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ENCAPSULATION OF METAL PARTICLES DURING HIGH TEMPERATURE REDUCTION OF Pt AND Rh ON TiO₂ CATALYSTS

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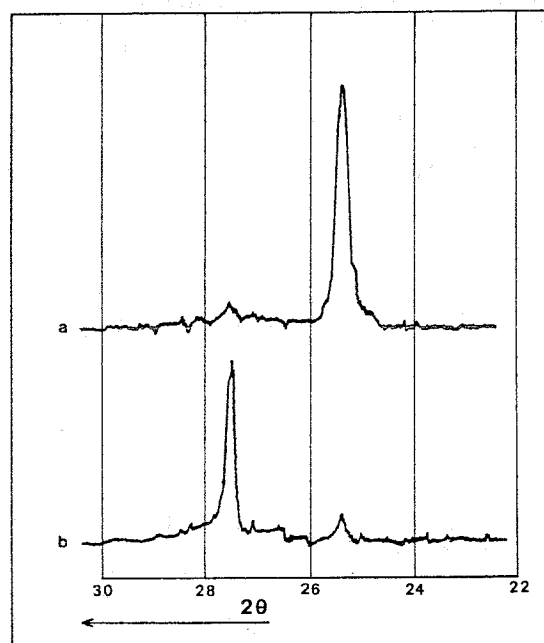
Abstract: For TiO₂ supported metal catalysts which were reduced above 1015 K a shielding of the metal particles from gases was observed, due to a phase transformation of anatase to rutile with a concurrent encapsulation of the metal particles.

The use of TiO₂ as a support in heterogeneous catalysis has attracted considerable interest after the discovery of the so-called strong metal-support interaction (SMSI). (1). Characteristic of the SMSI state is its anomalous chemisorption behaviour: When reduction treatments are carried out at progressively higher temperatures a simultaneous decrease in hydrogen and carbon-monoxide chemisorption capacities is observed, without any loss in specific metal surface area as observed by for instance electron microscopy. Chemisorption of nitrogen, however, was increased for TiO₂, Ni/TiO₂ and Rh/TiO₂ when reduced at 773 K (2,3). It has been suggested by several authors (4,5) that a reduction of the support, initiated by the catalytic properties of the supported metals, could play a decisive role in the SMSI behaviour.

In this communication results are presented obtained when TiO₂-supported metal catalysts are reduced at temperatures above 1015 K. A catalyst containing 4.1% Pt was prepared by means of a combined ion exchange and wet impregnation method (5), while a 3.2% Rh/TiO₂ catalyst was prepared by the standard pore volume impregnation method. The support used in both cases was anatase (Tioxide CLDD 1367) with a surface area of 50 m²g⁻¹ and a pore volume of 0.9 cm³g⁻¹. After reduction in flowing hydrogen at 570 K H/Pt and H/Rh values of respectively 0.65 and 0.37 were found. After reduction at 773 K these values decreased to near zero in both cases. The SMSI could be destroyed by an oxidative treatment,

followed by reduction at low temperature e.g. 573 K. When reduction temperatures at 1015 K or higher were used again no hydrogen chemisorption could be observed, but in this case oxidation followed by low temperature reduction did not restore the normal chemisorption properties of the supported metals. X-ray diffraction and XPS measurements shed more light on this behaviour.

In figure 1 the X-ray diffraction patterns of Rh/TiO₂ reduced at 973 and 1073 K are presented.



X-ray diffraction patterns (Cu-K α radiation)
1a : Rh/TiO₂ reduced at 973 K, passivated
1b : Rh/TiO₂ reduced at 1073 K, passivated

In the diffraction pattern no peaks due to metallic rhodium could be observed. It is clear that the high temperature reduction converts the anatase ($2\theta = 25.4^\circ$) to the more stable rutile phase ($2\theta = 27.6^\circ$). As might be expected this phase transformation brings about a strong decrease in the specific surface area of the support from $50 \text{ m}^2 \text{ g}^{-1}$ to $1 \text{ m}^2 \text{ g}^{-1}$. Measurements on the pure support demonstrated that the phase transformation was catalysed by the metal.

In figure 2 X-ray photoelectron spectra (Mg K α radiation) are presented of Rh/TiO₂ catalysts which had been reduced and subsequently exposed to air at 20°C (passivated). The spectrum of the sample reduced at low temperature shows two bands (Rh 3d_{3/2} and 3d_{5/2}), both of which consist of a main peak at lower binding energy and a shoulder at a somewhat higher binding energy (fig. 2a). The lower binding energy peaks (307 and 312 eV) are due to metallic rhodium and the shoulders around 309 and 314 eV are due to an oxidized form of rhodium. Apparently after the low temperature reduction oxygen can easily oxidize part of the rhodium. Most likely this oxidation (or corrosive chemisorption) takes place at the outermost regions of the metal particles (6,7). Figure 2b shows that after high temperature reduction and subsequent admission of oxygen only the Rh 3d_{3/2} and 3d_{5/2} metal peaks are present. Thus oxygen cannot oxidize the rhodium particles anymore. In agreement

with this conclusion temperature programmed reduction and oxidation studies demonstrated that after reduction above 1015 K hardly any hydrogen or oxygen consumption could be observed. A completely parallel behaviour was observed for Pt/TiO₂.

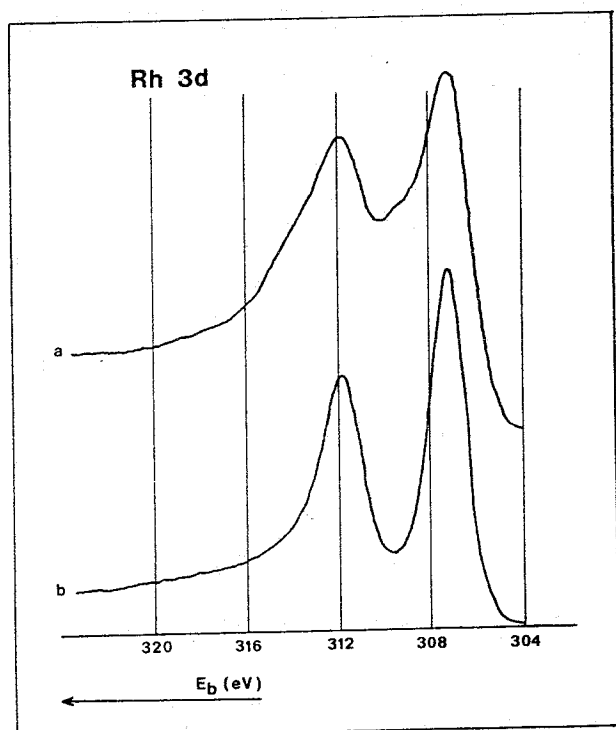
The XPS, TPR and chemisorption measurements prove that after prereduction at very high temperatures Pt and Rh on TiO₂ are in the metallic phase, but inaccessible to gases. The XRD and surface area measurements demonstrate that this same treatment causes a phase transformation of the support and a strong reduction in surface area. This strongly suggests that the shielding of the metal particles is due to encapsulation during the phase transformation of anatase to rutile. From the fact that the reduction at temperatures above 1015 K leads to a complete phase transformation and is catalyzed by the metal one might infer that at somewhat lower temperature mobility of the support might exist around the metal particles. An enhanced support mobility could cause a reversible covering of the metal particles, thereby explaining the SMSI phenomena. Further studies are in progress.

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Rh 3d XPS spectra of Rh/TiO₂ catalysts

2a : Rh/TiO₂, reduced at 573 K, passivated

2b : Rh/TiO₂, reduced at 1073 K, passivated