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CATALYST STRUCTURE STUDIED BY A LABORATORY EXAFS FACILITY: Ru/Al₂O₃

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A laboratory EXAFS spectrometer is described which features the utilization of higher order reflections from curved dispersing crystal. With this spectrometer a sufficient performance for structural analyses are obtained in the high energy region up to about 25 keV. It was applied to structurally characterize two kinds of Ru/Al₂O₃ catalysts, prepared from RuCl₃ and Ru₄(CO)₁₂, by the Ru K EXAFS combined with H₂ adsorption and EM observations. It was found that Ru metal particles of different sizes were formed depending on the starting material and the procedure. In the catalyst prepared from Ru₄(CO)₁₂, small metal particles, possibly consist of about 20 atoms, are formed. They are small enough to show a contraction of the nearest neighbor distance by 0.06 Å.

1. INTRODUCTION

Laboratory EXAFS spectrometers have advantages over synchrotron facilities in several respects; much faster and better interaction between the experiments and ideas, among others. In order to develop laboratory EXAFS facilities, a workshop was held in 1980 [1] and the possibility to construct ones that can supply data accurate enough for structural analysis was discussed. Since then several laboratory spectrometers have been constructed by employing focused optics in order to compensate relatively weak x-ray intensity from conventional x-ray generators [2-5]. Some have already been utilized to structurally characterize amorphous materials and liquids. All the studies so far reported, however, have been confined to the first raw transition elements only [6-11], the reason being in poor resolving power at higher energy region (>15 keV).

In this study an improvement of the resolution in the high energy region has been attempted by the use of the higher order reflections from dispersing crystals. In order to discriminate unwanted reflections which always accompany the desired one, a solid state detector was employed. As a result, a sufficient resolution as well as photon numbers for EXAFS analysis was obtained for the energy range up to about 25 keV.

By the use of the spectrometer, structures of two kinds of Ru/Al₂O₃ catalysts, prepared from RuCl₃ and Ru₄(CO)₁₂, were studied by the Ru K EXAFS (absorption edge 22.14 keV). It was found that very tiny metal clusters were formed in the catalyst prepared from Ru₄(CO)₁₂. They are so small that structural parameters differ significantly from those of bulk metal; the coordination number is

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about 6 instead of 12, the nearest neighbor distance contracts by 0.06 Å compared to that of the bulk metal, and they are easily oxidized if kept in air at room temperature.

2. EXPERIMENTAL

The spectrometer employed is the one previously reported [5]. It has a Rowland radius of 320 mm and is equipped with a Johansson cut and bent crystal. X-rays from a rotating anode x-ray generator are monochromatized by either Ge(220) or Ge(311) dispersing crystal, and the discrimination of the reflections by undesired orders is made by a combination of an SSD, and a 4 channel discriminator and scaler. Photons from up to 4 different orders of reflection can be accumulated separately, and the desired one is picked out after transferred to a microcomputer through a CAMAC bus. It was necessary to maintain total photon numbers from all the orders less than $10^8$ cps, in order to avoid a counting loss. This imposes a limitation to the available x-ray intensity. A use of aluminum foil filter was efficient for the elimination of lower order reflections. By the use of a rotating sample holder, I and $I_0$, which are the x-ray intensities with a sample in and out of the beam, were measured alternatively. Each absorption measurement required about 12 hours, collecting at least $2 \times 10^8$ photons as I at each data point. EXAFS analysis was performed as reported previously [7,8].

Ru/Al$_2$O$_3$ catalysts were prepared by impregnating $\gamma$-Al$_2$O$_3$ (Reference Catalyst of Catalysis Society of Japan, ALO-4) of a hexane solution of Ru$_3$(CO)$_{12}$ or aqueous solution of RuCl$_3$ as described previously [12]. The former will be abbreviated as catalyst A and the latter catalyst B. The contents of Ru were 4% in the former and 5% in the latter. The catalysts in a glass cell with very thin wall were reduced by H$_2$ at 450°C for 2 hrs. EXAFS measurements were performed with the sample sealed under vacuum after the reduction. In order to study the effects of oxidation, the catalysts exposed to air at room temperature were also studied.

3. RESULTS

An improvement of the resolving power by the use of higher order reflections is demonstrated in Fig. 1, taking Mo K doublet as an example. Resolution (FWHM) of 7 eV at 18 keV has been attained with Ge(660) reflection, which is sufficient for EXAFS analysis. Figure 2 shows EXAFS spectra of the Ru catalyst A and B, as well as that of Ru metal, taken with Ge(660) crystal. A comparison of the EXAFS function $\chi(k)$ for Ru metal and the two catalysts are shown in Fig. 3. It is evident from the figure that the $\chi(k)$ of the catalyst B, which is prepared from RuCl$_3$, almost coincides with that of the metal, except for a slightly fast damping in the high k region. This indicates that Ru atoms in the catalyst B are coordinated by other Ru atoms in the same way as in the bulk metal, possibly with a slightly larger disorder factor or with a smaller mean free path of the photoelectron. On the other hand, $\chi(k)$ of the catalyst A, which is prepared from Ru$_3$(CO)$_{12}$, is significantly different; amplitude is much smaller and the period is slightly longer. From these qualitative observations a decrease in the
coordination number and shorter nearest neighbor distance in the catalyst A can be anticipated.

Fourier transforms were made over k range of 3.55 to 14.55 Å followed by back-Fourier transforms of the first peak and the non-linear least-squares parameter fittings. The phase and amplitude factors reported by Teo and Lee [13] were employed in the calculation. The best fit values of the interatomic distances and the coordination numbers are shown in Table I.

