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LETTERS

The Structure of a Rh/TiO₂ Catalyst in the Strong Metal–Support Interaction State As Determined by EXAFS

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(Received: February 7, 1986)

Reduction of a highly dispersed 2.85 wt % Rh/TiO₂ catalyst at 473 K after previous calcination at 623 K resulted in EXAFS whose primary contributions are due to nearest rhodium (average coordination number of 3.1 and distance of 2.67 Å) and oxygen neighbors (coordination 2.5 and distance 2.71 Å). These oxygen neighbors originated at the metal–support interface. The average rhodium–rhodium coordination number did not change in the SMSI state produced by reducing the catalyst at 673 K. However, the average coordination distance contracted by 0.04 Å with an accompanying decrease of the Debye–Waller factor of the Rh–Rh bond of 0.0012 Å². This is due to the fact that in the SMSI state the surface of the metal particles is not covered with chemisorbed hydrogen. The SMSI state leads to a structural reorganization of the support in the vicinity of the rhodium metal particles. This can be concluded from the appearance of a Rh–Ti bond at 3.42 Å in the SMSI state coupled with the fact that the average coordination number of the rhodium–support oxygen bonds does not increase. Other types of rhodium–oxygen bonds could not be detected with EXAFS in this state. Thus, these results provide no evidence for coverage of the metal particle by a suboxide of TiO₂ in the SMSI state.

Introduction

High-temperature reduction drastically diminishes the capacity of TiO₂-supported metal particles to adsorb H₂ or CO. Since this suppression was first accredited to an interaction between the metal and the support, it was called the strong metal–support interaction (SMSI). Several models have been proposed to explain SMSI, such as alloy formation,¹ the electronic influence of a suboxide of TiO₂ beneath the metal particles,² and covering of the metal

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TABLE I: Fourier Transform Ranges of Reference Compounds and Crystallographic Data

<table>
<thead>
<tr>
<th>ref</th>
<th>compd</th>
<th>$k^*$</th>
<th>$\Delta k^*$, Å$^{-1}$</th>
<th>$\Delta R$, Å</th>
<th>$R_{1/2}$, Å</th>
<th>$N_{ref}$</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>R.</td>
<td>Rh foil</td>
<td>$k^2$</td>
<td>2.68-24.4</td>
<td>1.5-3.05</td>
<td>0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R.</td>
<td>RhO$_3$</td>
<td>$k^1$</td>
<td>2.7-18</td>
<td>0-2.05</td>
<td>2.05</td>
<td>6</td>
<td>12</td>
</tr>
<tr>
<td>R.</td>
<td>RhTi alloy</td>
<td>$k^1$</td>
<td>2.79-12.5</td>
<td>0-3.12</td>
<td>2.676</td>
<td>8</td>
<td>13</td>
</tr>
</tbody>
</table>

*Fourier transformation after subtraction of a calculated Rh-Rh EXAFS (N = 4, R = 2.949 Å, $\Delta k^2 = 0.006$ Å$^{-2}$) from experimental data.

particles by a suboxide of TiO$_2$ after a reduction at high temperature. Extended X-ray absorption fine structure (EXAFS) is an excellent tool to investigate local structure around a metal atom in a catalyst. Recently, the existence of 2.7-Å Rh-O (Rh-O$_2$ support) bonds in the metal-support interface in highly dispersed Rh/Al$_2$O$_3$ catalysts has been reported. Similar Rh-O bonds were found in a Rh/TiO$_2$ catalyst reduced at 473 K.

Here we present an EXAFS study of a 2.85 wt % Rh/TiO$_2$ catalyst after low (non-SMSI) and high temperature (SMSI state) reduction in order to make a careful study of the structural changes between the two states. The catalyst was very highly dispersed, which is vital for this type of study since only metal atoms in the interface will be sensitive to effects due to the support and only metal atoms on the surface will be sensitive to effects due to coverage.

