New evidence for the electronic nature of the strong metal-support interaction effect over a Pt/TiO$_2$ hydrogenation catalyst

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Analysis of the Pt 4*f* line asymmetry evidenced that the suppression of the hydrogenation activity of Pt/TiO$_2$ in the SMSI state is caused by a decrease in the *d*-electron density at the Fermi level of platinum particles, while the net charge of the metal particles remains unaltered.

Interest in the effect of strong metal-support interaction (SMSI) in M/TiO$_2$ systems (M = Pt, Rh, Pd, Ni, *etc.*) has increased since 1980 because the performance of these catalysts can change dramatically depending on the reduction temperature.[1] Despite intensive research efforts directed toward the elucidation of the nature of this phenomenon, its mechanism remains unclear. Several hypotheses have been proposed including encapsulation of metal particles by the support material or alteration of their electronic properties.[2–7]

In this study, we used a new method for the evaluation of the electronic state of supported metal particles. This method is based on the analysis of the lineshape asymmetry in the XPS spectra of the metal.[8] The importance of this parameter for studying the electronic state of supported metal clusters stems from the fact that the asymmetry of an XPS line is a function of the density of *d*-electrons at the Fermi level.[9] Taking into account that *d*-electrons are deeply involved in the catalytic conversion over metals, an analysis of the XPS line asymmetry may provide a new insight into the relation between the electronic structure of supported metals and their catalytic performance. Therefore, the aim of this study was to find a relationship between variations in the catalytic activity and the electronic state of metal particles upon transition of the Pt/TiO$_2$ catalyst between the SMSI and non-SMSI states.

In order to minimise experimental uncertainties resulting from possible phase transitions in the carrier material and from variations in the dispersion of platinum, a 3 wt% Pt/TiO$_2$ catalyst supported on high-purity rutile type TiO$_2$ with a narrow particle-size distribution was used. The catalyst was prepared by impregnation of TiO$_2$ (95 m^2 g^{-1}) with an aqueous solution of H$_2$PtCl$_6$ (Aldrich, 99.995%) followed by drying and calcination at 500 °C. The removal of residual chlorine was monitored by XPS.

After calcination, the catalyst samples were reduced in a hydrogen flow at 200 and 500 °C, and the particle size of platinum was estimated by transmission electron microscopy (EM-125 electron microscope operated at 75 kV) and from X-ray diffraction line broadening. The X-ray diffraction line broadening gave a particle size of ~6.0 nm for both samples, which is in a good agreement with the estimates on the basis of XPS data (see below). The TEM data also ensured the absence of bigger platinum particles (>10 nm) in both samples.

Table 1 Variations of the Pt 4$f_{7/2}$/Ti 2$p_{3/2}$ atomic ratio, Pt particle size, and binding energies (BE) of Pt 4$f_{7/2}$ and Ti 2$p_{3/2}$ lines with the reduction temperature.

Pre-treatment	Pt 4$f_{7/2}$/Ti 2$p_{3/2}$ intensity ratio	Particle size of Pt/nm[a]	Pt 4$f_{7/2}$ BE/eV	Ti 2$p_{3/2}$ BE/eV
H$_2$, 200 °C	0.015	5.7	70.9	458.9
H$_2$, 500 °C	0.013	6.5	70.8	458.9
O$_2$, 200 °C + H$_2$, 200 °C	0.013	6.5	70.8	458.8
H$_2$, 300 °C	0.014	6.1	70.7	458.9
H$_2$, 400 °C	0.013	6.5	70.8	458.9
H$_2$, 500 °C	0.013	6.5	70.7	458.8

[a]Calculated from XPS data using the Kerkof model.[5]

X-ray photoelectron spectra were obtained using an XSAM-800 spectrometer (Kratos) with AlK$\alpha_{1,2}$ radiation for spectra excitation. The binding energies of peaks were corrected with account of sample charging by referencing to the C 1*s* peak at 285.0 eV. The Pt/Ti surface atomic ratio was calculated from the integral intensities of XPS peaks using the Scofield photoionization cross-sections for AlK$\alpha_{1,2}$ excitation.[10] The particle size of Pt was calculated from the Pt 4*f* /Ti 2*p* intensity ratio using the Kerkof ‘stacking sheets’ model.[11] Reductive and oxidative pretreatments were performed using a home-made reactor attached directly to the analytical chamber of the spectrometer.[12] The samples were treated in flowing H$_2$ and O$_2$ and transferred to the spectrometer without exposure to ambient air.

A Pt foil was cleaned using a standard procedure[13] of several cycles of sputtering with Ar ions (2 kV, 0.25 μa, $t \sim 30$ min) followed by heating in oxygen ($p_{O_2} = 6\times10^{-5}$ mbar, $t = 45$ min). Surface contaminations were below the detection limits of XPS.

