rh/CeO_2

M. PAN, J. M. COWLEY and R. GARCIA*

Department of Physics, Arizona State University, Tempe, AZ 85287, U.S.A.
and *Facultad de Ciencias, Dpto. Quimica Inorganica, Universidad de Cadiz, Puerto Real (Apto. 40), Spain

(*Received* 31 *March* 1987)

Abstract—Using scanning transmission electron microscopy (STEM) and microdiffraction techniques, information on structures of small Rh particles (2–3 nm) and the interaction between Rh particles and Ce oxide support has been obtained. It was found that Rh particles (around 2 nm in size) were frequently in epitaxial relationship to the CeO_2. Microdiffraction patterns also suggested that all Rh particles exist as pure F.C.C. metal single crystals and no evidence was found for any twinning or for oxidation. Double diffraction effects were prominent and care was needed in interpreting the microdiffraction patterns.

INTRODUCTION

Characterization of crystal surfaces and small particles (< 5 nm) has been the interest for many electron microscopists in the past few years and significant progress has been made in this field along with the developments of many different techniques (Cowley, 1986). Among these studies a great deal of effort has been made to characterize the behavior of small particles (< 5 nm) in terms of the structures, the stability of structures under electron irradiation and the equilibrium states (Marks, 1985). This has been considered the basis for understanding surface structure and reactions and is directly related to research in chemical reactions, particularly in catalysts. For small particles (< 5 nm) X-ray diffraction and selected area electron diffraction (SAED) could not be used readily to study the structures due to the severe broadening of Bragg peaks caused by particle size effects. High resolution transmission electron microscopy (HRTEM) provides a direct way of viewing the structures of small particles and has been extensively used in recent years. With the improvement of resolution, down to 0.16 nm for the JEM-4000EX electron microscope, lattice imaging of small particles becomes more and more easy and considerable progress has been made in structure studies of small particles such as Au and Pt (Bovin *et al.*, 1985; Wallenberg *et al.*, 1986). The existence of supports, however, limits the structure imaging of small particles due to the fact that the phase contrast structures from supporting films could obscure, or, in some cases, even wipe out the contributions from the supported particles to the final images. The supporting materials, in this sense, act as a limiting factor in high resolution imaging of small supported particles.

In the case of the scanning transmission electron microscope (STEM), however, with an electron probe of 1–1.5 nm in diameter one is able to obtain both STEM images and diffraction patterns from individual regions 1–2 nm in diameter. The microdiffraction patterns can, in general, contain structure information on both the individual particles, and the supporting films. It is therefore possible to deduce not only the structure information of small particles but also the structure relationship between particles and their support, although the involvement of supporting materials may complicate the interpretation of microdiffraction patterns. Another important advantage of microdiffraction technique is that it can be easily associated with STEM bright and dark field (BF, DF) imaging, secondary electron imaging (SEM) and the techniques of microanalysis available with STEM electron microscopes. It should be pointed out that the 'microdiffraction' patterns are actually 'convergent beam electron microdiffraction patterns' because it is necessary to generate a convergent electron beam with convergence $\sim 3 \times 10^{-3}$ rad or more at the specimen

level in order to obtain a beam size of 1–1.5 nm or less. The accuracy of measuring lattice spacings from microdiffraction patterns is sacrificed in this case due to both the finite spot size in the diffraction patterns and the uneven intensity distribution within a spot disk caused by coherent illumination (Cowley and Spence, 1981). However information on local structures (1–2 nm) could be provided by the microdiffraction method used along with STEM BF and DF and the combination with HRTEM has proved to be powerful in the study of the structures of alumina-supported small Pt particles (Pan *et al.*, 1987).

EXPERIMENTAL OBSERVATIONS AND DISCUSSION

In the dedicated VG HB-5 STEM electron microscope in our laboratory, convergent electron beams 0.3 nm or less in diameter at the specimen level have been generated with a field-emission gun and rastered over the area, giving images with resolutions comparable with the incident electron beam size 0.3 nm. By stopping the beam at any selected point in the image a convergent electron microdiffraction pattern is then observed on the two-dimensional detector plane (Cowley, 1986). In order to obtain microdiffraction patterns having relatively well-defined sharp spots it is necessary to use a small objective aperture (10 μm) that results in an incident beam of diameter (1–1.5 nm).

The studies were carried out over the following samples:

(1) 2.5% Rh/CeO_2 reduced in H_2 at 350°C.
(2) 1% Rh/CeO_2 reduced in H_2 at 350°C.
(3) 1% Rh/CeO_2 reduced in H_2 at 500°C.

