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About the Structure of Small Metal Rh Particles on TiO_2: TEM Study

In recent years there has been a wide interest about the structure of small metal particles (less than 15 Å). The problem of the changes in catalytic properties of small metal particles when they are supported in oxides still presents many challenges. It has been suggested that small particles may form "rafts" (*1*), icosahedrons, decahedrons (*2*), or even atomic spreading on the surface of oxides like SiO_2, Al_2O_3, TiO_2, etc. (*3*).

In the present work we report TEM studies of Rh/TiO_2 using high-resolution electron microscopy (HRTEM) combined with imaging processing techniques, to characterize the structure of the particles on the support.

The images were computer-processed to enhance the contrast of weak features. Images revealed flat rhodium particles with a rough shape. In addition there are atomic rhodium "rows" deposited along the (110) planes.

The aim of this work is to gain further insight about the atomic distribution of small metal supported particles.

A Rh catalyst supported on TiO_2 was prepared by ionic exchange of $Rh(NO_3)_3$ H_2O in TiO_2 (pretreated with ammonia) at 343°K. The solution was contacted overnight, washed with deionized water, and dried at 373°K for 4 h. The metal loading measured by atomic absorption was 1.06% wt. The catalyst was calcined in air to 473°K for 2 h and reduced in hydrogen at 473°K.

The dispersion of rhodium calculated from the back-extrapolation of the hydrogen isotherm obtained at 298°K, was 100%, suggesting the existence of very small particles. The catalytic activity of this sample was measured in a continuous flow microreactor under atmospheric pressure. Two reactions were studied, the hydrogenation of benzene and the hydrogenolysis of pentane. From Table 1, it is observed that this catalyst shows slightly decreased hydrogenation activity and increased selectivity in the hydrogenolysis of the terminal bond for pentane. This behavior is the same as observed on catalysts supported on silica with the same dispersion (*4*). From these results it is observed that this sample reduced at 473°K shows a typical behavior of well-dispersed catalysts.

TiO_2 crystallites from the catalyst were mounted in TEM grids for observation. Samples were observed with a JEOL 100-C microscope fitted with ultrahigh-resolution pole piece (C_s = 1.7 mm). High-resolution lattice images were obtained including in the aperture a ⟨110⟩ reflection of the TiO_2. Figure 1 shows a typical lattice resolution image with a fringe distance of 3.25 Å, corresponding to rutile. On this picture Rh particles of 10–12 Å of diameter are readily seen. It has been shown by Avalos and Yacamán (*5*) that the particle visibility strongly depends on the substrate orientation and thickness. The orientation in which lattice fringes from the TiO_2 are observed is optimum for detection of very small metal particles. Nevertheless the main problem in obtaining reliable information about the structure of particles is the low signal/noise ratio. Contrast features from very small particles are usually masked by substrate contrast. This problem can be overcome by using image processing techniques to filter the noise and enhance the contrast. In order to process images, the photographic plates were digitalized using a microdensitometer with a spot size of 10 μm. Reconstructed images were dis-