The spectra were analysed by a curve fitting procedure using the Doniach–Sunjic function[14]

$$I(\varepsilon) \cong \frac{\Gamma(1-\alpha)}{(\varepsilon^2+\gamma^2)^{(1-\alpha)/2}}\cos[0.5\pi\alpha + \theta(\varepsilon)], \tag{1}$$

$$\theta(\varepsilon) = (1+\alpha)\tan^{-1}(\varepsilon/\gamma), \tag{2}$$

where ε is the kinetic energy of the photoelectrons, Γ is the gamma-function, γ is the lifetime width of the core hole created as a result of photoemission and α is the line asymmetry parameter.

The function was convoluted with a Gaussian curve for taking into account an experimental broadening (instrumental resolution, sample inhomogeneity, *etc.*).

Kinetic investigations of toluene hydrogenation activity under stationary conditions were carried out in a gradientless flow-cir-

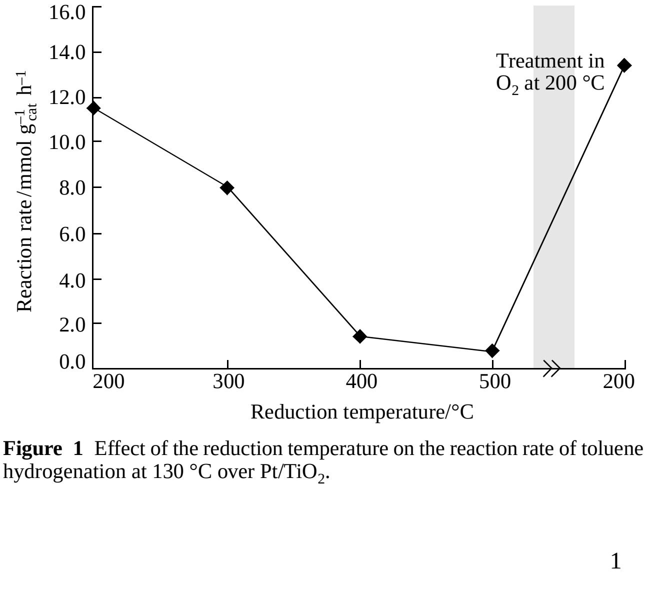

Figure 1 Effect of the reduction temperature on the reaction rate of toluene hydrogenation at 130 °C over Pt/TiO$_2$.

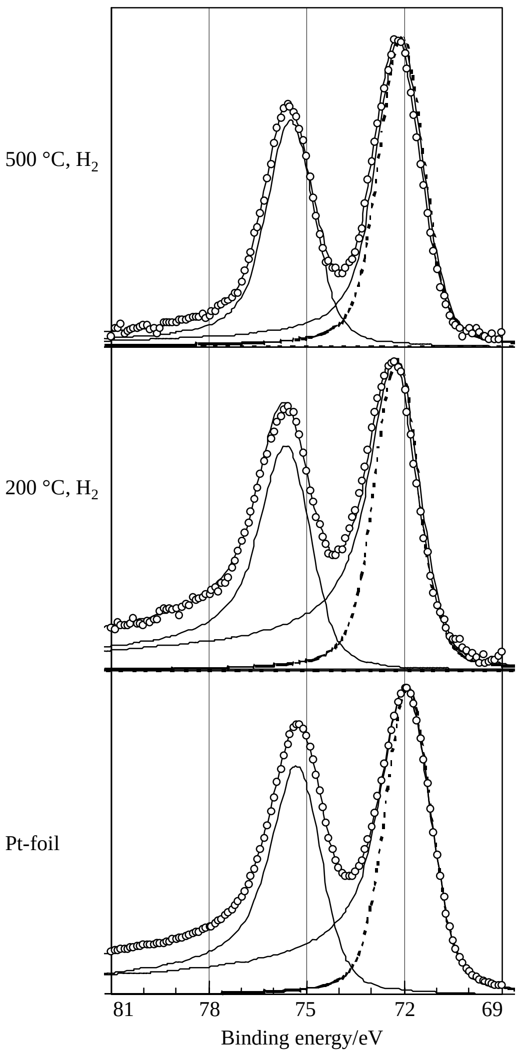

Figure 2 XPS spectra and the results of the curve-fitting analysis of the Pt 4*f* line in Pt/TiO$_2$ after reduction at 200 and 500 °C and in Pt foil. Dotted lines correspond to the Pt 4*f* line with $\alpha = 0$ and are shown for comparison.

culation system at atmospheric pressure with the on-line gas-chromatographic analysis of the reaction products. The reaction rates were measured at low conversions at 130 °C and $P_{C_7H_8}/P_{H_2} = 0.004$.

