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Characterization by TEM and Image Processing of Rhodium Supported on TiO_2

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It is shown by the use of digital image processing techniques in electron microscopy that the shape of small rhodium particles supported on titania depends on the hydrogen reduction temperature. In sample I (1 wt%) reduced at 473 K, one-dimensional rows and two-dimensional irregular arrays of rhodium were observed. In sample II (3 wt%) reduced at 573 K, three-dimensional rhodium particles about 2 nm in size were observed. In addition, an apparent support reduction around the particles was revealed.

INTRODUCTION

The understanding of catalytic phenomena has advanced in recent years with the availability of surface spectroscopy, high-resolution imaging, and diffraction techniques. In particular, electron microscopy has made enormous progress and now it is possible to obtain a good deal of information on the particle structure in the size range 2 to 50 nm. This has been the case for rhodium supported on SiO_2 and Al_2O_3 where an attempt to correlate surface and catalytic properties has been made (*1–3*). However, in cases where most of the atoms are on the surface we have a difficult task in characterization of the catalyst. Although atomic rhodium species and raft-like particles have been invoked to explain catalytic properties of highly dispersed rhodium (*2*), their characterization has not yet been presented.

Recent studies of Rh on TiO_2 by HREM coupled with digital image processing showed that rhodium atoms are on the surface structure of the support, forming one-dimensional structures and irregular agglomerates of two to three monolayers thick (*4*).

EXPERIMENTAL

Electron microscopic observations were carried out with a JEOL 100C electron microscope with an ultrahigh-resolution pole piece. Images were obtained at 330,000 and 440,000 magnifications; astigmatism was corrected using the phase contrast-features of the support carbon film. To perform digital image processing the photographic plates were digitalized using a microdensitometer with a pixel size of 10 × 10 m. Reconstructed images were displayed and processed using a Grinnell GMR-270 image processing system on line with a Prime computer Model 550. Contrast stretch algorithms were used and the final image was several times larger than the original electron optical magnification. The catalysts were prepared by ion exchange of $Rh(NO_3)_3$ (sample I) and $Rh(NH_3)_5Cl_3$ (samples II and III) on TiO_2 pretreated with ammonia. The solution was contacted overnight, washed with deionized water, and dried at 373 K for 4 h. The metal loadings measured by atomic absorption were 1.05 wt% (sample I) and 2.6 wt% (samples II and III). The catalysts were calcined in air

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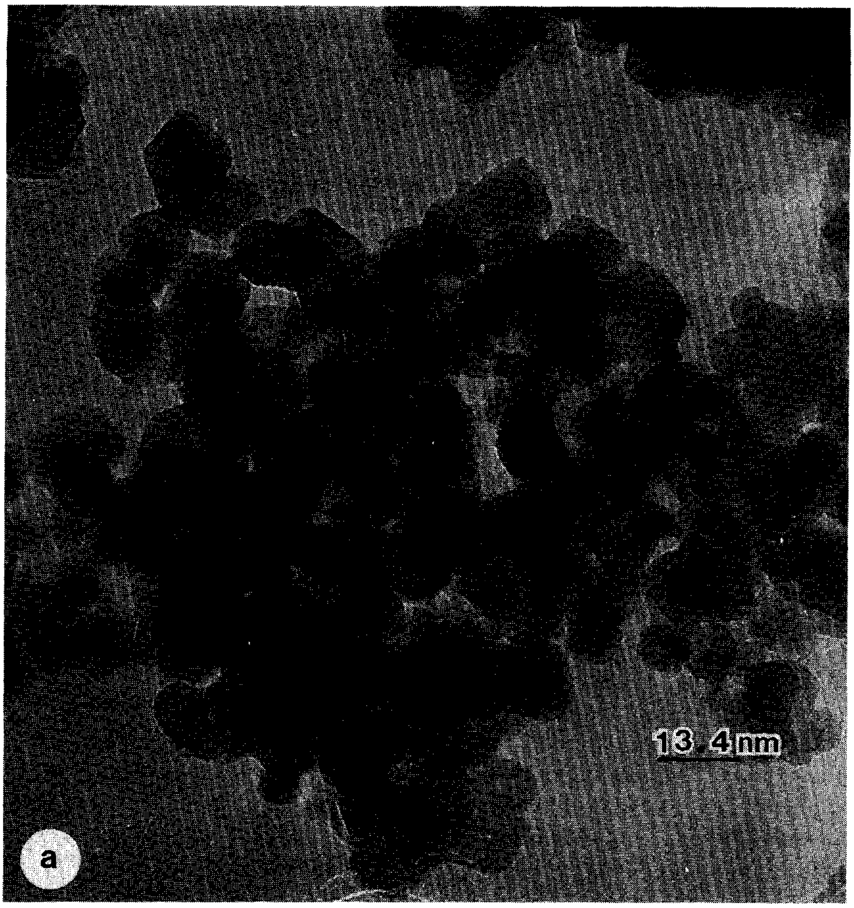

FIG. 1. (a) HREM micrograph of sample I, showing both the [110] lattice spacing of rutile and the rhodium particles 1.0–1.5 nm in size. (b) Magnified image of a single TiO_2 crystal showing small rhodium particles.

to 473 K for 2 h and reduced in hydrogen to 473 K (I) and 573 K (II). Before observation, the samples were exposed to air.

