Nanoparticles of Amorphous Ruthenium Sulfide Easily Obtainable from a TiO₂-Supported Hexanuclear Cluster Complex [Ru₆C(CO)₁₆]²⁻: A Highly Active Catalyst for the Reduction of SO₂ with H₂


Dedicated to Professor Horst Kisch on the occasion of his 60th birthday

Abstract: TiO₂-supported ruthenium-metal particles were derived from an anionic hexanuclear carbido carbonyl cluster [Ru₆C(CO)₁₆]²⁻ and compared with those prepared conventionally by impregnation of TiO₂ with a solution of RuCl₃ followed by reduction with H₂. The average sizes of the metal particles in both systems are similar, that is, 12 Å for molecular cluster-derived particles and 15 Å for those derived from the RuCl₃ precursor, although the size distribution is sharper in the former case. These supported particles efficiently promote the reduction of SO₂ with H₂ to give elemental sulfur. Their active form is ruthenium sulfide as confirmed by EXAFS and X-ray diffraction measurements. The nanoscale ruthenium sulfide particles, which originated from the cluster complex, have an amorphous character and show activity even at low temperature (463 K), whereas ruthenium sulfide formed from RuCl₃-derived metal dispersion is a pyrite-type RuS₂ crystallite and needs a temperature above 513 K to effect the same catalysis. Amorphous ruthenium sulfide maintains its nano-sized scale (∼14 Å) regardless of the reaction temperature, while RuS₂ crystallite aggregates to form larger nonuniform particles.

Keywords: amorphous materials • cluster compounds • nanostructures • reduction • ruthenium

Introduction

The structures and functions of very small metal particles, which are synthesized with molecular cluster complexes as precursors, have attracted considerable interest.[1] They often show catalytic properties different from conventional supported metals, and this has been attributed to, at least in part, the small size of the catalyst particles. However, most of the reactions examined with such nano-sized fine metal catalysts involve the hydrogenation of olefins, hydroformylations, hydrogenolysis of alkanes, and in some limited cases the reformation of naphtha to produce aromatics. We were originally interested if such a size effect could also be effective in rather drastic reactions, such as SO₂ reduction by H₂, since the catalytic reduction of gaseous SO₂ to elemental sulfur has attracted much attention as a possible strategy to abate SO₂ from combustion processes.[2-5] In our studies along this line, we previously reported that TiO₂-supported ruthenium catalysts, which were prepared from two different precursors, that is, the ruthenium carbido carbonyl cluster complex [(PPh₃)₂N][Ru₆C(CO)₁₆] (1) and the metal chloride RuCl₃ (2), showed the efficient reduction of SO₂ with hydrogen to give elemental sulfur at temperatures higher than 508–513 K.[6] One of the remarkable features of the RuTiO₂ catalyst (Ru(A)), derived from the cluster complex 1, was its quite high activity even at a lower temperature of 463–513 K, whereas TiO₂-supported metal particles (Ru(B)), made conventionally by the impregnation process from 2, needed a reaction temperature higher than 513 K (Table 1).
The metal dispersion on TiO₂ derived from the zero-valent mononuclear complex, that is, [Ru(cyclooctadiene)(cyclooctatriene)], as the precursor exhibited exactly the same temperature dependency as in the case of Ru(B), and therefore even if a trace amount of Cl⁻ ion remains on the metal surface from RuCl₃, it should have no effect in the present SO₂ reducing reaction.[6] In this work, the TiO₂-supported particles derived from 1 and 2, before and after catalysis at various temperatures, were characterized in detail to elucidate the origin of the difference in their activities. Characterization based on transmission electron microscopy (TEM), Ru K-edge X-ray absorption fine structure (EXAFS) spectroscopy, and X-ray diffraction (XRD) measurement indeed showed that Ru(A) and Ru(B), as well as their sulfide derivative, have significantly different characteristics in the present reaction involving sulfur. However, the main reason for this difference was concluded to be not the size of the catalyst particles, as initially expected, but rather their morphology. The present results suggest the existence of unprecedented amorphous ruthenium sulfide as a nanoparticle dispersion and that it plays a significant role in catalytic activity.