The dependence of the rate of toluene hydrogenation on the reduction temperature is depicted in Figure 1. The reaction rate abruptly decreases with increasing reduction temperature above 300–400 °C. However, the oxidation of the catalyst reduced at 500 °C in O$_2$ at 200 °C followed by the reduction at 200 °C completely restores the activity.

It was found that the oxidation–reduction cycles could be repeated five times without appreciable changes in the reaction rates. Clearly, the catalyst demonstrates the behaviour typical of reversible transition between non-SMSI and SMSI states.

The XPS spectra of the Pt 4*f* line (Figure 2) indicated that the binding energy of the Pt 4*f* line in the catalyst reduced at 200 °C is higher by ~0.4 eV as compared to the position of the Pt 4*f* line of platinum foil, which is typical of supported metals. The curve fitting analysis of the line shape reveals a very similar value of the Pt 4*f* line asymmetry α for platinum foil and Pt/TiO$_2$ reduced at 200 °C.

The reduction at 500 °C does not affect the position of the Pt 4*f* line (Figure 2, Table 1). However, it leads to the pronounced narrowing of the line (Figure 2). Note that, after reduction at 500 °C, the Pt 4*f* line becomes narrower than that in Pt foil, which is unexpected for supported metal. The curve fitting analysis demonstrates that the narrowing resulted from a significant decrease in the asymmetry parameter α (Figure 2).

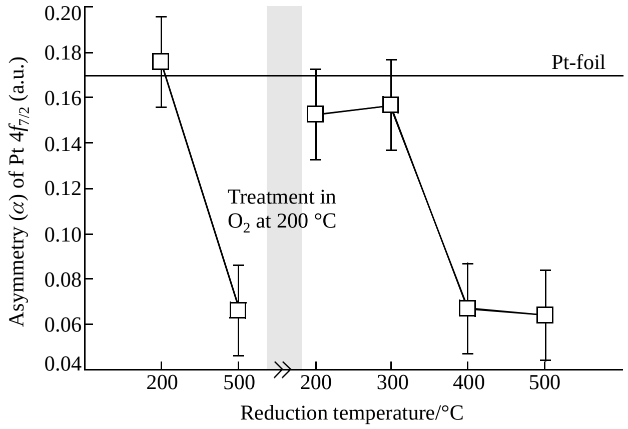

Figure 3 Dependence of the Pt 4$f_{7/2}$ line asymmetry (α) on the reduction temperature.

The dependences of the catalytic activity (Figure 1) or the Pt 4$f_{7/2}$ line asymmetry (Figure 3) on the reduction temperature reveals a good correlation between these parameters. An increase in the reduction temperature results in a simultaneous decrease in the catalytic activity and in the α value. On the other hand, the oxidation of the deactivated catalyst followed by the reduction at 200 °C completely restores the activity and the α value.

The above data allowed us to interpret the observed effect. Two main mechanisms were proposed for the explanation of changes in the catalytic performance of the catalyst in the SMSI state. One mechanism implies the decoration or encapsulation of metal particles with the support material species. The other mechanism assumes the alteration of the electronic properties of the metal particles due to their interaction with defects on the support surface created in the course of high-temperature treatment.

However, the Pt 4*f*/Ti 2*p* atomic ratio remained almost unchanged upon the treatments (Table 1). Therefore, we can presume that the decoration or encapsulation of the metal particles with the support moieties seems not to be the governing factor of the catalytic performance. The constancy of the Pt 4*f*/Ti 2*p* intensity ratio also implies the absence of any pronounced sintering of metal particles (Table 1).

On the other hand, a decrease in the catalytic activity is consistent with the changes of the electronic state of the metal particles deduced from the variations of the Pt 4*f* line asymmetry. The decrease in the line asymmetry is presumably caused by a decrease in the local density of a *d*-state at the Fermi level. In turn, the structure of the *d*-band is the crucial factor determining the reactivity of metal surface.[15,16] This allows us to suggest that the strong metal–support interaction can result in the lowering of the density of *d*-electrons on the Fermi level of the metal particle, thus decreasing the overall activity of the catalyst.

It is noteworthy that the Pt 4$f_{7/2}$ line asymmetry in the SMSI catalyst ($\alpha = 0.06$) becomes close to that for Au ($\alpha = 0.03$ for Au 4$f_{7/2}$). The *d*-electron density of states for gold is low, which is in a good agreement with the low catalytic activity of Au in the reaction requiring the activation of H–H, C–H or C–C bonds.

Thus, the results of this study indicate that the strong metal–support interaction induced by the high-temperature reduction presumably decreases the density of *d*-electrons at the Fermi level thus suppressing the activity of metal clusters. Another important finding is that the interaction between a metal particle and the support may affect the distribution of *d*-electrons in the metal cluster and change its catalytic performance, while the net charge of the particle remains nearly constant.

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