It is concluded from the results above that the Ru atoms in the catalyst B is predominantly metallic. The interatomic distance is the same as that of the metal and the difference in the coordination number is within the experimental error. Indeed, as is also shown in Table I, an observation of electron microscope (EM) revealed the presence of metal clusters with mean diameter of 71 Å, which is large enough to show no significant surface effects.

On the other hand, the environment of Ru atoms in the catalyst A is fairly different from that of the metal; the nearest neighbor distance is shorter by as much as 0.06 Å, and the coordination number is almost the half. No observation of metal particles was made on this catalyst by EM, and X-ray diffraction (XRD) did not give any distinct peak. All these observations lead to the conclusion.

![Figure 2. EXAFS spectra of Ru metal (M), catalyst A (from Ru₃(CO)₁₂), and catalyst B (from RuCl₃). The energies for A and B are displaced. Inserted is a k weighted Fourier transform of Ru metal (phase and amplitude uncorrected).](image)

![Figure 3. Extracted EXAFS oscillations of Ru metal (dots), catalyst A (triangles), and catalyst B (solid lines).](image)

Table I. Characterization of Ru/Al₂O₃ catalyst prepared from Ru₃(CO)₁₂ (A) and from RuCl₃ (B).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Diameter/(Å)</th>
<th>EXAFS DATA</th>
<th>r/(Å)</th>
<th>N*²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂ adsorption</td>
<td>EM</td>
<td>XRD</td>
<td></td>
</tr>
<tr>
<td>A (from Ru₃(CO)₁₂)</td>
<td>10</td>
<td>nd*³</td>
<td>nd*³</td>
<td>2.59</td>
</tr>
<tr>
<td>B (from RuCl₃)</td>
<td>46</td>
<td>71</td>
<td>nd*³</td>
<td>2.65</td>
</tr>
</tbody>
</table>

*¹ Interatomic distance of Ru metal is 2.88 Å.
*² Coordination number of Ru metal is 12.
*³ Not detected.
that the Ru atoms in catalyst A exist in much smaller metal clusters than those of the catalyst B, resulting in the low coordination number and the shorter interatomic distance.

The changes in the EXAFS spectra when these catalysts were exposed to air give another clue to the understanding of the structure of these catalysts. As is shown in Fig. 4, EXAFS function of catalyst A after exposure to air becomes a single, monotonously decreasing oscillation with lower frequency, suggesting that the atoms surrounding each Ru atom are not Ru, but light atoms, and the oxygen is the only candidate in this case. In the Fourier transform of the extracted oscillation only one peak appears, which corresponds to Ru-O distance. There also appears a sharp peak near the absorption edge, which is absent in metals and is often characteristic of the absorption spectra of oxides. In the catalyst B, the metal like oscillation remains after the exposure to air as is shown in Fig. 5, but another oscillation with lower frequency is superposed. As a result, the associated Fourier transform shows two major peaks; one is Ru-Ru and the other is, most likely, Ru-O. All these evidences suggest that metal atoms on the surface are easily oxidized by the exposure to air. Since the metal particle sizes in the catalyst A is so small almost all the Ru atoms are oxidized, while in the catalyst B only those atoms on the surface are oxidized, the bulk remaining as metallic.

![Figure 4. An EXAFS spectrum of catalyst A after exposure to air and the associated k^2 weighted Fourier transform (phase and amplitude uncorrected).](image1)

![Figure 5. An EXAFS spectrum of catalyst B after exposure to air and the associated k^2 weighted Fourier transform (phase and amplitude uncorrected).](image2)

4. Discussion

EXAFS analysis of Ru/Al₂O₃ samples combined with EM, XRD, and H₂ adsorption studies showed that depending on the preparation method, Ru metal clusters of various sizes are formed. The metal particle size in the catalyst B was determined by EM to be about 70 Å, and the nearest neighbor distance and the coordination number obtained from EXAFS are almost the same as those of bulk metal in this case. The cluster size in the catalyst A is, however, too small to be determined from EM, but the coordination number of 6 was obtained from EXAFS.

A rough estimation of the cluster size is possible from the coordination number. Taking the hcp structure which bulk Ru metal assumes as a basis, two simple models that have the coordination
number of about 6 can be conceived; an infinite two dimensional closed pack model gives the coordination number of 6, and that of a hcp structure consisting of 20 atoms (three layers, with 5, 10, and 5 atoms in each layer) happened to be 6.3. The latter model is more likely to be close to the case, because the former requires fairly large number of atoms in order for the coordination number to be nearly 6. From the H₂ adsorption study by assuming a cubic shape, the average half side of the particle was estimated to be about 10 Å. A 20 atom model fits this result, because it can be approximated to be an ellipsoid with diameters of about 11 and 7 Å, which almost is identical to a cube with half side of 10 Å.

Another interesting result is the considerable contraction of the nearest neighbor distance in catalyst A. Contractions due to surface stress can be expected for very small particles and several examples have already been reported. Montano et al. [14] reported a decrease of about 0.04 Å in the nearest neighbor distance of Ag particles in solid argon with average sizes ranging from 25 to 150 Å. In a separate publication they observed a significant contraction of Fe-Fe distance, although the particle size was not known [15]. Moraweck et al. [16] have reported a contraction of Pt-Pt distance by 0.12 Å in a Pt/Y-zeolite sample. The observation here has added another evidence that the contraction does occur in very small particles.

Asakura et al. [17] studied the structure of Ru/γ-Al₂O₃ and Ru/SiO₂ prepared from Ru₃(CO)₁₂ by EXAFS and observed Ru-O bond as well as Ru-Ru bond (2.64 Å) for Ru/Al₂O₃. They attributed the Ru-O bond to the one between the metal and the surface oxygen of the support. In the result presented here, no evidence for Ru-O bond was obtained with the sample kept in vacuo after reduction. The reason of the discrepancy is not known at this point.

References