### Results

The TiO₂-supported cluster complex was prepared by impregnation of TiO₂ with a solution of 1 in THF and transformed to metal dispersion Ru(A) by heating the incipient sample at 573 K for 1.5 h under vacuum and then heating at the same temperature for three hours under a stream of H₂. By using the same procedure, precursor 2 was converted to TiO₂-supported metal dispersion Ru(B). The catalytic reduction of SO₂ at 7 Kelvin was interrupted after two hours, and the gray powders of [RuS(A)]₇ and [RuS(B)]₉, which were formed from Ru(A) and Ru(B), respectively, were subjected to EXAFS and XRD spectra measurements, as well as the observation of particle size by TEM.

**Transmission electron microscopy:** The TEM image of Ru(A) (Figure 1a) shows an exceptionally narrow size distribution of metal particles dispersed on TiO₂, with an average size of 12 ± 1.7 Å. The image of Ru(B) (Figure 1b) indicates that the average particle size is 15 ± 2.6 Å, and the particles are not as uniform as in the case of Ru(A). Energy-dispersive X-ray (EDX) analysis was used to confirm that the dark spots observed were actually images of Ru metal.

When Ru(A) was exposed to a gaseous mixture of SO₂/H₂ (1/2 v/v) at 443 K for two hours, only a slight conversion (2.8%) of SO₂ to elemental sulfur was observed (Table 1). However, the particle-size changed during that process: the resulting particles, denoted [RuS(A)]₄₄₃, became smaller (average size 8 ± 2.6 Å), but still maintained a sharp size distribution (Figure 2a). In contrast, upon treating Ru(B) under the same conditions, the resulting particle [RuS(B)]₄₄₃ tended to be larger with an even wider distribution compared

### Table 1. Reduction of SO₂ with H₂ to elemental sulfur over TiO₂-supported ruthenium catalysts carried out at various temperatures.[a]

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Conversion [%]</th>
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<tr>
<td></td>
<td>T [K]</td>
</tr>
<tr>
<td>443</td>
<td>463</td>
</tr>
<tr>
<td>1</td>
<td>2.8</td>
</tr>
<tr>
<td>2</td>
<td>1.7</td>
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![Figure 1. TEM images and histograms of the TiO₂-supported Ru particles. a) Ru(A); b) Ru(B).](image-url)
to that of the parent Ru(B) (Figure 2b). This property of [RuS(B)] for aggregation is more pronounced at higher temperatures, as shown in Figure 3b: [RuS(B)]\textsubscript{473} particles have average sizes of 30 ± 7.8 Å. Likewise, the average size for [RuS(B)]\textsubscript{523} particles was observed to be 30 ± 6.3 Å, which act as a catalyst at 523 K (Table 1). The changes in particle size and distribution with the reaction temperature are much less in the system with Ru(A): [RuS(A)]\textsubscript{473} still has a narrow distribution, with a particle size of 14 ± 1.8 Å (Figure 3a), while [RuS(A)]\textsubscript{523} has a mean particle size of 14 ± 3.5 Å, as summarized in Table 2.

**Ruthenium EXAFS spectra:** Figure 4 displays the original raw EXAFS data. Figures 5 and 6 show the normalized raw EXAFS data. Figures 5 and 6 show the normalized
oscillation $c(k)$ and the associated $k^3$-weighted Fourier transforms, respectively, for the supported Ru catalysts before (a and e) and after (b–d and f, g) the catalytic run at each reaction temperature. Figure 7 shows the results of respective curve-fitting analysis.

The Fourier transform for the initial metal dispersion of Ru(A) exhibits a single strong peak (Figure 6a). By comparison with the EXAFS oscillation and its associated Fourier transform spectra of authentic Ru metal powder, this peak was confirmed to represent the nearest neighboring Ru–Ru bond. TiO$_2$-supported Ru metal has been reported to lack the Ru–O bond.$[^7,8]$ Furthermore, in the present case, the one-shell Ru–Ru model gave a satisfactory fit, as shown in Figure 7a, while two-shell (Ru–O + Ru–Ru) fitting did not give reasonable parameters. The corresponding Fourier transform for Ru(B) (Figure 6e) again has a strong single peak due
to the Ru–Ru bond and agrees well with the EXAFS spectrum reported in the literature for Ru metal supported on TiO₂.⁹ Structural parameters are summarized in Table 3.

