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NOTE

Comparison of Metal–Support Interactions in Pt/TiO_2 and Pt/CeO_2

Since the phenomenon of strong metal–support interaction (SMSI) on Group VIII metals supported on TiO_2 was first reported by Tauster *et al.* (1), a great deal of work has been done toward understanding the nature of the interaction between metals and reducible supports. When supported on TiO_2, Group VIII metals undergo a drop in alkane hydrogenolysis activity and H_2 chemisorption ability after being subjected to high temperature (>773 K) reduction (HTR) under H_2. Since the work of Tauster *et al.* (1), a growing body of evidence has shown that this suppression is due to the migration of reduced titania (TiO_x) species onto the surface of the metal crystallites (2–4). For the Rh/TiO_2 system, this model has been confirmed directly by the observation of amorphous overlayers on the Rh particles viewed edge-on using transmission electron microscopy (TEM) (5).

Another interesting aspect of SMSI is the increase in CO hydrogenation activity exhibited by metals supported on TiO_2 (6). Either special interfacial sites (7) or the spillover of reactive intermediates (8, 9) onto the support are thought to be responsible for this enhancement. Our previous work (10) also showed that when CO hydrogenation was carried out on Pt/TiO_2 samples, there was an apparent reversal of the SMSI state. Specifically, we found that the drop in hydrogenolysis activity caused by HTR was reversed when the catalyst was used in the CO hydrogenation reaction. Based on these results, we concluded that the enhancement of CO hydrogenation activity on TiO_2-supported Pt was not directly related to the onset of the SMSI state.

Other reducible oxides have been reported to exhibit support interactions similar to the classic SMSI phenomenon. The response of the CeO_2 support is of particular interest in view of its importance as an additive in automotive catalysts and due to the necessity of catalyzing hydrocarbon reactions on these catalysts. Several researchers have reported the occurrence of strong metal support interactions on Pt/CeO_2 (11), Ni/CeO_2 (12), Ir/CeO_2 (13), and Rh/CeO_2 (14). While in some cases (11, 14), these interactions have been described in terms of the classic SMSI that occurs on TiO_2-supported catalysts, other workers (12, 13) propose alternative explanations, including electronic effects. Zafiris and Gorte (15, 16), performed CO, H_2, and NO chemisorption on model CeO_2-containing catalysts and showed that the interactions between Pt and CeO_2 are relatively weak and similar to those between Pt and Al_2O_3 while the interactions between Rh and CeO_2 are strong.

TEM studies of the effect of evaporated Ce on the microstructures of Pt and Rh particles supported on silica and alumina have been performed by Schmidt and co-workers (17, 18). The presence of Ce modified the shape of the Pt particles, in that cube-shaped particles of Pt (otherwise seen on the silica and alumina supports) were not seen after H_2 reduction at 923 K. Reactivity measurements were done on Rh/CeO_2 where the presence of CeO_2 was found to enhance the CO hydrogenation activity and also cause a drop in ethane hydrogenolysis activity by approximately two orders of magnitude on reducing the catalyst at 873 K. Their studies, however, did not reveal any significant changes in the microstructure of Rh particles that could explain the drop in hydrogenolysis activity after HTR. It should be noted that the catalysts studied by Schmidt and co-workers involved 200-Å particles supported on planar supports and treated at temperatures as high as 1023 K.

In our previous work on CeO_2-containing Pt catalysts (19), we found that the interaction between Pt and CeO_2 was apparently similar to that of Pt/TiO_2 in that high-temperature reduction (HTR, reduction at 773 K under H_2) resulted in a large drop in hydrogenolysis activity that was reversible after the catalyst was subjected to oxidation at 773 K. In order to gain insight into the mechanisms whereby the behavior of Pt is modified by ceria, we have observed the microstructure of Pt/TiO_2 and Pt/CeO_2 catalysts using high-resolution TEM after similar pretreatments. Catalysts were observed both after low-temperature reduction, high-temperature reduction, and high-temperature oxidation. High-temperature oxidation was performed under an O_2/He gas mixture containing 10% O_2. Low-temperature reduction was performed under 20 sccm of flowing H_2 at 673 K while high-temperature

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reduction was performed under 20 sccm of flowing H_2 at 773 K. After reduction, the sample was cooled to room temperature under flowing hydrogen. Following this, the hydrogen flow was stopped and helium was allowed to flow through the system to purge out the hydrogen. The catalyst sample was then passivated under an O_2/He gas mixture containing 10% O_2. The catalyst was then removed from the reactor and stored in airtight vials.

