Metal-support interaction in Pt/SiO_2 model catalyst studied by TEM

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Instead of “real” supported catalysts consisting of randomly oriented and irregularly shaped metal particles on high surface area porous supports, well-oriented and regularly shaped metal particles were grown on planar thin supports and the structural changes in a chemical environment during activation or reaction were characterised by electron microscopy [1-2]. In the present work, Pt particles epitaxially grown on (001) NaCl single crystals were covered with a supporting film of amorphous silica. Subsequently, the NaCl was dissolved in distilled water and the films were mounted on gold grids for electron microscopy [2]. After an oxidising treatment (O2, 673K, 1h) the samples were exposed to 1 bar H2 at 873K for 1h. Selected area electron diffraction (SAED), bright field images, microdiffraction and high-resolution images were taken by a Philips CM200 FEG microscope in order to analyse and to understand the metal-support interaction.

The as-prepared Pt particles (Fig. 1a) exhibit regular shapes and a size of 8-15 nm. After the treatment, particles consisting of two coalesced parts (denoted as A) and large particles with irregular forms (denoted as B) were observed (Fig. 1b). These particles are about 20 nm in size and randomly oriented.

The SAED patterns of the sample before and after the treatment are shown in Figs. 2a and b, respectively. Fig. 2a indicates that all the as-grown Pt particles exhibit the same orientation. Comparatively, Fig. 2b shows series of rings together with some diffuse spots. The interplanar distance values *d* (± 1%) corresponding to the rings and to the diffuse spots were calculated. Moreover, microdiffraction patterns were taken from single particles. The formation of Pt silicides Pt_3Si (cubic), Pt_3Si (monoclinic), $Pt_{12}Si_5$ (tetragonal) and was confirmed besides not reacted Pt.

Figs. 4a-d are the HREM images of the particles before and after the treatment with Fourier transforms inserted. In Figs. 4b-d, well-crystallised cubic and monoclinic Pt_3Si and $Pt_{12}Si_5$ can be seen. Pt_3Si phases were usually observed in particles with straight edges, while the large particles with round edges contain $Pt_{12}Si_5$. Therefore, a topotactic structural transformation from Pt to either cubic or monoclinic Pt_3Si has taken place. $Pt_{12}Si_5$ was possibly formed by melting and recrystallisation.

The present observations confirm the mechanisms of metal–support interaction involving the dissociative adsorption of H_2 on Pt particles and the reduction of silica [3]. In addition, we suggest that at 873 K the Pt particles become highly mobile on the reduced SiO_2 surface. This facilitates the coalescence of neighbouring Pt particles and the migration of the Si atoms into the Pt particles. On the other hand, the exothermal dissociative adsorption of H_2 on Pt particles could result in a local temperature increase. This may explain the appearance of high temperature phases of monoclinic Pt_3Si [3] and $Pt_{12}Si_5$. All the suggested processes (coalescence, melting and recrystallisation, and Si migration) lead to the observed restructuring of the as-grown half octahedral Pt particles [4].

References

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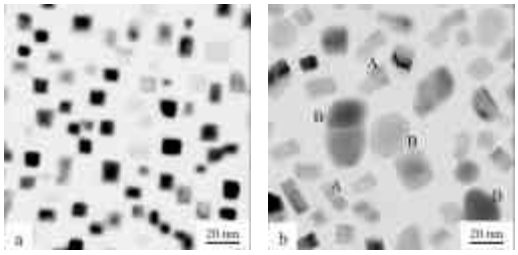

Fig. 1 TEM images of Pt supported on SiO_2 (a) before and (b) after treatment in H_2 at 873 K.

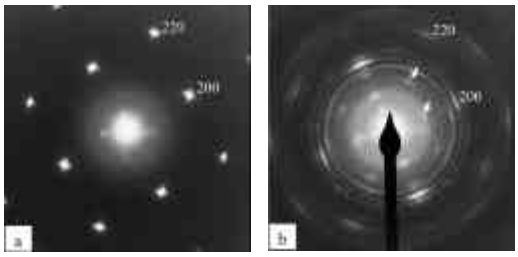

Fig. 2 SAED patterns of Pt supported on SiO_2 (a) before and (b) after treatment in H_2 at 873 K.

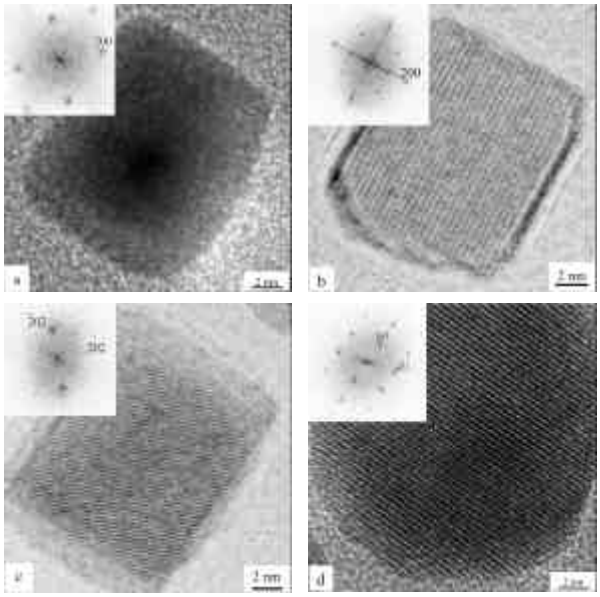

Fig. 3. HREM images of particles (a) as grown, (b) Pt_3Si with $L1_2$ structure, (c) monoclinic Pt_3Si and (d) [2,7,6] projected $Pt_{12}Si_5$, after the treatment. The corresponding Fourier transforms are inserted.