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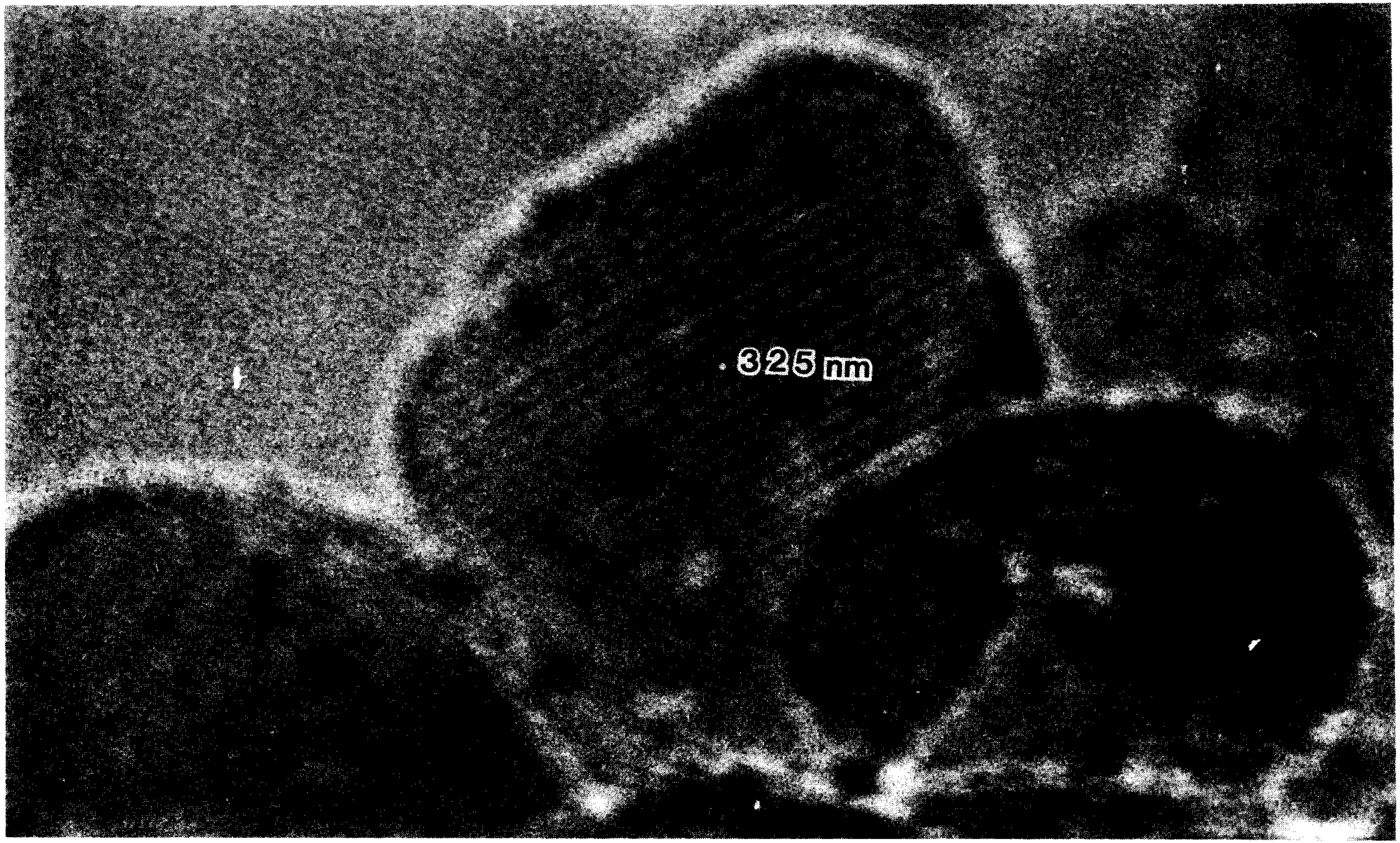

FIG. 1. High-resolution image of a TiO_2 catalyst showing lattice resolution of the (110) planes. Rhodium particles are apparent in the image.