All these samples contained well-separated small Rh particles. With the increase of the reduction temperature, the particle size increased

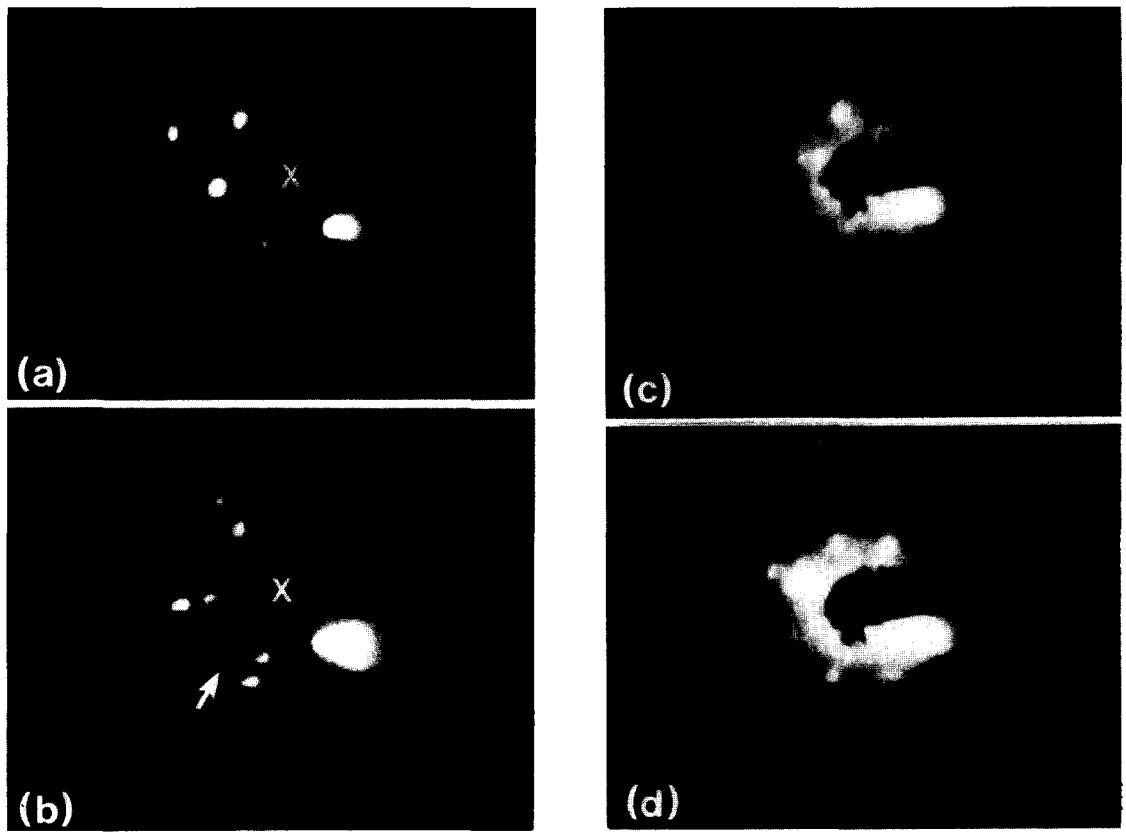

Fig. 1. Microdiffraction pattern showing a well-defined epitaxial relationship of Rh particles (2–3 nm) on CeO_2. (a) CeO_2 and (b) $Rh + CeO_2$ in [111] orientation. (c) CeO_2 and (d) $Rh + CeO_2$ in [100] orientation. "X" shows the position of primary beam.

