High resolution electron microscopy characterization of sulfided palladium particles on amorphous SiO_2

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The microstructure of palladium particles deposited on a porous silica support was examined by high resolution microscopy following various sulfidation treatments. For catalysts sulfided by the reaction itself (hydrodesulfurization of thiophene), the micrographs show large particles where an amorphous sulfide layer surrounds the Pd core; in the case of small particles, the presence of PdS_2 was identified. For catalysts sulfided under 20% H_2S/H_2 at 623 K, the particles show lattice planes compatible with PdS_2 and PdS. By increasing the sulfidation temperature to 723 K, faceted PdS particles are mostly formed. Some structural defects related to the sulfidation treatment are also shown.

Keywords: sulfidation; electron microscopy; palladium catalysts; noble metal sulfides

1. Introduction

Sulfidation of noble metal particles is involved in such important catalytic processes as reforming, selective hydrogenation and hydrodesulfurization. However, in spite of this industrial relevance, the microstructural changes that occur during the sulfidation process are still unknown to a large extent. This lack of information is mainly due to the small size of the catalytic particles, that exclude the use of X-ray diffraction techniques. Recourse to high resolution microscopy is a very appropriate technique to overcome this limitation.

The interaction of sulfur with noble metal catalysts has been studied by several authors [1–11]. Their results have generally established that the adsorption of sulfur is strong and leads to characteristic phenomena such as surface reconstruction [1–3] phase segregation [4] and selective poisoning [5–7].

In previous work [8] we performed a TEM study of palladium particles deposited on silica, which were sulfided with a H_2S/H_2 gas mixture at several temperatures. Electron microscope images showed spreading, sintering and faceting of

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particles as a function of the extent of sulfidation. Also, the thiophene HDS activity of these catalysts was such that both the reaction rate and the activation energy decreased as the degree of sulfidation increased, suggesting differences in the surface species formed at each temperature.

In order to obtain more information about the microstructural modifications of Pd particles during the sequential sulfidation treatment, high resolution electron microscopy characterization was performed on the catalysts. Image processing was used to improve the visibility of fringes and allow a better determination of lattice spacings, making phase identification possible.

2. Experimental

The experimental conditions for catalyst preparation and the sulfidation treatment have been reported elsewhere [8]. High resolution electron microscopy (HREM) was performed in a Jeol 4000 EX electron microscope (0.17 nm point-to-point resolution). Particles were examined by HRTEM at various stages of sulfidation. Bright field and atomic resolution imaging were used to determine morphology and microstructure.

Image processing by filtering in the Fourier space, as described by Artal et al. [9], was used to separate the amorphous (substrate) from the crystalline contributions, producing enhanced images where the interplanar spacing measurement was more reliable, and the structural details, more clearly visible and interpretable.

3. Results

Figs. 1a–1f show typical high resolution images of palladium particles obtained after reduction in hydrogen at 673 K. Fig. 1a shows a large particle (around 24 nm), where the lattice spacing is noticeable. In order to better estimate the interplanar spacing, a section of the image was digitized (fig. 1b), the Fourier transformed and processed to produce an image like the one shown in fig. 1c. From this picture, (111) Pd planes (0.22 nm) were easily identified. A twin, typical of this material is also seen. On the other hand, small particles (less than 3 nm) appear as single crystals as shown in fig. 1d. The (111) Pd planes are also identified, as shown in figs. 1e–1f.

Figs. 2a–2h show the particles after the catalytic test of thiophene hydrodesulfurization at 573 K was performed. Fig. 2a is a micrograph of a typical large particle where a metal core (identified by the presence of lattice fringes) is surrounded by an amorphous envelope. The contrast enhanced image shown in fig. 2c allows the determination of lattice fringes as PdS_2 (111) planes (0.34 nm). The two small particles that appear in fig. 2d have different characteristics, in contrast with the uniformity of the large particles. The particle on the left-hand side, isolated in figs. 2e