Table 3. Structural parameters of Ru(A) and Ru(B) determined from EXAFS data.

<table>
<thead>
<tr>
<th></th>
<th>d [Å]</th>
<th>ΔE [eV]</th>
<th>Δσ [Å]</th>
<th>R [%]</th>
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</thead>
<tbody>
<tr>
<td>Ru(A)</td>
<td>7.0</td>
<td>2.67</td>
<td>4.9</td>
<td>0.023</td>
</tr>
<tr>
<td>Ru(B)</td>
<td>9.2</td>
<td>2.66</td>
<td>9.8</td>
<td>0.037</td>
</tr>
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</table>

[a] The Ru–Ru distance determined by X-ray analysis of the metal is 2.65 Å.

The coordination number of the Ru–Ru bond was 7.0 for Ru(A) and 9.2 for Ru(B), which is consistent with the smaller size of Ru(A) observed by TEM (Table 2).

The Fourier transform of EXAFS data for [RuS(A)]₄₄₃, which is the species formed when Ru(A) is treated with a SO₂/H₂ gas mixture at 443 K (Table 1), is shown in Figure 6b. The spectrum is completely different from that of the parent Ru(A). The direct Ru–Ru bond is now very weak, while one strong peak is seen for the Ru–S bond, as assigned based on the spectrum of authentic RuSₙ (n = 2). The curve-fitting analysis based on two shells (Ru–S + Ru–Ru) gave the reasonable parameters listed in Table 4, while the fitted curve...
is shown in Figure 7b. The $N_{\text{Ru-S}}$ value was only 0.4; the $N_{\text{Ru-S}}$ was 5.3. The Ru–S bond length of 2.31 Å is comparable to the corresponding value of 2.351 Å found in the pyrite-type single crystals of RuS$_2$. At 473 K and 523 K, the cluster-derived particles showed good catalytic activity (Table 1) and the corresponding EXAFS data (Figures 5c, 6c; 5d, 6d) of the supported particles [RuS(A)$_{123}$] and [RuS(A)$_{323}$] were essentially the same as those for [RuS(A)$_{443}$]. For the curve-fitting shown in Figure 7d ([RuS(A)$_{123}$]), a one-shell approximation based on Ru–S was good enough (Table 4).

The EXAFS data for [RuS(B)$_{123}$] and [RuS(B)$_{323}$], obtained from noncatalytic and catalytic runs, respectively (Table 1), were similar to those of the corresponding [RuS(A)] analogues, as shown in Figures 5f-7f and 5g-7g. The Fourier transformed data in the range of 1.5–2.5 Å show a single peak. These were fit (Figure 7f and g) with curves generated from one-shell (Ru–S) parameters (Table 4).

All of these EXAFS data prove that the initially formed TiO$_2$-supported metal nanoparticles, Ru(A) and Ru(B), are converted to metal sulfide species upon reacting with a SO$_2$/H$_2$ gas mixture above 443 K, regardless of whether the temperature is high enough to achieve active catalysis.

**X-ray diffraction (XRD) analysis:** Since the metal loading of 1.5 wt% used for TEM and EXAFS studies was too low for XRD measurements, TiO$_2$ was loaded with the metal in 15 wt%. Figure 8a shows the XRD of blank TiO$_2$. As expected from the EXAFS data, both [RuS(B)$_{123}$] and [RuS(B)$_{323}$] (Figure 8b) show two peaks at 20 = 32 and 46°, which are assignable to the [200] and [220] faces, respectively, of the RuS$_2$ pyrite phase. The RuS$_2$ [311] face at 20 = 54° is overlapped by the strong peaks of TiO$_2$.

