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Electron Diffraction and Anomalous X-Ray Diffraction of Rhodium Oxide Platelets on Alumina

In the course of investigating the properties of severely calcined Rh on Al_2O_3 catalysts, we found interesting anomalies when we tried to characterize the particle size of the rhodium oxide by using only X-ray diffraction and chemisorption measurements.

All the 1% Rh catalysts were made following the procedure given previously (*1*) for 1% Ir on alumina, but using rhodium chloride as the source of metal. In all cases, the calcinations were carried out by putting the catalysts in a muffle furnace at 25°C, then heating over a period of several hours to the calcination temperature in static air, and then holding overnight at this temperature.

Calcination at 650°C (see Fig. 1) produced samples that gave metal dispersions (calculated from two CO isotherms (*2*) measured volumetrically) of about 0.48, or the equivalent of 20-Å particles, assuming hemispherical geometry. For the samples calcined at 760°C, the metal dispersion was 0.063, corresponding to hemispherical 170-Å particles. While the presence of 20-Å particles would not normally be expected to be detectable by Rh peaks in the X-ray spectrum, the 170-Å particles are in a favorable range for X-ray measurement (for details and discussion of the X-ray procedure used, see Ref. (*1*)). In fact, none of the X-ray spectra (taken after the 760°C calcination) showed any peaks of Rh_2O_3 (after calcination) or of rhodium metal (after calcination followed by reduction). This was most surprising as a catalyst containing 0.3% Ir and 0.3% Pt, prepared by the identical procedure, showed 340-Å Ir particles and 620-Å Pt particles after calcination at 760°C for 48 h, followed by reduction (Example 3, Ref. (*1*)). Chemisorption data (which gives an average value for both the Ir and the Pt) gave a calculated particle size of 300 Å, in good agreement with these X-ray values.

Data obtained by electron microscopy, using procedures detailed earlier (*3*), explain this anomaly, as in both samples (650 and 760°C calcinations) a significant number of large (500–1000 Å) particles of rhodium oxide were seen in the Phillips 300 microscope. The only difference in the two samples was that more particles were seen in the samples calcined at the higher temperature. In both samples, however, the particle size was essentially the same.

Good electron diffraction patterns were recorded for about 10 of these particles, and every one was a single crystal of Rh_2O_3, as shown by the fact that no diffraction rings were seen other than those characteristic of the alumina. Only small spots were seen, and their spacing indicated that they were single crystals of Rh_2O_3 (Fig. 2). Table 1 shows that very good agreement was found between the *d* spacings obtained by electron diffraction, and those of the standard ASTM X-ray diffraction values for Rh_2O_3.

The footnote in the table is the key to the mystery. The 114 orientation was observed only once in the 10 patterns analyzed, and this orientation gives the strongest line in the X-ray spectrum. As it appears from the electron micrographs that the Rh_2O_3 crystals are much thinner than either their length or width, it seems probable that most platelets are oriented with their 114 plane perpendicular to the large face. As the electron beam is also perpendicular to the large