Transmission electron microscopy was performed on a 200-kV JEM-2000FX electron microscope with a point resolution of 3.0 Å at the University of New Mexico. High-resolution TEM was done using a 400-kV JEM-4000EX electron microscope at Arizona State University. Catalyst powders were supported on holey carbon films mounted on Cu grids. No solvents were used at any stage of the sample preparation to prevent any contamination. The grids were simply dipped into the powders and the excess shaken off. Both fresh and aged samples were examined in the two electron microscopes after model reaction tests.

In this study, we have used nonporous oxides to constrain the location of the Pt particles to the exterior surface of the oxide support (20). The technique of surface profile imaging (21) was then used to study the surface structure of the supported particles on the atomic scale without overlapping contrast in the high-resolution image resulting from the support itself. Typical high-magnification views from the Pt/TiO_2 sample are shown in Fig. 1. In the HTR state, the Pt particles ranged in size from ~1.5 to 12 nm and their surfaces were covered with some sort of overlayer. On well-faceted {111} surfaces, the overlayers were invariably crystalline (see the region labeled "A" in Fig. 1a), whereas other surfaces had rather rough or disordered overlayers (see the region labeled "B" in Fig. 1). When the same catalyst was observed in the fresh state, i.e., after oxidation treatment at 773 K followed by low-temperature reduction (see Fig. 1 (b), it showed Pt particles with surfaces that were quite clean and devoid of the overlayers visible for the HTR state.

No similar overlayers were observed for the Pt/CeO_2 catalyst in the HTR state; and no difference in structure was noticeable between the Pt particles in the HTR state and those after oxidation followed by low-temperature reduction (see Figs. 2a and 2b). However, it generally appeared that the Pt particles were more difficult to locate in the oxidized state, which could have been due to the smaller Pt particles being completely oxidized. Raman spectroscopy showed a major Pt–O vibration on oxidized Pt/CeO_2 that was absent on a Pt/Al_2O_3 sample subjected to similar conditions (22). In the HTR state, the Pt particles were often found in a parallel epitaxial alignment with the ceria support. The lattice mismatch between the support and the supported particles was accommodated by an array of edge dislocations at the Pt/CeO_2 interface. One such interface is clearly visible in profile view in Fig. 2a; every two lattice planes of the CeO_2 support match three lattice planes of the Pt particle. This mismatch requires ~6% distortion of the normal Pt lattice plane spacing. The epitaxial relation is also apparent from Moiré fringes visible in the projection view images, such as Fig. 3. This Pt lattice distortion at the interface may contribute to the unusual catalytic properties of this metal–CeO_2 interface, for example, by affecting the mobility of oxygen, thus affecting the reducibility of CeO_2 in contact with platinum.

In previous work on Rh/TiO_2, we reported (5) the development of amorphous overlayers on Rh metal surfaces after high-temperature reduction. These overlayers were removed under oxidizing conditions. The presence of these overlayers on the metal surface leads to a drop in the metal signal as seen by surface-sensitive spectroscopy (4), and these overlayers can therefore be directly related to the drop in H_2 chemisorption after high-temperature reduction. Similar overlayers were also recently reported (23) for Rh/TiO_2 after 773 K reduction under H_2. Profile view imaging has not yet been extensively used to study the Pt/TiO_2 catalyst system. A previous report (24) had documented the formation of Ti–Pt intermetallic compounds when the catalyst was heated to high temperatures (>873 K) under H_2; however, the results were not correlated with catalytic properties. The work reported here provides direct confirmation of the encapsulation model for Pt/TiO_2 catalysts in the SMSI state, which has been previously confirmed in the Rh/TiO_2 system.