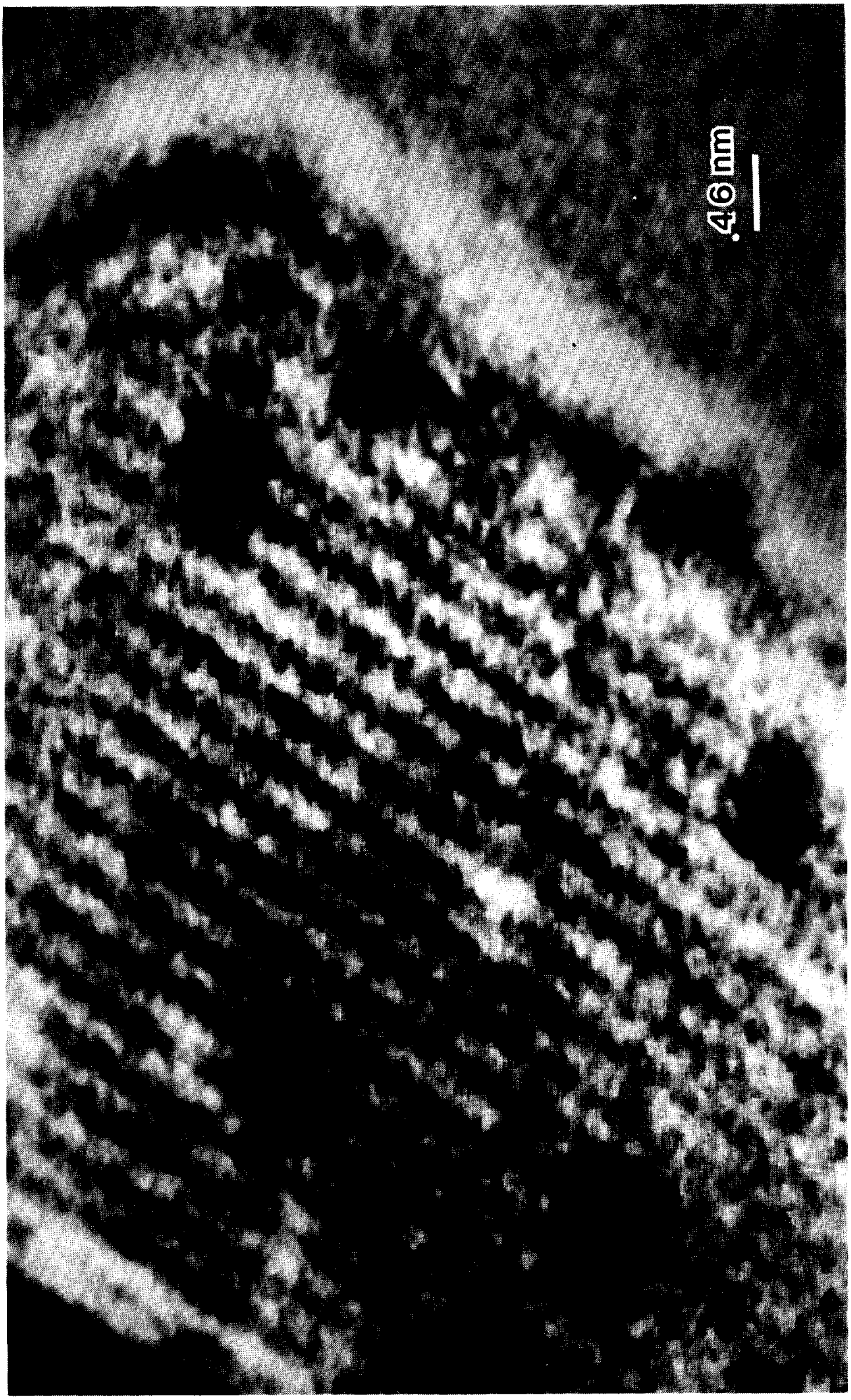

FIG. 2. Computer reconstructed image of the Rh/TiO$_2$ catalyst. The magnification is 20 times larger than Fig. 1.