Experimental Section

A 2.85 wt % Rh/TiO$_2$ catalyst was prepared by ion exchange using Rh(NO$_3$)$_3$ and anatase (130 m$^2$ g$^{-1}$, 0.63 mL g$^{-1}$). After adsorption, the catalyst was dried overnight at 383 K, subsequently calcined for 2 h at 623 K, and stored for further use. The dried and calcined catalyst was pressed into a thin self-supporting wafer and mounted in an in situ EXAFS cell. The thickness of the wafer was chosen to give $\mu$/x $\approx$ 2.5 at the rhodium K-edge. The reduction was carried out under flowing H$_2$ for 2 h at 473 K with the temperature being increased at a rate of 2.5 K min$^{-1}$. The sample was then cooled to room temperature under flowing H$_2$, and EXAFS spectra were recorded at 90 K with the catalyst exposed to 1 atm of static hydrogen. The same procedure was applied for the subsequent reduction at 673 K.

The EXAFS spectra of the rhodium K-edge were recorded in situ on X-ray beam line 1-5 at the Stanford Synchrotron Radiation Laboratory (SSRL) with a ring energy of 3 GeV and ring currents applied for the subsequent reduction at 673 K.

The high-quality raw EXAFS spectra for the sample reduced at 473 and 673 K are shown in Figure 1, a and d, respectively. Before Fourier transformation the raw experimental data were smoothed by a cubic spline background subtraction. Normalization was performed by division to the height of the edge. Reference compounds which were used to obtain phase and backscattering functions were analyzed in the same way as the catalyst samples.

Figure 1. (a, d) Rh K-edge EXAFS data for the normal (473 K reduction) (a) and SMSI state (673 K reduction) (d) of the 2.85 wt % Rh/TiO$_2$ catalyst. (b, e) Magnitude of the Fourier transform of the EXAFS data of the normal (b) and SMSI state (e). The transforms were taken by using $k^2$ weight over a range of 4-10 Å$^{-1}$ and are corrected for the Rh-Rh phase and amplitude. (c, f) Comparison of the imaginary parts of the Fourier transform of the experimental (solid lines) and calculated (dashed lines) data. (c) The normal state is compared with a calculated Rh-Rh + Rh-O spectrum. (f) The SMSI state is compared with a calculated Rh-Rh + Rh-O + Rh-Ti spectrum.

Table I gives the crystallographic data and Fourier transform ranges of the reference compounds.

The magnitudes of the $k^2$-weighted Fourier transforms of the experimental data obtained after reduction at 473 and 673 K are displayed in Figure 1, b and e, respectively. Before Fourier transformation the raw experimental data were smoothed by removing noise (harmonic numbers higher than 200) via Fourier filtering. The Fourier transforms are corrected for the Rh-Rh phase shift and backscattering amplitude. Reliable data for phase and backscattering amplitude have been obtained from EXAFS measurements on rhodium foil. If only a single rhodium coordination shell was present, the Rh-Rh phase and amplitude corrected Fourier transform should have shown one single symmetrical peak whose maximum was at the proper Rh-Rh distance. Clearly, in both EXAFS spectra there are other contributions present. To separate these contributions from the dominant Rh-Rh contribution and to determine their structural parameters, the difference file technique and the use of phase and/or amplitude corrected Fourier transforms have been applied. These data analysis procedures have been extensively described in ref 5 and

TABLE II: Structural Parameters* Obtained from the EXAFS Analysis

<table>
<thead>
<tr>
<th></th>
<th>Rh-Rh</th>
<th></th>
<th></th>
<th>Rh-O</th>
<th></th>
<th></th>
<th>Rh-Ti</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
<td>$R$, Å</td>
<td>$\Delta r^2 \times 10^3$, Å²</td>
<td>N</td>
<td>$R$, Å</td>
<td>$\Delta r^2 \times 10^3$, Å²</td>
<td>N</td>
<td>$R$, Å</td>
</tr>
<tr>
<td>$T_{\text{red}} = 473$ K</td>
<td>3.1</td>
<td>2.67</td>
<td>5.0</td>
<td>2.5</td>
<td>2.71</td>
<td>0</td>
<td>2.67</td>
<td>2.2</td>
</tr>
<tr>
<td>$T_{\text{red}} = 673$ K</td>
<td>3.3</td>
<td>2.63</td>
<td>3.8</td>
<td>2.1</td>
<td>2.67</td>
<td>2.2</td>
<td>2.65</td>
<td>3.0</td>
</tr>
<tr>
<td>estd error</td>
<td>±0.3</td>
<td>±0.01</td>
<td>±0.2</td>
<td>±0.5</td>
<td>±0.02</td>
<td>±1</td>
<td>±0.5</td>
<td>±0.02</td>
</tr>
</tbody>
</table>