In contrast, Pt/CeO_2 catalyst (as shown in Figs. 2 and 3) as well as Rh/CeO_2 catalysts (25) do not exhibit any overlayers after high temperature reduction. Similar results were obtained previously for Pt/CeO_2 reduced at 773 K (26). These observations suggest that the mechanism by which the ceria support interacts with Pt is very different from that occurring with titania supports. Another significant observation is that the Pt particles are often epitaxial with the ceria support, as also seen for Rh/CeO_2 (23), with the lattice mismatch between the support and metal being accommodated by misfit dislocations at the interface. It is tempting to attribute the mobility of lattice oxygen in ceria, and the ease with which H_2 is able to reduce ceria in contact with the metal, to the nature of the metal/ceria interface.

The particle shapes and exposed facets do not appear to be affected by the nature of the support, which is further consistent with the turnover frequency for *n*-butane hydrogenolysis (in the preoxidized and low-temperature reduced state) on Pt/ceria being similar to that of Pt on other supports (19). The TEM observations do not provide any evidence for a metal–ceria interaction that could result in a drop in hydrogenolysis activity with high temperature reduction. However, the enhanced activity for CO

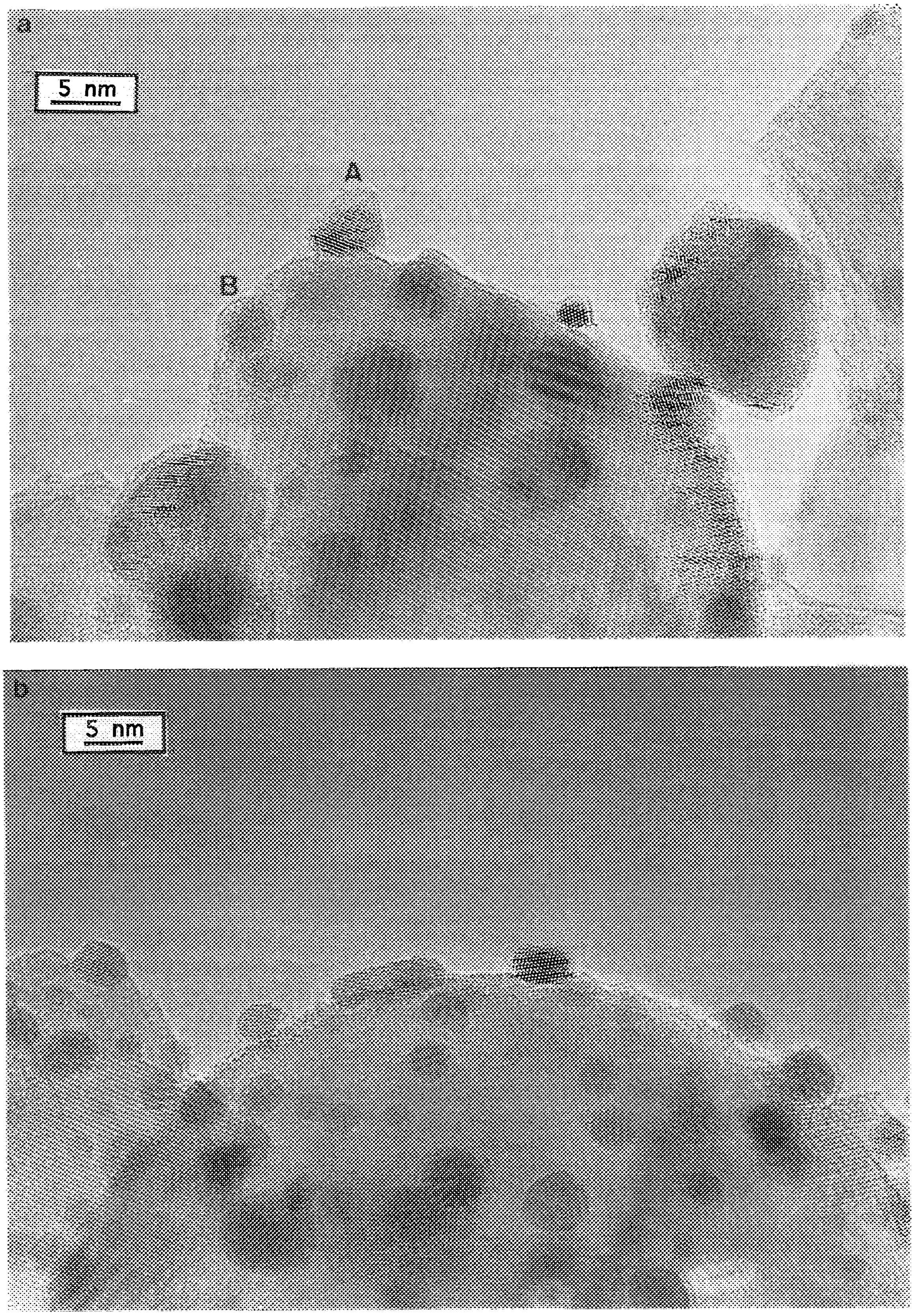

FIGURE 1

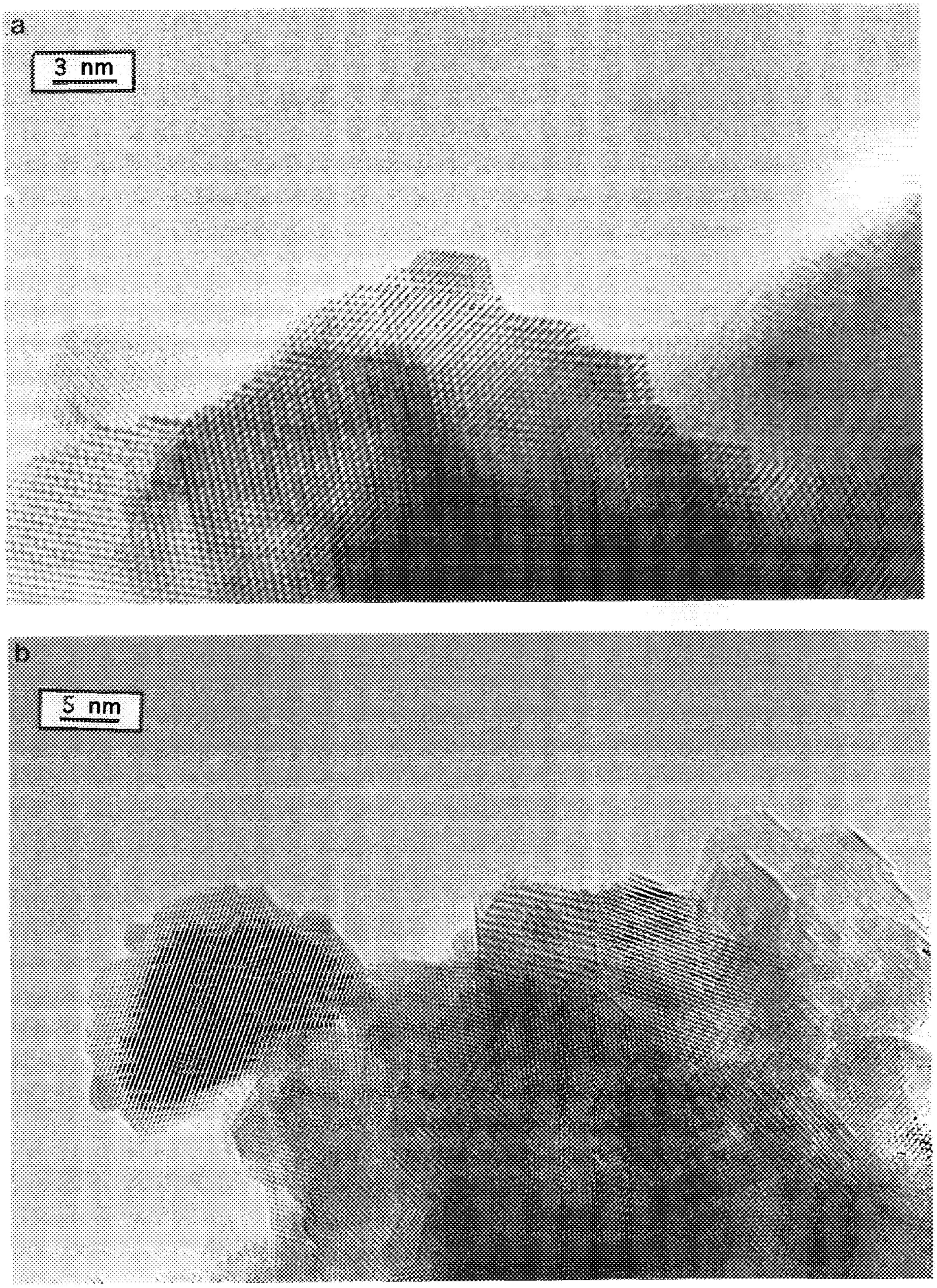

FIGURE 2

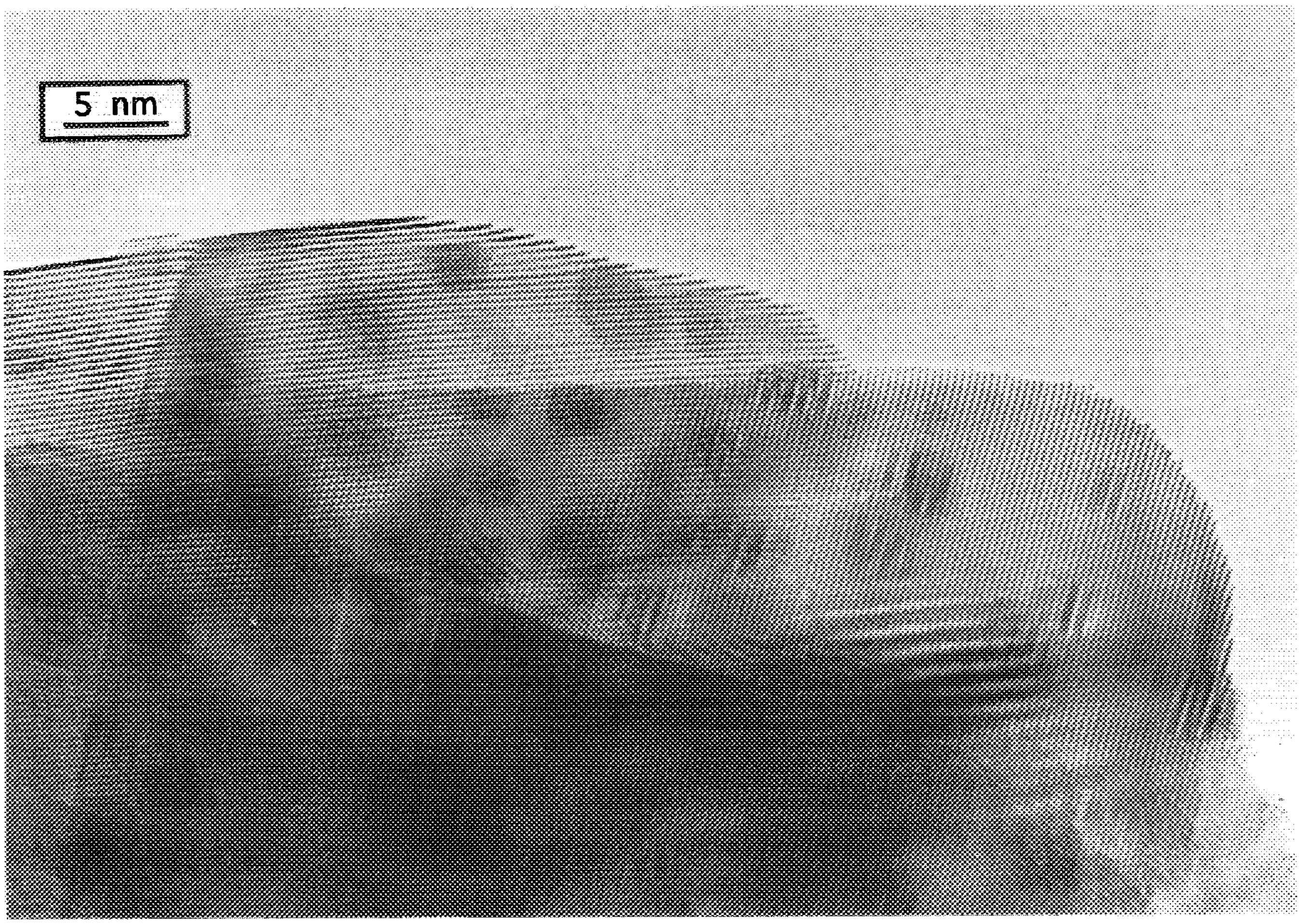

FIGURE 3

hydrogenation on Pt/CeO_2 compared with Pt/Al_2O_3 provides a clear manifestation of the role of the support interaction in modifying the behavior of the metal surface (19).

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