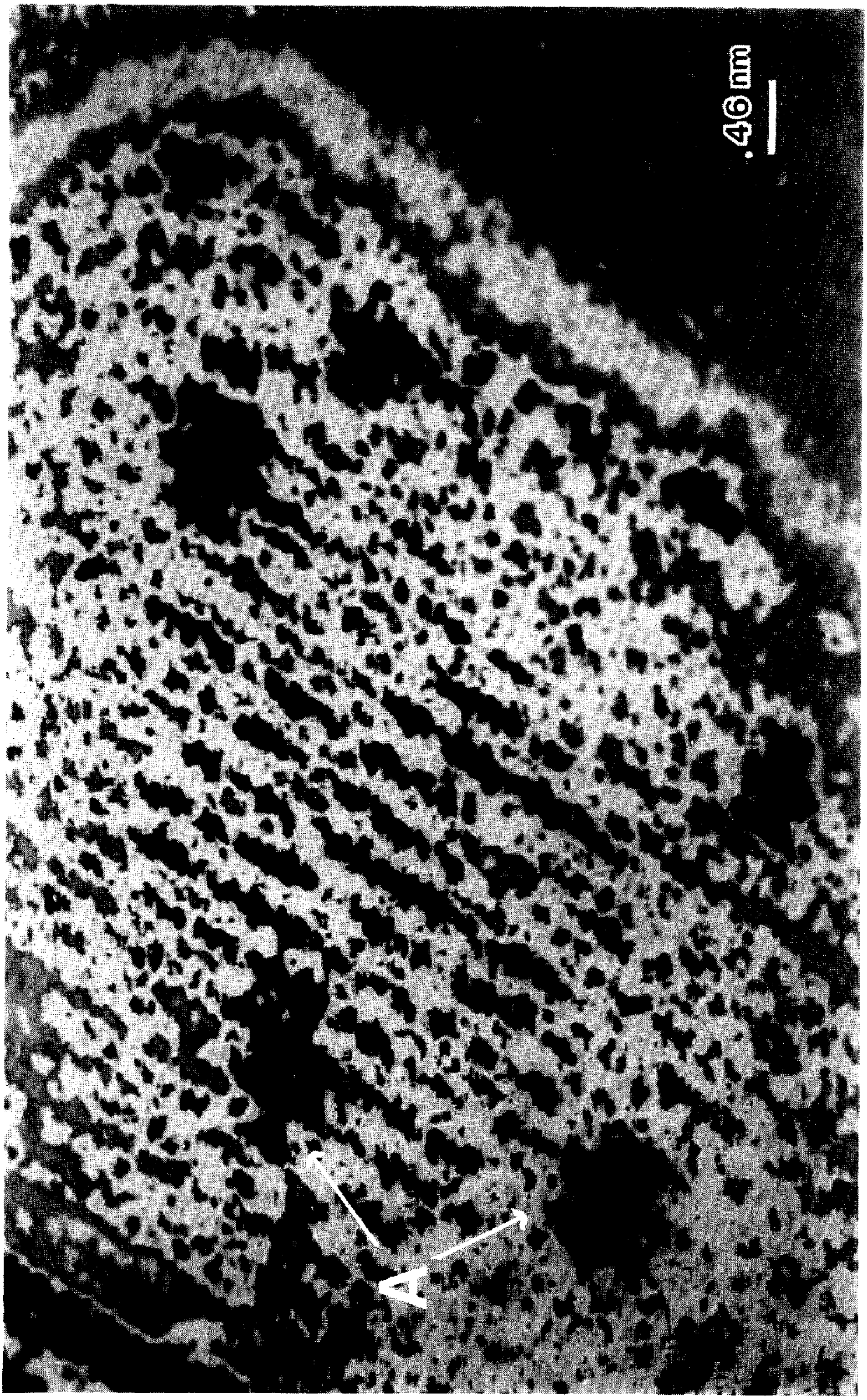

FIG. 3. Enhanced contrast image. Rhodium is present as flat particles (region A) or intercalated along (110) planes.

TABLE 1

Chemisorption and Catalytic Activity of Rhodium Supported on Different Substrates

Sample	Dispersion H/Rh	Hydrogenation of benzene TON (h^{-1} 50°C)	Hydrogenolysis of pentane		
			TON (h^{-1} 50°C)	Selectivity	
				$C_1 + C_4$	$C_2 + C_3$
Rh/TiO_2	100	200	170	0.30	0.70
Rh/SiO_2	95	250	121	0.24	0.76
Rh/MgO	90	300	24	0.28	0.62