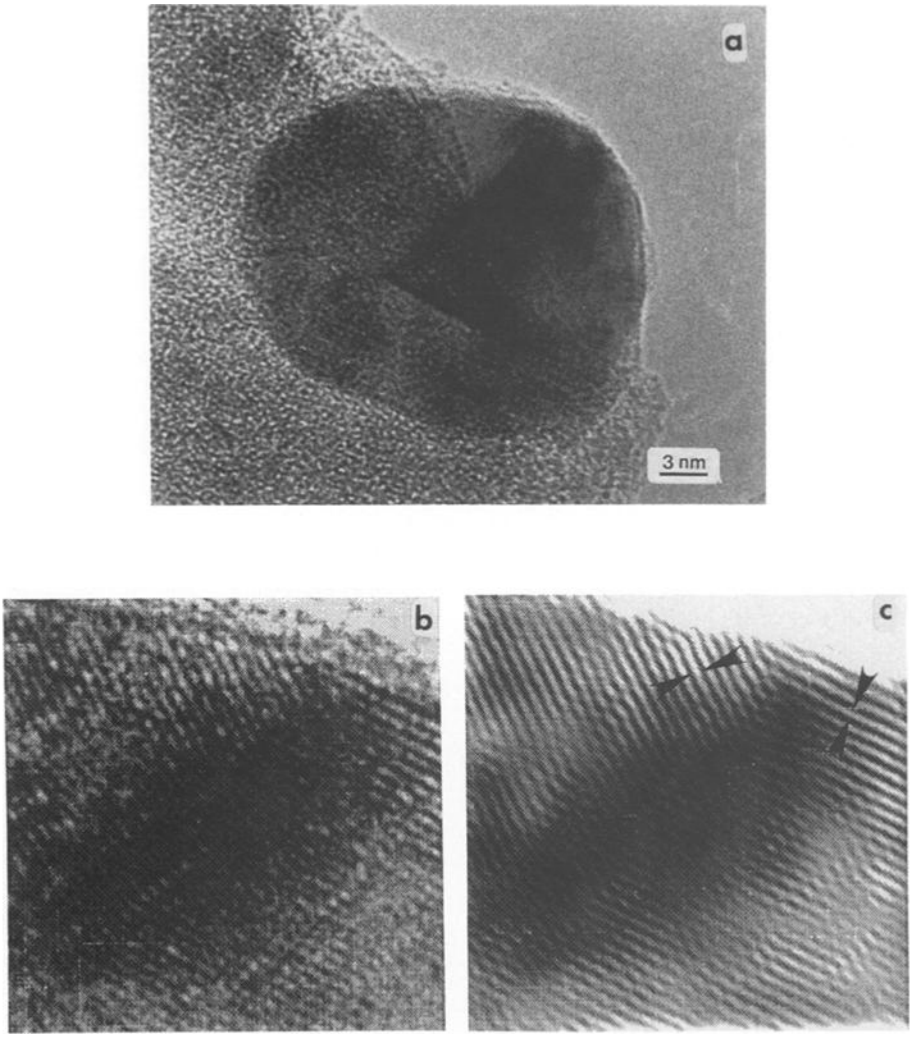

Fig. 1. (a) HREM image of a Pd/SiO_2 catalyst after reduction in hydrogen at 673 K. (b) Digitized section of the particle in (a). (c) Fourier filtered and enhanced image corresponding to (b). Markers indicate (111) Pd fringes (0.22 nm). (d) HREM of a catalyst as in (a) but showing smaller particles. (e) Digitized image. (f) Fourier filtered and enhanced image of (d). Markers indicate (111) Pd fringes (0.22 nm).

and 2f, shows an atomic resolution image of PdS_2 seen along the [101] zone axis, whereas the particle on the right-hand side, isolated in figs. 2g and 2h, shows lattice planes identified as the (200) planes of Pd (0.20 nm).