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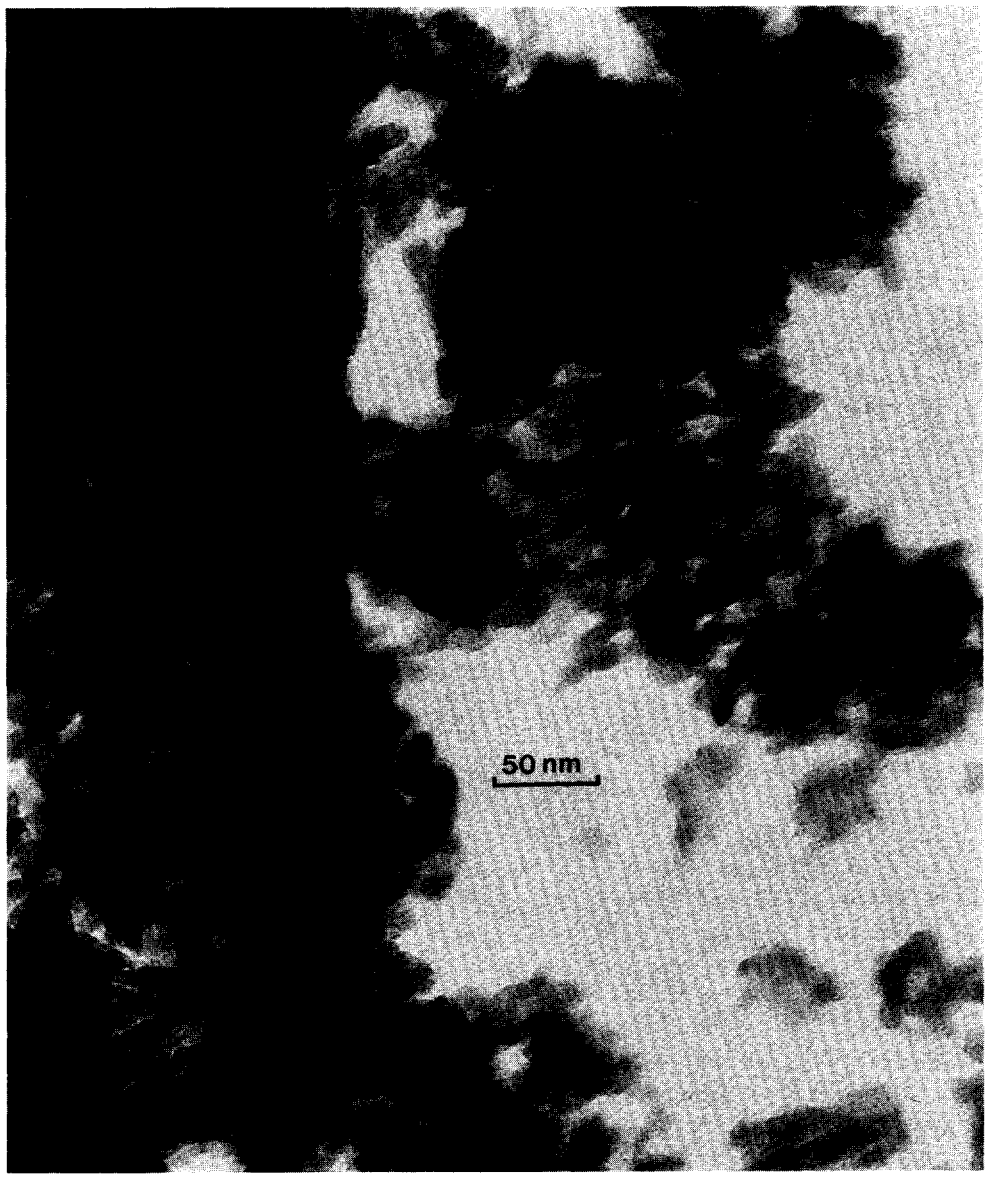

FIG. 1. Electron micrograph of 1% Rh on Al_2O_3, after calcination at 650°C.

face as a consequence of sample preparation, it follows that the strongest line in the X-ray spectrum is associated with the smallest crystal dimension. It is still not clear why no lines of Rh_2O_3 were detected in the X-ray spectra, as particles thicker than about 50 Å should be readily detectable. We conclude from this that the thickness is probably less than 50 Å. Unfortunately, it is very difficult to get any estimate of thickness directly from TEM photographs.

Some electron microscope studies were made of these calcined catalysts, after reduction at 500°C and passivation at room temperature. Particles of rhodium were seen, but smaller, with an upper limit in size of about 300 Å. As previously mentioned, such samples gave no Rh lines in the X-ray spectrum, so we assume that the