RESULTS

Sample I (Reduced at 473 K)

Some preliminary results of this sample were reported previously (*4*); further studies are now presented. Figure 1 shows a high-resolution image of the catalyst; to obtain a better resolution this picture was taken on a hole upon the sample grid. We can observe TiO_2 superimposed crystals showing the [110] lattice resolution of rutile. Rhodium particles 0.8 to 1.5 nm are observed on these images. To characterize the particles' shape, the contrast was enhanced using digital image processing. TiO_2 single-crystal areas showing particles were retained for analysis to avoid misinterpretations originating from the overlap of two or more titania crystals. In the upper right section of the image shown in Fig. 1, particles on a single crystal are observed. A computer-processed image of this area is shown in Fig. 2; irregularly shaped particles are observed. They are distributed along the lattice spacing of the support and are connected, with some rows showing the same lattice periodicity of the support. That

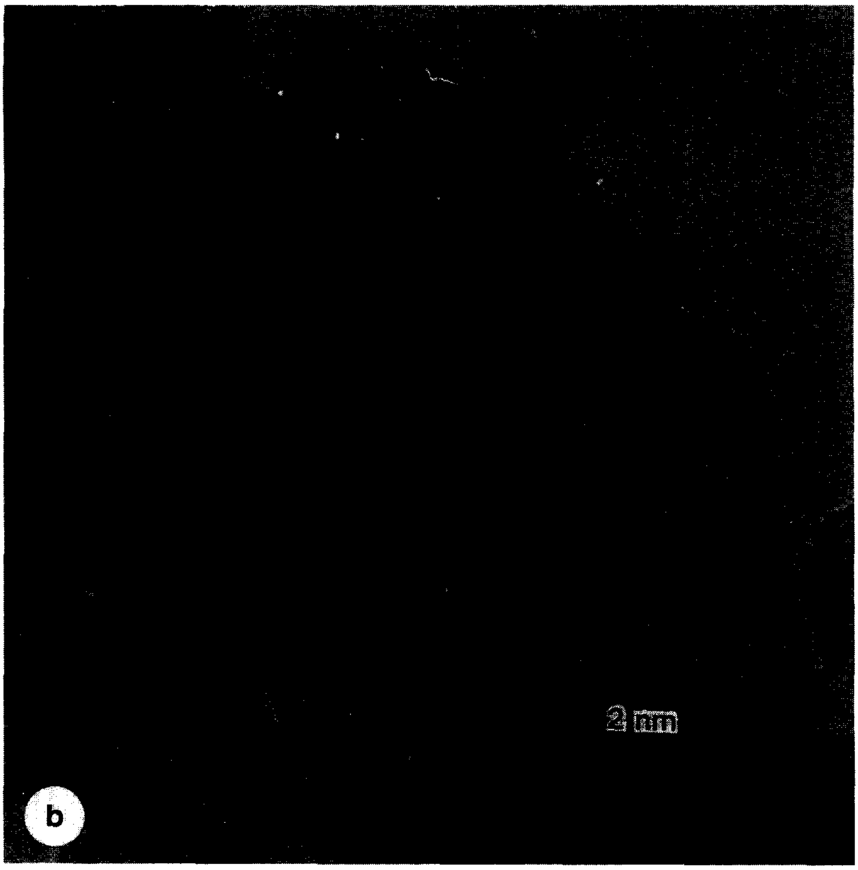

FIG. 1.—*Continued.*

the contrast intensity of these rows was similar to that of agglomerates suggests that it is provided by rhodium atoms. From similar results it was previously concluded that Rh forms two types of structures, one-dimensional and flat irregular aggregates, over the [110] face of rutile (*3*).

Sample II (Reduced at 573 K)

This sample was prepared by increasing the metal loading to 3 wt% and the reduction temperature to 573°K.

A high-resolution axial bright-field lattice image of this sample is shown in Fig. 3, the [110] rutile lattice planes and several Rh particles deposited on it are clearly observed. Computer-enhanced contrast images of two particles are shown in Fig. 4; both particles are surrounded by a halo, which indicate that the support has changed and reacted at these areas. This change in contrast could be produced for TiO_2 reduction near the metal particles, suggesting that the particle–support interface is modified by thermal treatment. It should be mentioned that the halo contrast is not due to carbon contamination around the particle. This was sustained by the fact that particles in sample I observed under similar microscope, vacuum, and preparation conditions did not show such halo.

In Fig. 5 the particle shape is irregular but a single core is observed, in contrast with the particle shape in Fig. 6 that shows two cores fused into a larger particle. The contrast observed at the center of both par-

FIG. 2. A digital processed image of the particles shown in Fig. 1b.