Images of particles sulfided at 623 K in 20% H_2S/H_2 are shown in fig. 3. From these images, it looks clear that the characteristic picture of a catalyst containing metal particles has drastically changed. A complex network of lattice planes dis-

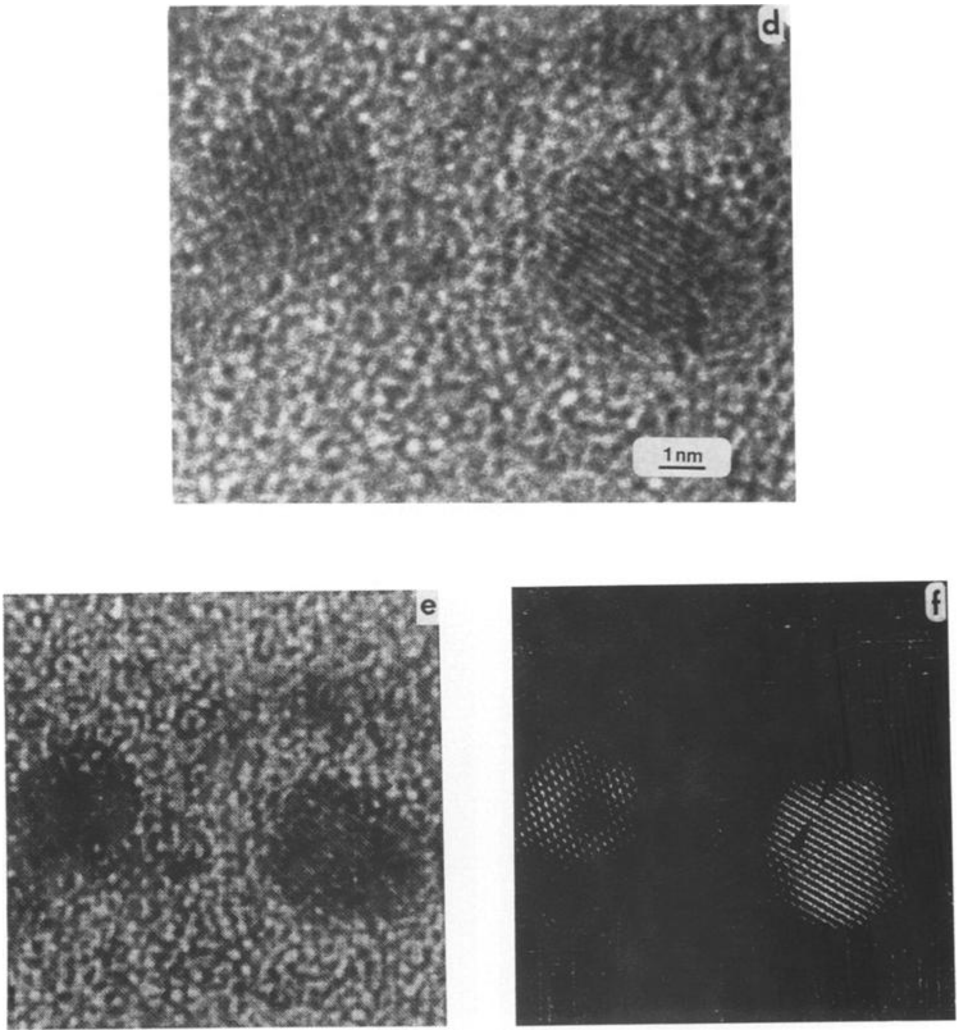

Fig. 1. (continued).

tributed throughout the surface now appears, suggesting that a broad restructuring of the material has taken place. From computer reconstructed images like those shown in fig. 3c, the following planes were identified (111), (220), (212) and (200) of PdS, along with (121), (210), (222), and (232) of PdS_2.