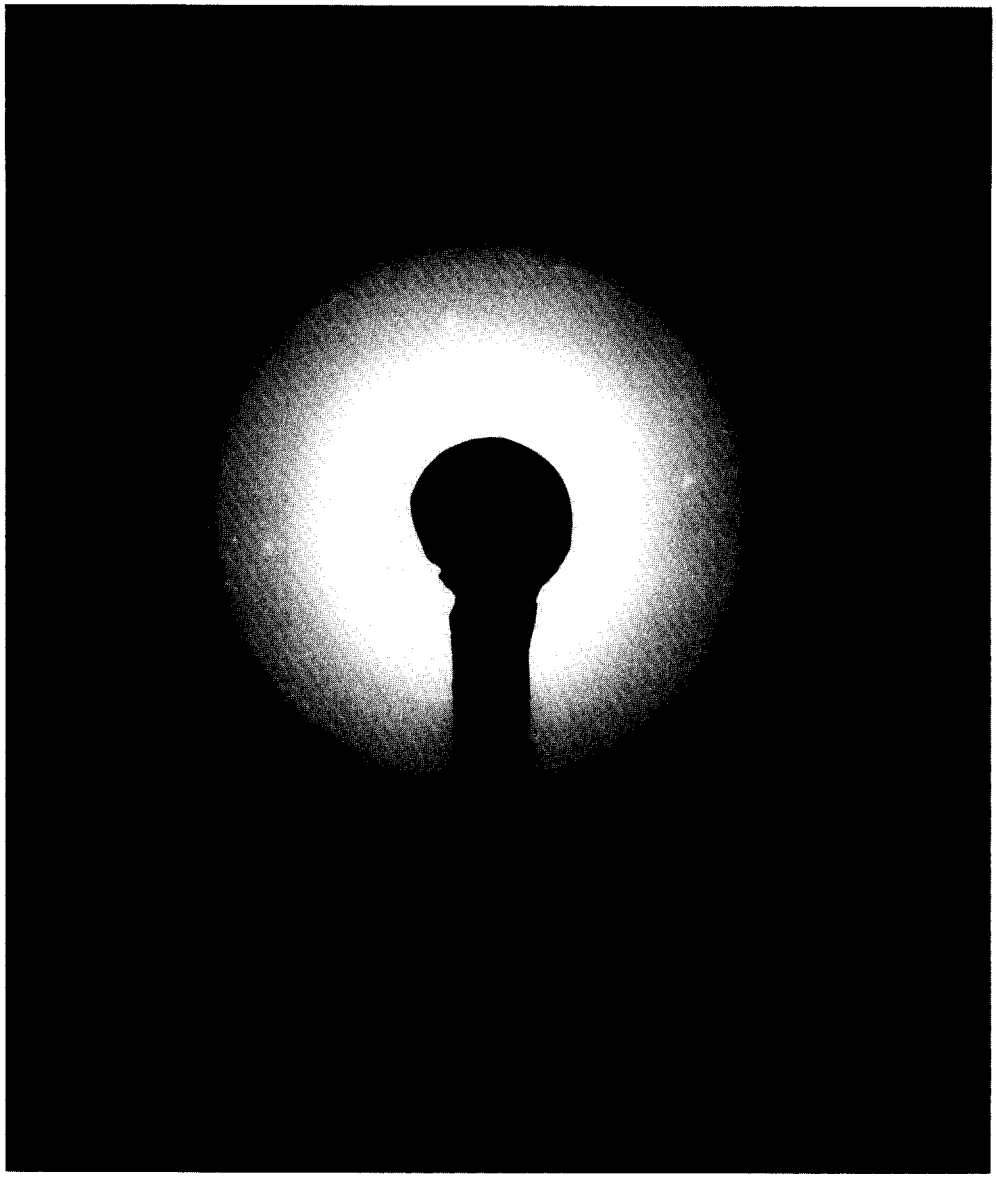

FIG. 2. Electron diffraction pattern of particles shown in Fig. 1.

particles have essentially the same morphology, with all dimensions reduced by the shrinkage inherent in the transition from Rh_2O_3 to Rh. We cannot be certain of this, however, as such particles are too small to be studied by electron diffraction in our microscope.

As far as the interpretation of the chemisorption data is concerned, it seems probable that there is a bimodal particle size distribution of the Rh in the sample calcined at 650°C: some is in the form of the large platelets seen in the microscope while the rest (about half) is probably atomically dispersed in rafts one atom thick, as found with noncalcined 1% Rh on alumina samples (*4*). In the latter work, using a reduction temperature of 470°C, a dispersion of 1.06 was measured with H_2 chemisorption, in substantial agreement with other work-

TABLE 1

Indexing of Electron Diffraction Patterns of Rh_2O_3

d(Å)		hkl
Experimental	ASTM (X-ray)	
3.70	3.68	004
3.64	3.62	111
2.72	2.722	020
2.61	2.623	114[a]
2.56	2.574	200
1.73	1.747	223
1.70	1.698	131
1.49	1.495	314
1.28	1.286	400
1.24	1.242	331

[a] Strongest line in the X-ray spectrum. Observed only once in 10 electron diffraction patterns.

ers (*5*), who reduced 1% Rh on different alumina at 500°C, and obtained a dispersion of 1.0.

This interpretation is confirmed by the TEM data obtained on the 760°C calcined samples—the same size particles were seen of the single crystal Rh_2O_3, but many more particles were seen than in the case of the 650°C calcined sample. The chemisorption data on this sample indicated a metal dispersion of 0.063 or, in other words, if the same bimodal distribution was present, most of the Rh was in the 500- to 1000-Å Rh platelets, and very little in the form of atomically dispersed rafts.

Hence, it is clear that air calcination of rhodium on alumina catalysts can produce, very surprisingly, single crystals of Rh_2O_3 oriented mainly with their 114 planes perpendicular to their large face. This is in marked contrast to the behavior after calcination of other noble metals such as Pt and Ir on the same alumina, which results in approximately spherical particles (*1*) which are not single crystals.

In conclusion, this work clearly shows that the absence of a line in the X-ray diffraction spectrum should not be interpreted to mean that one necessarily has particles of dimension less than about 50 Å. The latter criterion has been used in many cases to show that noble metal catalysts are well dispersed. Depending on the metal, the support, and the pretreatment, large particles of noble metal can be present which have no X-ray diffraction spectrum.

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