In contrast, both [RuS(A)$_{123}$] and [RuS(A)$_{323}$] showed the same XRD pattern (Figure 8c), which had a very broad peak in the range 20 = 30–55°, as is evident by comparison with the XRD pattern of pure TiO$_2$. Annealing of the [RuS(A)$_{323}$] sample under Ar at 723 K for two hours (Figure 8d) and further at 773 K for two hours (Figure 8e) yielded a sample with an XRD pattern that was essentially the diffraction of pyrite-type RuS$_2$ crystalline. To confirm further that the broad XRD peak observed in Figure 8e is due to ruthenium sulfide and not to impurities, a typical sulfidation method with conditions for metals was applied for Ru(A), that is, the reaction was performed at 573 K with H$_2$S/H$_2$ (1/9 v/v) in place of SO$_2$/H$_2$. The XRD pattern of the resulting ruthenium sulfide had exactly the same broad peak as that in Figure 8e, and annealing of this sample at 773 K gave the expected [200] and [220] peaks of the crystalline RuS$_2$. Similar sulfidation of Ru(B) with H$_2$S/H$_2$ proceeded only above 673 K, and its XRD pattern was very close to that shown in Figure 8b. Based on these observations, the broad peak present in Figure 8e is assigned to the amorphous phase of ruthenium sulfide.

XRD peaks of the parent metal dispersions Ru(A) and Ru(B) could be observed only in low 20 region due to low intensities of the diffraction. XRD of Ru(B) showed, albeit unresolved, overlapped peaks assignable to [002] and [101] faces of the hcp phase of the metal crystallite, whereas the corresponding diffraction for Ru(A) is broader and the peak top position is apparently different from those of the authentic Ru metal (Figure 9).
and is formed in the SO₂ reducing reaction of metal Ru(A), is highly active as a catalyst at a low temperature of 463–503 K. In contrast, the other ruthenium sulfide [RuS(B)], formed from Ru(B), is inactive in the same temperature range (Table 1) and works only at higher temperatures.

XRD can provide information on structural differences between the two ruthenium sulfides. Sulfide [RuS(B)] is evidently an ubiquitous pyrite-type crystallite of RuS₂ supported on TiO₂, while [RuS(A)] is amorphous (Figure 8). Successful curve-fitting analysis of the EXAFS data for [RuS(A)], with calculations based on crystalline RuS₂ (Figure 7), suggests that the relative orientation of the Ru and nearest S atoms in the amorphous phase is similar to that in the more common pyrite-type form (Table 4). Although there have been a number of reports concerning Ru sulfide, only two have reported the preparation of an amorphous form.[15, 16] The reported XRD of amorphous Ru sulfide consists of two broad overlapping humps with 2θ ranging from approximately 20–55°, although the peak-head positions are evidently different in the two reports. To the best of our knowledge, [RuS(A)] obtained in the present study is the first example of a supported amorphous species of a ruthenium sulfide dispersion and also the first case in which reactivity of amorphous ruthenium sulfide was examined.

Comparison of the ruthenium sulfides prepared here by TEM indicates that the sulfidation of Ru(A) during the reaction with SO₂/H₂ causes partial fragmentation of the metal particles into smaller metal sulfide particles at low temperature, that is, [RuS(A)]₁₄₋₁₈ has an average size of 8 Å (Figure 2a). Although some re-aggregation takes place at higher temperatures, the particle size remains rather small, for example, [RuS(A)]₁₀, and [RuS(A)]₁₂ each measured ≈ 14 Å (Table 2). Thus, it is very likely that amorphous ruthenium sulfide [RuS(A)] has weak interaction between the RuS₂ units, which does not allow greater aggregation. In the case of Ru(B), the behavior toward sulfidation through the reaction with SO₂/H₂ is very different from that with Ru(A); at 443 K, the reaction induced partial aggregation rather than fragmentation and resulted in a broad distribution of the particle size of 20–25 Å (Figure 2b). The tendency of crystalline RuS₂ for rather random aggregation is even more pronounced at higher temperature, at which it gives ruthenium sulfide [RuS(B)] with the particle size scattered over a wide range of 18–47 Å (473 K) and 17–33 Å (523 K), as shown in Figure 3b.