*N = average number of neighbors. $R = $ average coordination distance. $\Delta r^2 = $ the Debye-Waller factor relative to the reference compound.

Figure 2. A comparison of the magnitudes and imaginary parts of the Fourier transforms of the difference files for the normal (a) and SMSI (b) states. The transforms are $k^2$-weighed, corrected for Rh-O phase, and taken over a range of 4-9 Å⁻¹. Also shown as dotted curves are the imaginary parts of the Fourier transforms of the calculated spectra for Rh-O (a) and Rh-O + Rh-Ti (b).

The best two-shell fit in k space was obtained using one Rh-O and one Rh-Ti contribution. The structural parameters which led to the best agreement between the calculated Rh-O + Rh-Ti EXAFS function and the difference spectrum both in k space and in r space between their corresponding Fourier transforms are summarized in Table II. Figure 2b shows that the imaginary parts of both transforms are very similar. Within the region for back-transformation again, small differences in the regions of 1.4-2.2 Å and 3.6-4.2 Å can be seen.

The amplitude of the calculated Rh-O and Rh-O + Rh-Ti EXAFS functions can be best compared with those of the calculated Rh-Rh and the experimental EXAFS data by transforming all functions under identical conditions. The magnitudes and imaginary parts of these transforms are displayed in Figure 3, a,c and b,d, respectively. The imaginary parts show clearly that by adding the different contributions interferences are created which give peaks in the magnitude of the resulting transform (dashed curve) at positions different from those of the individual components.

The agreement between the calculated Rh-Rh + Rh-O ($T_{\text{red}} = 473$ K) and Rh-Rh + Rh-O + Rh-Ti ($T_{\text{red}} = 673$ K) EXAFS functions and the corresponding experimental data can be seen in Figure 1, c and f, where the imaginary parts of the two corresponding EXAFS functions are plotted for both reduction temperatures. It can be seen that almost all features of the experimental data are reproduced by the calculated EXAFS functions. Still detectable but small differences can be noticed which correspond to those found for the difference files (see Figure 2a,b).
given in Table 11. The average Rh-Rh coordination number of
R.

The coordination number of the particles of five metal atoms, four of which are in contact with
tetrahedral sites are occupied by Ti$^{4+}$ ions.\(^{(16)}\) The following structural
model can now be derived based on the Rh$_3$Ti coordination.\(^{(15)}\) Since we found no evidence for
coverage of the metal particle that closely resembles a shear plane in Ti$_4$O$_7$. Surprisingly, in
these results there is no evidence for coverage of the metal particle with a suboxide of TiO$_2$, the model that has been generally ac-
cepted during the past years as the origin for the anomalous properties of the metal particle.\(^{(3)}\) Since we found no evidence for
alloy formation as well, we feel that the special, probably electronic
properties of this suboxide are responsible for the SMSI state. To clarify this, however, more research will have to be done. The results of such research and of a more detailed analysis of the
spectra discussed here will be the subject in a more extensive
publication.

**Acknowledgment.** This work was done at SSRL (Stanford University), which is supported by the Department of Energy, The National Science Foundation, and the National Institutes of Health. We gratefully acknowledge the assistance of the SSRL staff and the assistance of Dr. Gajardo and Dr. Michel in the preparation and characterization of the catalyst. This study was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO). D.C.K. thanks ZWO for supplying a travel grant (R71-34).

**Registry No.** Rh, 7440-16-6; TiO$_2$, 13463-67-7; H$_2$, 1333-74-0.

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