FIG. 3. HREM micrograph of sample II, showing the [110] lattice spacing of rutile and the rhodium particles 2.0–2.5 nm in size.

FIG. 4. Digital processed image of particles shown in Fig. 3.

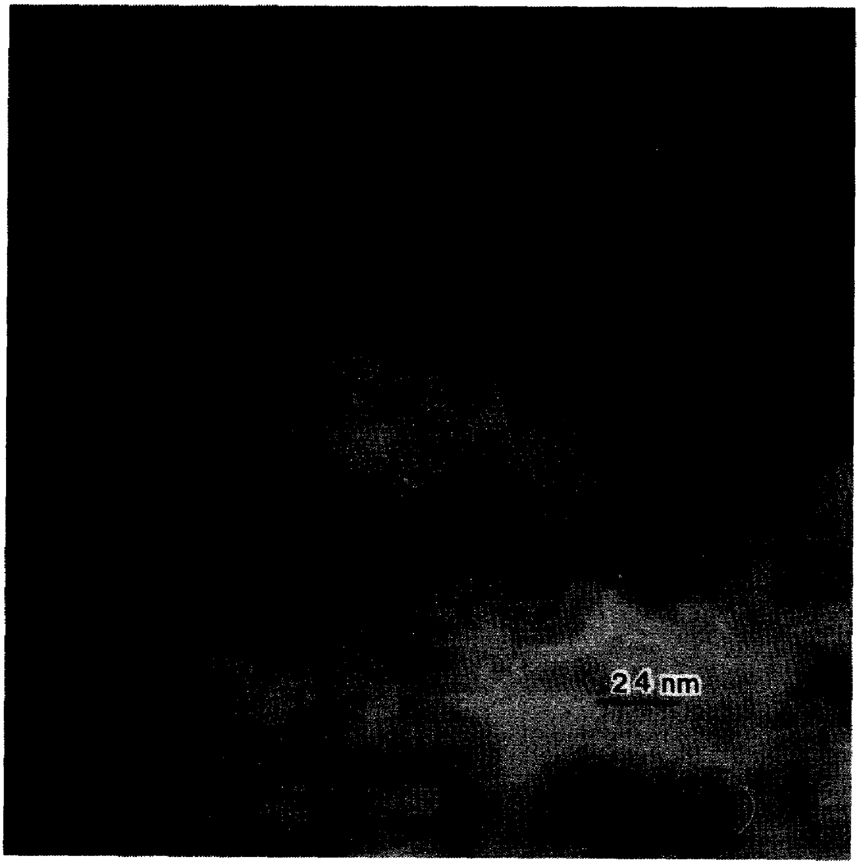

FIG. 5. Enhanced-contrast image showing an irregular single-core particle.

FIG. 6. Enhanced-contrast image of an enlarged particle showing two cores.

ticles suggests that they are three-dimensional, involving between five and six atomic layers from the support surface.

DISCUSSION

The morphology of rhodium particles supported on TiO_2 has been a subject of discussion for quite some time. Several authors claimed that rhodium forms "rafts" on the surface of alumina (*2*). Some others suggest the existence of Rh ions to explain the influence of additives in the syngas conversion (*6*). Recent studies by Prins and coworkers (*7*) suggest that the existence of rafts could be related to the presence of Rh_2O_3. Electron microscopic observations have been interpreted in some cases as the existence of two- and one-dimensional particles which could be explained by interaction with the support. Our results obtained from the sample reduced at 473 K support this interpretation. The main characteristics of this model are the interactions with some planes of the support, and the fact that rhodium atoms could be spreaded on the surface. The causes of this interaction are primarily the ion-exchange method (*8*) and, secondly, the electrostatic attractions with some anions on the surface. This interaction with [110] TiO_2 planes must produce one-dimensional "rows" the first time and two-dimensional ensembles by atomic diffusion as temperature and time increase. The distance of rhodium atoms between two rows is longer than that required to form metallic bonds giving a highly coordinate unsaturated character to these atoms. At low temperatures and low loadings, this kind of arrangement is what we expected. This one-dimensional structure may correspond to the ionic species observed by Worley *et al.* (*6*). The addition of rhodium atoms by diffusion between these "rows" leads to the formation of two-dimensional ensembles (flat irregular) as suggested previously. These particles, which seem to be the main contributors to the total rhodium deposited in this sample, have been probed and found to be catalytically active in benzene hydrogenation (*9*), in contrast with very diluted samples where a strong inhibition of this reaction was observed (*10*).

The sample with 3 wt% Rh loading reduced at 573 K showed well-defined particles (2 nm) on a [110] TiO_2 face. On this sample the main observations are the following: The surface around the particle has reacted with the surroundings. The particles are three-dimensional and several layers high; in some cases, two particles are fused forming an enlarged one. It has been reported that the [110] face is highly resistant to reconstruction; therefore, a catalytic effect of the rhodium particles could be assumed. If it is assumed that reduction of the support starts at 573 K, then a high concentration of Ti reduced species should exist around the particle. Migration of these species onto the particle at higher temperatures could explain several established facts about SMSI (*11*).

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