Finally, the microstructure of particles sulfided at 723 K is shown in fig. 4. The general appearance of this sample is similar to the sample sulfided at 623 K, with some important differences. First, the lattice spacings all belong to PdS (the PdS_2 phase is no longer observed). Second, a number of particles like the one in fig. 4b show some facets. In this case, the particle exhibits (102) and (201) PdS planes,

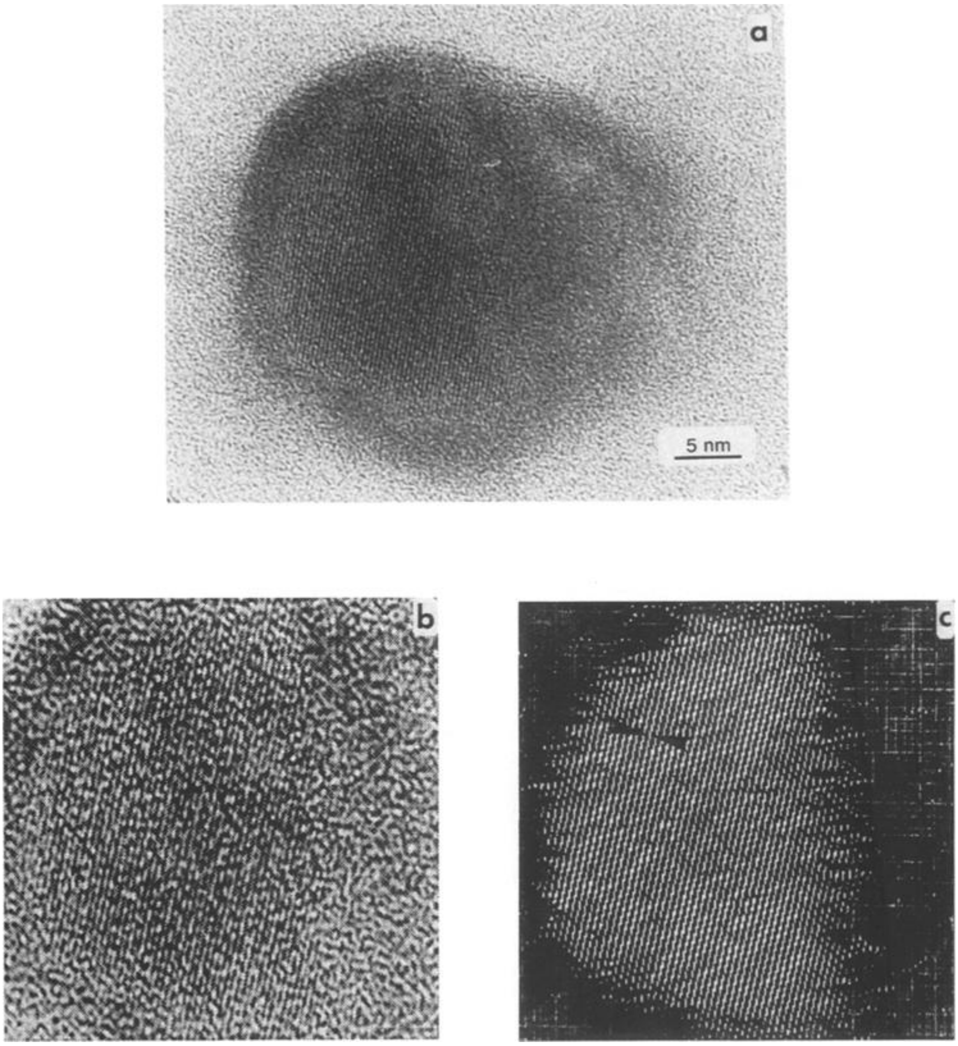

Fig. 2. (a) HREM image of the catalyst after hydrodesulfurization test. (b) Digitized portion of (a). (c) Enhanced image of (a). Markers indicate (111) PdS_2 fringes (0.34 nm). (d) HREM with the same conditions as in (a), but different area. (e, f) Left-hand side particle in (d) corresponding to PdS_2 seen along the [101] zone axis. (g, h) Right-hand side particle in (d) corresponding to (200) Pd (0.20 nm).

therefore, the particle is observed along the [010] zone axis. The defect at the center of the particle is identified as a dislocation.