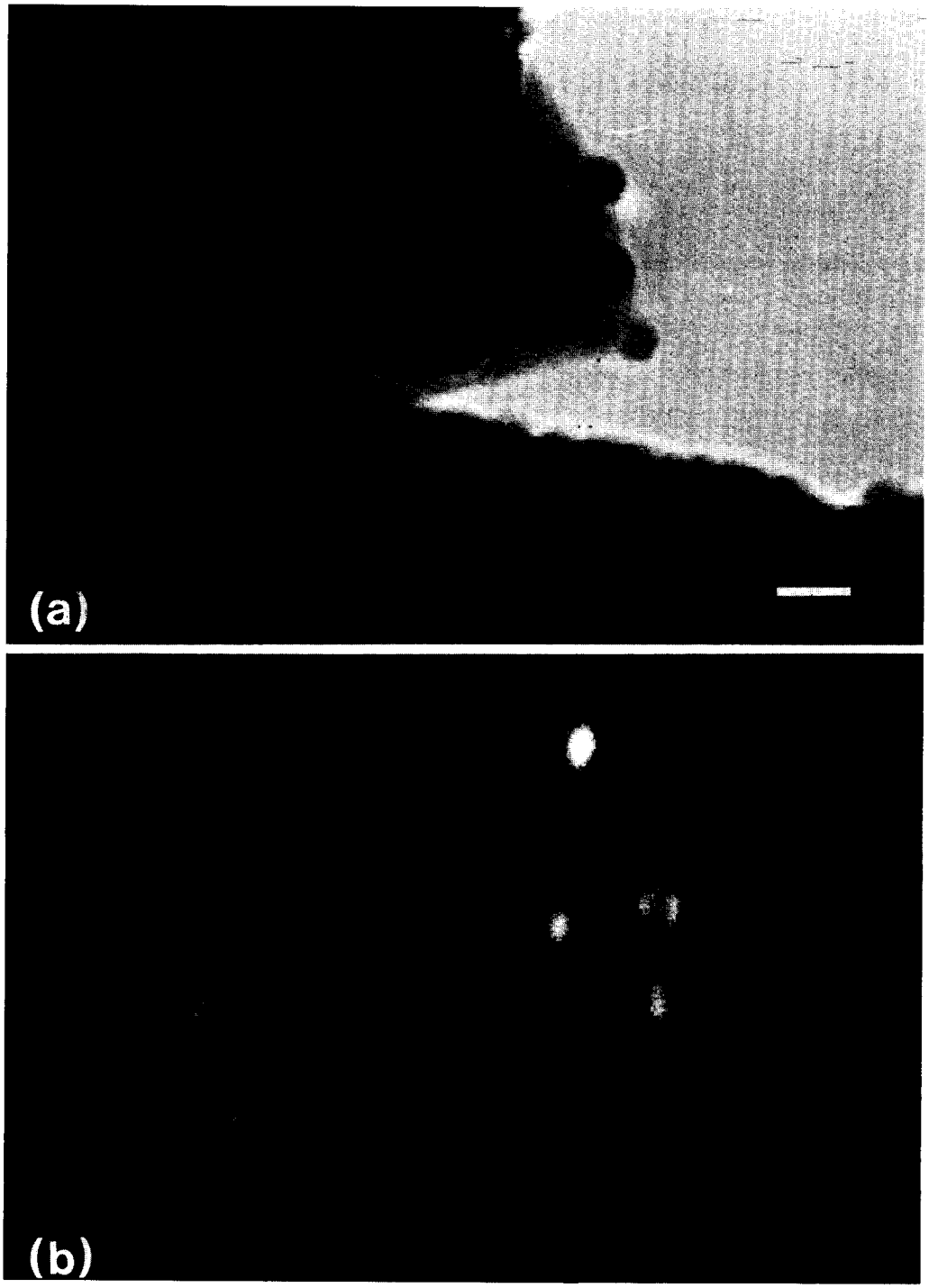

Fig. 2. (a) Bright field STEM image of Rh/CeO_2 sample. (b) Dark field STEM image of the same region by (200) reflection of Rh metal. Mark = 5 nm.

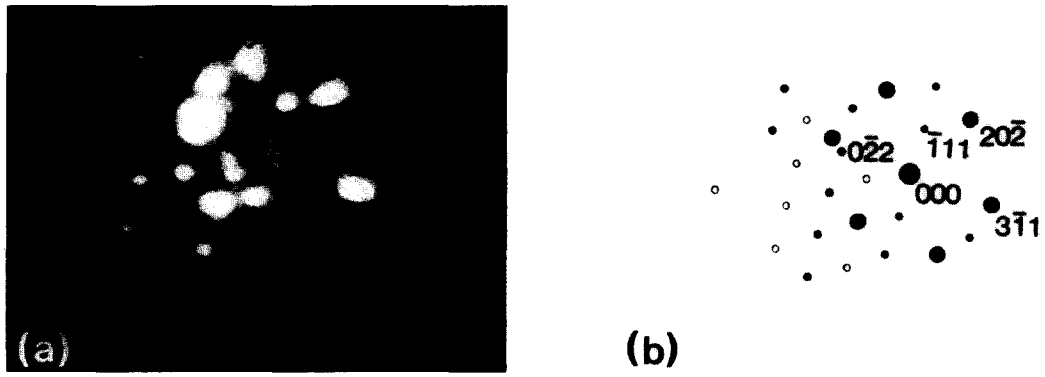

Fig. 3. (a) Microdiffraction pattern containing double diffraction spots due to overlapping of two CeO_2 microcrystals oriented along the [211] and [141] zone axes respectively. (b) Corresponding explanatory diagram. The open circles represent double diffraction spots. "X" shows the position of primary beam.

as well. Most of the Rh particles, which have been examined, were in the size range of 2–3 nm. The samples for electron microscopy investigation were prepared in the usual way. Powder of Rh/CeO_2 was ground into fine powder in suspension in hexane and put into an ultrasonic generator to obtain a good dispersion of the fine-ground powder. An electron microscope grid with carbon coating was then dipped into the suspension and allowed to dry in air.