The striking difference between the two ruthenium sulfide catalysts, one originating from the [Ru₅] cluster complex 1 and the other from ruthenium salt 2, may be traced back to the different morphologies of the initially formed metal particles Ru(A) and Ru(B), which are intermediate precursors for the sulfide species. Aside from sulfidation by a gas mixture of SO₂/H₂ (1/2 v/v) as discussed above, the more common sulfidation process with a gas mixture of H₂S/H₂ (1/9 v/v) also gave amorphous ruthenium sulfide from Ru(A) and pyrite-type crystallite from Ru(B), as observed by XRD analysis (Figure 8). Furthermore, the fact that a higher temperature is needed for the sulfidation of Ru(B) (673 K) by H₂S/H₂ relative to the reaction with Ru(A) (573 K) is another indication of the higher reactivity of Ru(A). The
XRD observations displayed in Figure 9 suggest that TiO2-supported Ru(A) and Ru(B) vary with regard to structure: Ru(A) is much more reactive probably because it has significant structural defects or more amorphous-like, compared to crystalline metal Ru(B), and furnishes nanoparticles of amorphous metal sulfide on sulfidation.

Conclusion

By comparing the TiO2-supported metal particles Ru(A) and Ru(B) and their sulfide derivatives [RuS(A)] and [RuS(B)], several features became clear.

1) Though the size distribution is sharper in Ru(A), the average particle size of the two forms is rather similar (Ru(A) 12 Å, Ru(B) 15 Å). However, they differ in structures: Ru(A) probably has significant structural defects, while Ru(B) is a conventional hcp crystallite.

2) Ru(A) readily undergoes sulfidation with a H2S/H2 gas mixture at 573 K to give amorphous ruthenium sulfide, while Ru(B) requires a temperature of 673 K and gives ruthenium sulfide in the form of pyrite-phase crystallite.

3) Upon reaction with a gas mixture of SO2/H2, both metal species are converted to Ru sulfide. Ru sulfide derived from Ru(A) consists of amorphous RuS2, while Ru(B) gives the conventional RuS2 pyrite phase. The amorphous ruthenium sulfide formed in situ from Ru(A) catalyzes the reduction of SO2 to elemental sulfur by H2 at a much lower temperature (463 K) than does the crystalline ruthenium sulfide derived from Ru(B) (513 K).

4) Ruthenium sulfide crystallite [RuS(B)] aggregates to a larger and nonuniform dispersion at higher temperature. In contrast, amorphous ruthenium sulfide [RuS(A)] maintains a small particle size under various temperatures for the catalytic reaction. This probably is due to the much weaker interunit interaction among RuS2 units in the amorphous phase.

5) Ru EXAFS analysis suggests that the relative orientation of Ru and S atoms in the RuS2 species of the amorphous phase is similar in average to that in the crystalline pyrite phase. Ruthenium cluster complexes are thus good precursors for amorphous metal sulfide supported on TiO2, which is expected to have high activity under rather mild conditions. Further studies on its reactivity in other catalyst reactions are now in progress.

Experimental Section

Sample Preparation: The anionic carbido carbonyl cluster complex, \[[\text{PPPh}_{3}]_{2}\text{N}]_{2}\text{[Ru}_{6}\text{C(CO)}_{16}]\] (1), was prepared by the method described in the literature.\(^{37}\) Cluster 1 was supported on TiO2 (Japan Aerosil P25, mean particle size 21 nm) by impregnation at 298 K for 1 h with dry THF solution under an Ar atmosphere, and subsequent removal of THF in vacuo. The amount of Ru metal loaded was fixed at 1.5 wt% unless stated otherwise. Dried incipient catalysts were heated in vacuum for 1.5 h at 573 K and then reduced for 3 h under a stream of hydrogen at 573 K to give Ru(A). In the same manner, RuCl3 · 3H2O (2) on TiO2 was reduced to give Ru(B). The catalytic reduction of SO2 was carried out in a gas flow system (flow rate 60 cm3 min\(^{-1}\)) as described in a previous report.\(^{38}\) After the catalytic reaction, elemental sulfur remaining on the catalyst surface was flushed with argon for 2 h at the reaction temperature. The supported catalyst sample was then transferred under Ar to a glass cell with Kapton films on both sides and subjected to EXAFS measurements. Sulfidation of the supported metals Ru(A) and Ru(B) by H2S was carried out under a mixture of H2S/H2 (1/9 v/v), with a flow rate of 44 cm3 min\(^{-1}\) at atmospheric pressure. In this manner, Ru(A) and Ru(B) underwent sulfidation at 573 K and 673 K, respectively. After 3 h, the sample was cooled to room temperature and flushed with nitrogen for 1 h.