4. Discussion

It has been traditionally recognized that sulfur adsorption causes restructuring of the metal surface, altering the catalytic activity of the catalyst towards structure

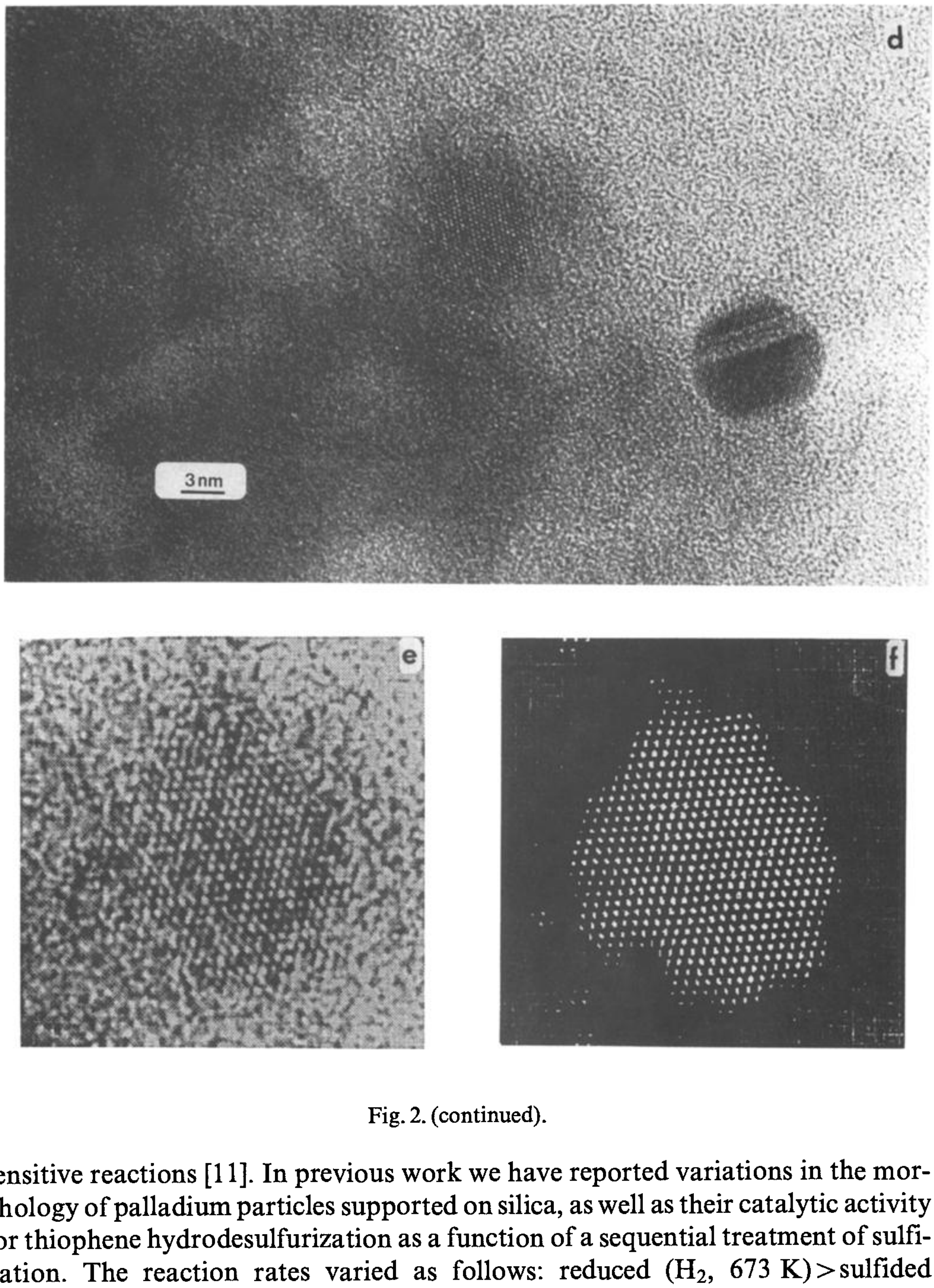

Fig. 2. (continued).

sensitive reactions [11]. In previous work we have reported variations in the morphology of palladium particles supported on silica, as well as their catalytic activity for thiophene hydrodesulfurization as a function of a sequential treatment of sulfidation. The reaction rates varied as follows: reduced (H_2, 673 K) > sulfided (523 K) > sulfided (623 K) ≈ sulfided (723 K). Characterization by TEM of model palladium catalysts exposed to the same sulfidation treatment revealed that the size and morphology of the metal particles varied. At low temperature (< 623 K) a