played and processed using a Grinnell GMR-270 image processing system on line with a Prime Computer Model 550. Contrast stretching algorithms were used and the final image magnification was 20 times larger than the original electron optical magnification. To produce the image 256 gray (or color) tones were used in order to ensure enough particle visibility. A typical reconstructed image is shown in Fig. 2. In this micrograph all the contrast features showing dark tones correspond to the Rh metal, and the intermediate tone to the TiO_2 substrate. By increasing this contrast, Fig. 3 is obtained. In this image, the Rh metal is in the form of irregularly shaped particles of 10 Å and as "rows" along the substrate. The particles show a change of contrast in the center indicating a variation of thickness. By knowing the change in intensity corresponding to a given color it was determined that this variation in contrast corresponds to a monoatomic step in thickness. Therefore the particles are very flat with an approximate shape as illustrated in Fig. 4. They can be considered as platelets with a thickness of two monolayers. On the other hand from Fig. 3 it is clear that many atoms are located so as to form rows along the substrate. By crystallographic analysis it was concluded that the TiO_2 surface in contact with the Rh was the (110) surface with the particles located in rows along the ⟨001⟩ direction. The (110) surface of TiO_2 has been shown to be a stable surface (with no faceting or reconstruction) by LEED studies (*6*). Thickness fringes on the TiO_2 substrate confirmed that the surface was flat. Further evidence is provided by the fact that the lattice fringes are not shifted by thickness changes on the substrate. Figure 5 shows a model of the (110) rutile surface indicating the possible location of the Rh atoms.

Theoretical results by Joyner (*9*) predict that metal–support interactions are strongly dependent on particle size. In particular, it is suggested that only in the case where the particles are one or two layers thick (as in this case of Rh on TiO_2), the support effect will be strong and independent of particle size.

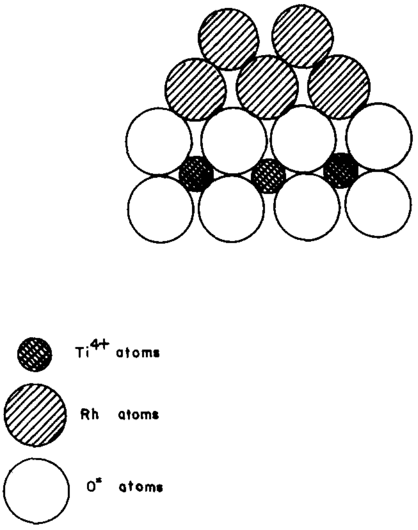

FIG. 4. Approximate shape of the particles as reconstructed from the contrast changes in Fig. 2.

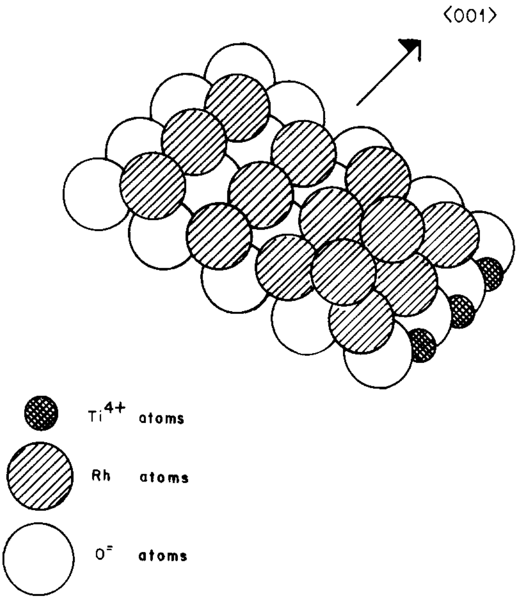

FIG. 5. Model of the (110) surface of TiO_2 showing the possible location of Rh atoms.

From our model it is expected that high-temperature treatments in hydrogen will produce O^{2-} vacancies where rhodium atoms will be substitutionally introduced as proposed by Galli (*7*). EXAFS results obtained by Haller (*8*) for catalysts reduced at 773°K give evidence to a direct Rh–Ti bonding, which could be well explained by incorporating Rh atoms on O^{2-} vacancies. This metal–support interaction observed on catalysts reduced at low temperature, may give an insight about the behavior of samples in the SMSI state by assuming that O^{2-} vacancies are produced in the support with incorporation of Rh atoms in the structure.

In conclusion, we observed that small Rh particles supported on TiO_2 presented a selective interaction with the (110) surface of rutile. The metal is forming two kinds of structures, flat platelets (two monolayers) and atomic rows along the ⟨001⟩ direction.

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