Our experimental observations showed that Rh particles with size 2–3 nm often exhibit a well-defined epitaxial growth behavior on the crystals of the CeO_2 support. Both Rh and CeO_2 have FCC lattices with unit cell dimensions of 0.3804 and 0.5411 nm respectively. Microdiffraction patterns in Figs. 1a and 1c are from CeO_2 crystallites with the beam close to the [111] and [100] directions. Figures 1b and 1d contain the diffraction patterns from supported Rh particles 2–3 nm in diameter close to the above regions, being also close to the [111] and [100] orientations. In both of these cases the epitaxial growth of Rh microcrystallites 2–3 nm on the CeO_2 support was well-defined as parallel alignment, as clearly revealed in the microdiffraction patterns. It was noticed that the spot marked with an arrow in Fig. 1b resulted from double diffraction processes.

As suggested by microdiffraction patterns, all Rh particles were in the pure metallic state. No patterns were observed which could be attributed to RhO_2 or any other known Rh oxide. Figure 2a shows a BF STEM image containing Rh particles with sizes from 2 to 5 nm. The microdiffraction patterns from these Rh particles could all be attributed to Rh metal and showed, once again, a well-defined epitaxial relationship. The DF image was formed by (200) reflection of Rh metal and it could be seen that Rh particles less than 2 nm showed a good contrast as shown in Fig. 2b.

Among the Rh particles 2–3 nm, which have been investigated, few showed evidence of twinned or multiply-twinned structures in their microdiffraction patterns. The multiply-twinned structures have been proposed to be the stable structures for very small particles and the experimental evidence for these structures has been found for small particles 1–5 nm of Au and Pt (Marks and Smith, 1983; Cowley and Roy, 1981) by both HREM and microdiffraction techniques. In this case it is believed that the proportion of twinned or multiply-twinned Rh particles is considerably less than 5%.

As mentioned above, double diffraction effects often occurred in microdiffraction patterns from overlapping crystals. This is simply a multiple scattering diffraction effect and usually makes microdiffraction patterns complicated. It is, therefore, necessary to identify these double diffraction spots in order to avoid any misleading conclusions. The microdiffraction pattern, shown in Fig. 3a, is a typical example. It was obtained from two overlapping CeO_2 microcrystals in the [211] and [141] directions respectively. Figure 3b is the corresponding explanatory diagram showing the superposition of diffraction patterns and double diffraction spots.

CONCLUSIONS

Epitaxial relationship has been established for small Rh particles 2–3 nm on CeO_2 crystalline substrate. Most of the Rh particles show single

crystal, FCC structure and it is believed that the proportion of twinned or multiply-twinned particles is considerably less than 5%. No evidence has been found for the oxidation of Rh metallic particles.

Acknowledgements—The work was supported by DOE grant DE-FG02-86-ER45228 and made use of the resources of the ASU Facility for HREM supported by NSF grant DMR-8306501.

REFERENCES

Bovin, J.-O., Wallenberg, L. R. and Smith, D. J., 1985. Imaging of atomic clouds outside the surfaces of gold crystals by electron microscopy. *Nature*, **317:** 47–49.

Cowley, J. M., 1986a. High resolution imaging and diffraction studies of crystal surfaces. In: *Electron Microscopy*, 1986, Imura, T., Maruse, S. and Suzuki, T., eds., The Japanese Society for Electron Microscopy, Tokyo, Vol. 1, 3–8.

Cowley, J. M., 1986b. Electron diffraction phenomena observed with a high resolution STEM instrument. *J. Electron Microsc. Tech.*, **3:** 25–44.

Cowley, J. M. and Spence, J. C. H., 1981. Convergent beam electron microdiffraction from small crystals. *Ultramicroscopy*, **6:** 359–366.

Cowley, J. M. and Roy, R. A., 1981. Microdiffraction from gold microcrystals. In: *Scanning Electron Microscopy*, Johari, O., ed., SEM, Chicago, 143–152.

Marks, L. D., 1985. Imaging small particles. *Ultramicroscopy*, **18:** 445–452.

Marks, L. D. and Smith, D. J., 1983. HREM and STEM of defects in multiply-twinned particles. *J. Microsc.* **130:** 249–261.

Pan, M., Cowley, J. M. and Chan, I. Y., 1987. The structure of Pt particles on γAl_2O_3 support. *J. Appl. Cryst.*, in press.

Wallenberg, L. R., Bovin, J.-O., Petford-Long, A. K. and Smith, D. J., 1986. Atomic-resolution study of structural rearrangements in small platinum crystals. *Ultramicroscopy*, **20:** 71–76.