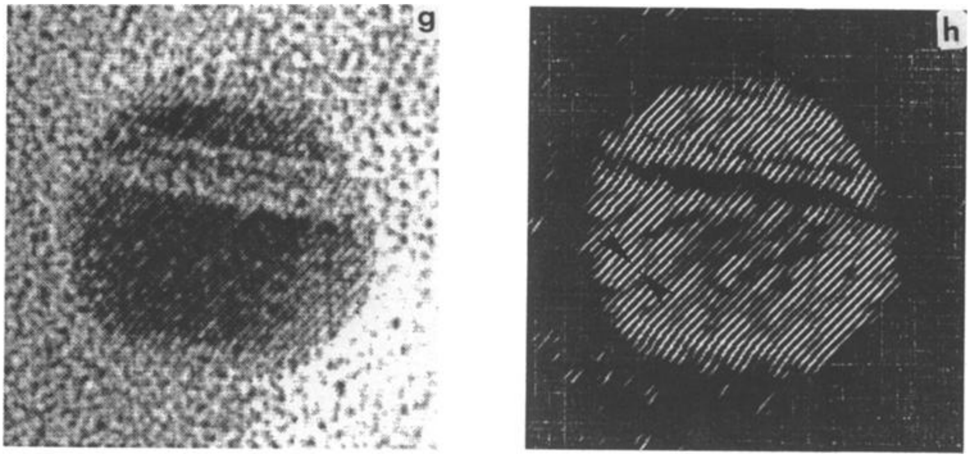

Fig. 2. (continued).

sulfide shell was formed around the particle. At higher temperatures the particles became completely sulfided and spreading and sintering of particles occurred.

In this work, HREM showed that such changes in size and morphology of the Pd particles are related to changes in structure, i.e. different sulfide phases. For reduced catalysts subjected to the catalytic reaction three cases are observed: (a) in large particles, the formation of an amorphous sulfide layer surrounding a metal core, similar to the process of sulfidation mentioned above; (b) in some small particles, the formation of PdS_2; (c) in other small particles, the persistence of Pd metal, which remains unsulfided. The occurrence of these different phases (the amorphous skin and PdS_2, in contrast with the single PdS phase predicted by thermodynamics for the Pd–H_2S system [12], indicates that the temperature–gas–time history is very important in determining the particle structure. In fig. 2d, the observation of two particles very near each other, yet having different structure (Pd and PdS_2) suggests that some planes or faces are being sulfided more rapidly than others. It is well known that sulfur is a selective poison that adsorbs preferentially at edge sites because they exhibit greater bond strength than ordered surfaces [13]. The formation of sulfided phases different from those predicted by the equilibrium has been observed for ruthenium [14] and nickel [15] particles exposed to H_2S environments. Structural differences between small and large particles may be explained assuming that sulfidation takes place by diffusion of sulfur into the inner layers of palladium, modifying the metal–metal bonds and forming an amorphous sulfide. After complete sulfidation a phase change occurs, going from the amorphous sulfide to a metastable phase like PdS_2.

For catalysts sulfided under 20% H_2S/H_2 at 523 K for 2 h, the images showed mainly PdS_2 particles with some PdS particles. These results reflect a tendency to reach equilibrium. When the temperature of sulfidation was increased to 623 K, the