EXAFS measurements and analysis: Ru K-edge EXAFS measurements were performed at room temperature at beamline 10B of the Photon Factory at the High Energy Accelerator Research Organization (KEK-PF) in Tsukuba. The accumulation ring energy was 2.5 GeV and the ring current was 450 – 300 mA. The beamline 10B makes use of the channel-cut double crystal monochromator of Si(311). The incident and transmitted X-rays were monitored by ion chambers filled with Ar for \(L_e\) and Kr for \(K_{\alpha}\). The photon energy was calibrated by equalizing the derivative maximum of the absorption edge of Ru powder at 22193.1 eV. The background was subtracted by fitting the polynomial to the pre-edge region and extrapolating it to the postedge region. The edge jump of the subtracted spectrum was normalized at 22313.8 eV.

The EXAFS data were analyzed by the EXAFS program.\(^{38,39}\) Background subtraction was performed by calculating the three-block cubic spline, followed by normalization using the Victoreen parameter. Fourier transformation of the \(k^2\)-weighted \(\varepsilon\) function was carried out over the range \(r_{\text{max}} = 3\) and \(k_{\text{max}} = 170 – 190\) Å\(^{-1}\). The window function (Hanning function) was multiplied by the \(k\) width of \((k_{\text{max}} – k_{\text{min}})/20\) on both ends of the FT \(k\) range. Inverse FT was performed in the \(r\) range of \(r_{\text{min}} = 1.3 – 1.4\) and \(r_{\text{max}} = 3.9 – 4.1\) Å multiplied by the window Hanning function with width 0.1 Å on both ends. Curve-fitting analysis was performed by using a method based on the formula of the plane wave single-scattering theory, with empirical phase shift and amplitude functions extracted from ruthenium metal powder for the Ru–Ru bond (metallic), from RuO2 for the Ru–O bond, and from RuS, \((x = 2)\) for the Ru–S bond. The coordination number \((N_i)\), bond length \((d)\) and Debye–Waller factor \((\sigma)\) were determined in the fitting procedure. In Tables 3 and 4, Debye–Waller factors thus obtained are listed in the form of \(Ae^\sigma\) Å, that is, with reference to the corresponding values for the standard compounds (Ru metal, RuO2, and RuS).

Transmission electron microscopy: Microscopy studies were performed by using a field emission Vacuum Generator JEM-2000EXII operated at 200 kV. The spatial resolution of the microscope was estimated to be \(\approx 3\) Å. Specimens were prepared by dipping a copper-mesh-supported holey carbon grid into an ethanol suspension of the sample.

X-ray diffraction measurement: The amount of Ru metal loaded on TiO2 was 15 wt% in XRD studies. XRD analysis of the catalyst samples [RuS(A)] and [RuS(B)] was provided on a MAC Science M18XHF X-ray diffractometer with rotating anode generators and a monochromatic detector. CuK\(_\alpha\) radiation (\(\lambda = 1.542\) Å) was used at 45 kV and 400 mA. For crystal phase identification, the typical operation parameters were divergence slit of 1', scattering slit 1', receiving slit 0.3 mm, and a scanning rate of 2° min\(^{-1}\) with a 0.02° data interval. XRD patterns were collected in the 29 domain ranging from 10 to 100°. XRD measurement of intermediate metal particles (Ru(A) and Ru(B)) was carried out on a Rigaku RINT/RAPID diffractometer with CuK\(_\alpha\) (\(\lambda = 1.542\) Å) radiation at 40 kV/36 mA with radiation time of 15 min.

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