

Migration of Supported Metals during Preparation for Electron Microscopy

Transmission electron microscopy (TEM) is one of the best methods for characterizing small supported metal particles, even those with diameters <1 nm (1-4). We report TEM of small Rh particles on SiO_2 which demonstrates sample preparation technique has a strong influence on the number and type of small (1-3 nm) Rh particles visible not only on the support, but also on the neighboring grid coating; the results indicate mobility of the Rh particles during sample preparation.

The Rh/ SiO_2 was prepared by mixing silica (Cab-O-Sil, M-5 grade), calcined at 473 K for 12 h, with a hexane solution of $[\text{Rh}(\text{allyl})_3]$, to yield the SiO_2 -bound, diallyl rhodium complex $[\{\text{Si}\}-\text{O}-\text{Rh}(\text{allyl})_2]$ (5-7). H_2 at 298 K reduces the organometallic complex, leading to formation of highly dispersed rhodium aggregates (6, 7). Two samples of Rh/ SiO_2 prepared in this way, having metal loadings of 0.7 and 1.4 wt%, were used in an investigation by ^1H NMR and TEM (8) involving treatment of the samples with H_2 .

TEM was used to characterize the rhodium particle sizes before and after treatment with H_2 at 473 K. Samples were prepared for microscopy by ultrasonically dispersing the catalyst powder in reagent-grade methanol (Fisher) (or, alternatively, isopropanol or acetone), followed by deposition of the suspension onto carbon-Formvar-coated copper grids. The samples were examined with a Philips EM 400T microscope and a 100-keV incident electron beam.

The micrographs of both the unheated samples showed the presence of nearly uniform distributions of rhodium aggregates, approximately 1 to 3 nm in diameter

(smaller particles could not be resolved) (Fig. 1). After heating in H_2 at 473 K, the sample containing 1.4 wt% Rh showed a much broader distribution of particle sizes, the majority being in the range 4 to 5 nm, whereas the sample containing 0.7 wt% Rh showed no evidence of significant aggregation. In all of the samples, however, the presence of small, nearly spherical particles was noted both on the silica and on the grid. The particles on the grid were all less than 3 nm in diameter; the larger particles (formed by aggregation in one of the samples) were observed on the silica but not on the grid.

The particles were characterized further with scanning transmission electron microscopy and energy dispersive analysis of X rays. Areas in the vicinity of the rhodium particles on the carbon-Formvar coating were analyzed. No trace of silica was found in these areas. Attempted elemental analyses of the small particles themselves were not accurate, since the particles were too small.

In experiments with the sample containing 0.7 wt% Rh, a greater number of particles was observed off the silica, and an alternative grid preparation was used. The carbon-Formvar-coated grid was simply dipped into the dry catalyst powder and shaken to remove the excess. TEM of this sample under the conditions stated above revealed no metal particles other than those on the silica support (Fig. 2). Moreover, the particles on the silica were far less clearly visible than those observed with the dispersion technique of preparation.

Since the sizes and shapes of the particles observed on and off the silica support were indistinguishable, we infer that small rhodium particles migrated off the silica

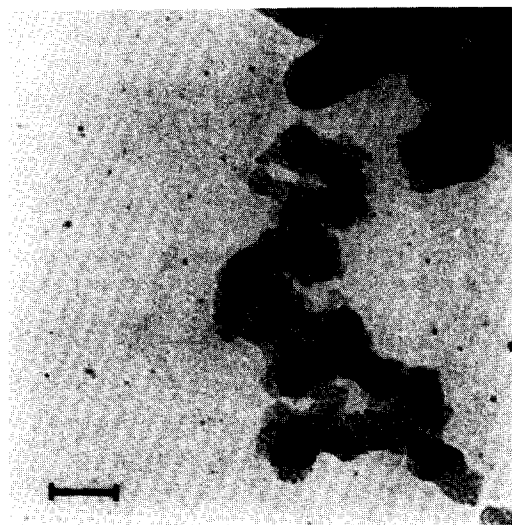


FIG. 1. Electron micrograph of Rh/SiO₂ (0.7 wt%) after grid preparation by the ultrasonic dispersion technique. The scale bar represents 20 nm.

and onto the carbon-Formvar coating of the grid. We conclude that the ultrasonic vibrations used to disperse the samples had sufficient energy to cause the smaller rhodium particles to separate from the silica support. This conclusion is consistent with the fact that silica has a weak binding interaction with metals in comparison with, say, γ -Al₂O₃ (9,11). The small rhodium particles appear to be spherical, having only relatively small areas of contact with the support; in contrast, the larger rhodium aggregates had much greater areas of contact and were found to be more stable on the silica (12-16).

Ruckenstein and co-workers (12, 13, 15) investigated the effects of temperature, periodic oxidation, and the metal-support interaction of Pt/Al₂O₃ on migration of the platinum and concluded that migration can occur under similar circumstances. Baker (14) reported a correlation of size and shape of platinum particles with mobility during treatment. All of these reports unambiguously demonstrate that metals migrate under conditions of reaction. Our observations indicate that the process of TEM sample preparation itself can produce the

migration of metal particles which have relatively weak interactions with the support. The clarity of the images of the small rhodium particles observed with the samples prepared by the ultrasonic dispersion method suggests that the particles may have migrated off the silica, been suspended in the liquid, and then randomly re-deposited in the drying process.

Many characterizations of catalysts by TEM are performed with holey carbon films so that catalyst particles dangling over the holes can be examined, and one should be aware of the possibility that many of the smaller metal particles may migrate off the catalyst support and not be seen at all. It is also possible that metal particles observed on the support will have been redistributed by the ultrasonic dispersion. These effects could well lead to incorrect measurements of particle size distributions. Particularly susceptible to these effects would be samples with weak metal-support interactions, which may require alternative grid preparations.

The migration phenomena may prove useful in diagnosing the existence of weak metal-support interactions and characteriz-



FIG. 2. Electron micrograph of Rh/SiO₂ (0.7 wt%) after grid preparation by the dry dipping technique. The magnification is as in Fig. 1.

ing the relations between the sizes of metal aggregates and their bonding to various supports.

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