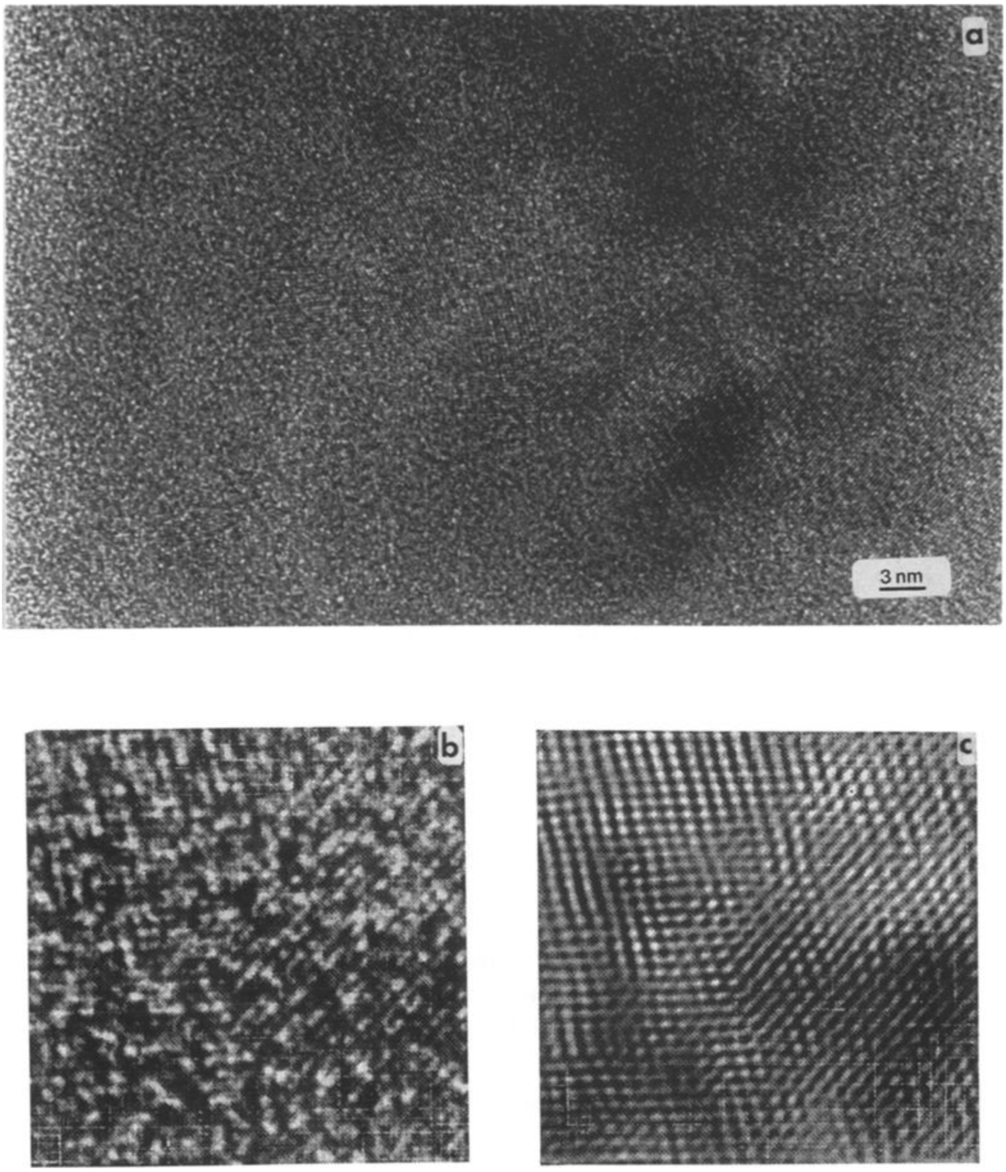

Fig. 3. (a) HREM image of catalyst after sulfidation treatment at 623 K. (b) Digitized portion of (a). (c) Enhanced image showing lattice planes barely visible in (a).

amount of PdS particles as compared to PdS_2 particles increased, while spreading of particles may account for the broadly restructured material observed. Spreading is believed to occur due to different wetting properties of sulfides as compared to metals and has been observed in rhodium and platinum sulfide particles [10].

Finally, at 723 K, the thermodynamically predicted phase was the only struc-

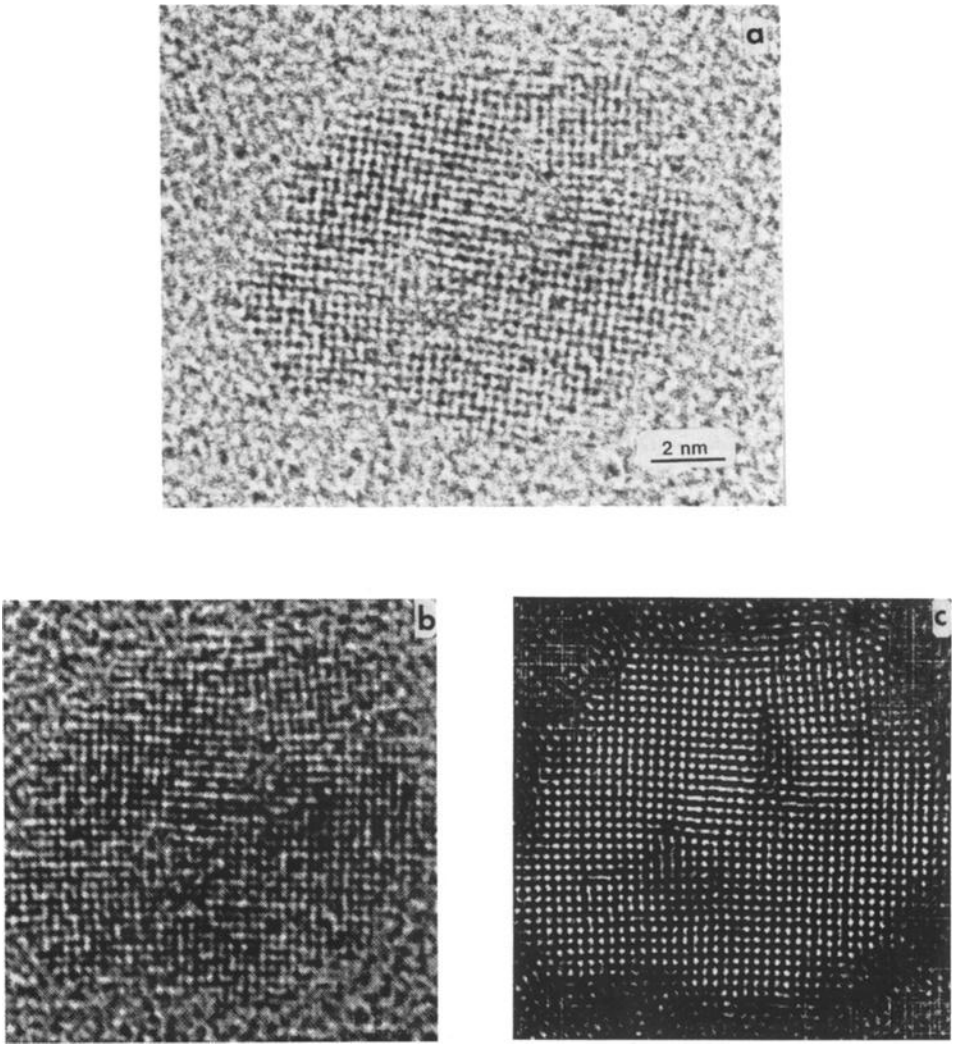

Fig. 4. (a) HREM image of catalyst after sulfidation treatment at 723 K. (b) Digitized portion of (a). (c) Enhanced image showing a PdS particle seen along the [010] zone axis.

ture observed. The morphology of particles became completely different from that of former metal particles and spreading was general throughout all the silica surface.

Faceting has been observed during the interaction of sulfur with platinum [16] and palladium–gold [4]. The driving force is a decrease of the free surface energy of metal surfaces [13]. Thus, a surface that initially has an unstable orientation develops a faceted structure with low energy planes like (100).

5. Conclusions

Results suggest that the mechanism of sulfidation of metal particles goes through a long series of consecutive steps, which include surface sulfidation, bulk sulfidation (amorphous phase), phase transition to a metastable phase and phase transition to a thermodynamically predicted stable phase. During these steps spreading and faceting can also take place. The relative contribution of these processes to the particle morphology is strongly dependent on the temperature–time–gas history of the metal–sulfur interaction.

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