# Efficient Reduction of Sulfur Dioxide with Hydrogen over TiO$_2$-Supported Catalysts Derived from Ruthenium Salts and Ruthenium Cluster Complexes

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Catalytic reduction of SO$_2$ to elemental sulfur was carried out over supported ruthenium catalysts that were derived not only from hexaruthenium carbonyl cluster complexes but also from RuCl$_3$ as the precursor. The activity was largely dependent on the kind of metal oxide support used. Compared to the known systems, the TiO$_2$-supported ruthenium catalysts operated with higher efficiency at lower temperature. Moreover, the selectivity was totally to elemental sulfur, forming no detectable amount of unfavorable H$_2$S. H$_2$S-free catalysis appeared to be a common feature of ruthenium catalysts regardless of the kind of precursors. The TiO$_2$-supported catalyst derived from [N(PPh$_3$)$_2$]$_2$[Ru$_6$C(CO)$_{16}$] was much more active within the 463–508 K temperature region than the catalyst conventionally prepared from RuCl$_3$, while both showed similar activity at more elevated temperatures. The kind of cation in anionic cluster complexes and the presence of an interstitial atom are important factors in generating supported catalysts that operate under mild conditions.   © 2002 Elsevier Science (USA)

*Key Words:* ruthenium cluster; ruthenium chloride; titanium oxide; sulfur dioxide; hydrogenation; catalytic reduction; supported metal catalyst.

## INTRODUCTION

Since environmental protection regulations will become stricter in the near future, the removal of SO$_2$ in oxygen-free exhaust gases from coal-fired power plants, combustion engines, industrial boilers, and other sources has recently attracted significant attention. Commercial SO$_2$ abatement technologies typically use wet scrubbing systems based on lime (1, 2). However, the disposal of large amounts of solid waste (e.g., gypsum) and industrial effluent generated from these systems presents another environmental problem. One of the most desirable products from SO$_2$ is probably harmless elemental sulfur, which is easy to handle, store, and convert into useful chemicals. Recently, the catalytic reduction of SO$_2$ to sulfur was studied using carbon

monoxide (3–7), hydrogen (8–17), and methane (18–24) as reducing agents. In the reduction by carbon monoxide, more than 80% conversion of SO$_2$ was observed in the Co$_3$O$_4$/TiO$_2$ catalyst at 623 K (6). A problem often encountered in using CO as the reductant is the formation of toxic COS, particularly in the low-temperature region. Reduction by methane was carried out using ceria-based copper (23, 24), Al$_2$O$_3$-supported molybdenum (18, 19), and Al$_2$O$_3$-supported cobalt–molybdenum catalysts (20), but the reaction temperatures required were generally very high (723–1113 K). By using hydrogen, SO$_2$ can be converted to sulfur at a much lower temperature (8). For example, the Al$_2$O$_3$-supported sulfided cobalt–molybdenum with a rather high metal loading ($\approx$10%) could give approximately a 60–90% yield of sulfur with excess H$_2$ at 533–623 K. However, the stoichiometric feed ratio, i.e., 2 equiv H$_2$ versus SO$_2$, resulted in lower activity (9). One problem often observed in the SO$_2$ hydrogenation system is the formation of H$_2$S as a toxic by-product (9–12, 15, 17).

Several years ago, we examined reactions of the hexanuclear ruthenium cluster complex [PPN]$_2$[Ru$_6$C(CO)$_{16}$] (**1**, PPN=(PPh$_3$)$_2$N$^+$) with SO$_2$ and H$_2$ to develop a model system for the catalytic reduction taking place on nanoscale metal particles (25, 26). The gaseous SO$_2$ molecule trapped on the cluster undergoes S–O bond splitting by the action of Lewis acids to give a $\mu_3$-SO unit which in turn is easily reduced by H$_2$ to give metal sulfide complexes. A noticeable feature of the model reaction is that fission of metal–metal bonds, i.e., partial fragmentation of the metal cluster skeleton, coincides with metal sulfide formation. To determine whether the parent cluster complex **1** or its derivatives could be a precursor of an actual catalyst to reduce SO$_2$, we impregnated metal oxide supports with solutions of the ruthenium cluster complexes. After converting the supported cluster complexes to nanosized metal particles, the catalytic activity for SO$_2$ reduction by H$_2$ was tested. At the same time, dispersed ruthenium metal on a metal oxide support was prepared by a conventional method using ruthenium chloride as the precursor, and the catalytic activity

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was compared to the metal catalyst derived from the cluster complexes. Although in recent years (27) a number of supported fine metal particles were prepared from molecular cluster complexes (metal carbonyl clusters), most were related to the hydrogenation of olefins, hydrogenolysis of alkanes, and, in limited cases, naphtha reforming for the production of aromatics. The present report describes the first example in the application of cluster complexes to a more drastic but environmentally important $SO_2$ reduction catalysis.

## METHODS

### Preparation of Supported Metal Catalysts

The ruthenium carbonyl cluster precursors, $[PPN]_2[Ru_6C(CO)_{16}]$ (**1**) (28), $[PPN]_2[Ru_6(CO)_{18}]$ (**2**) (28), $Ru_6C(CO)_{17}$ (**3**) (29), $[PPN][Ru_6H(CO)_{18}]$ (**4**) (30), mononuclear cyclic olefin complex $Ru(cod)(cot)$ (**7**, cod = cyclooctadiene, cot = cyclooctatriene) (31), and the iron cluster $[PPN]_2[Fe_6C(CO)_{16}]$ (**8**) (32), were prepared by methods described in the literature. The change in the cationic part of **1**, i.e., preparation of cluster complexes $[PPh_4]_2[Ru_6C(CO)_{16}]$ (**5**) and $[Et_3BzN]_2[Ru_6C(CO)_{16}]$ (**6**) ($Et_3BzN=(C_2H_5)_3(PhCH_2)N^+$), was performed in a similar manner to the preparation of **1**. Cluster complexes were supported on $TiO_2$ (*a*, Nihon-Aerosil, Titanium oxide P25, surface area 50 $m^2$ $g^{-1}$; *b*, Catalysis Society of Japan, JRC-TIO-1, surface area 73 $m^2$ $g^{-1}$; *c*, Catalysis Society of Japan, JRC-TIO-3, surface area 40 $m^2$ $g^{-1}$), $Al_2O_3$ (Nihon-Aerosil, Alon C, surface area 100 $m^2$ $g^{-1}$), $SiO_2$ (Fuji-Silysia, CARiACT P-10, surface area 280 $m^2$ $g^{-1}$), $MgO$ (Catalysis Society of Japan, JRC-MGO-4 (500A), surface area 32 $m^2$ $g^{-1}$), $ZrO_2$ (Toso, TZ-PX-15, surface area 68 $m^2$ $g^{-1}$), $HfO_2$ (Soekawa 325 mesh), active C (Wako), $VO_2$ (Soekawa, 200 mesh), and $V_2O_5$ (Soekawa, 200 mesh)) by an impregnation technique. The air- and moisture-sensitive natures of these supported metal clusters required that manipulation be performed under argon atmosphere using dehydrated and degassed tetrahydrofuran (THF). The metal oxide was mixed with a THF solution of a metal carbonyl cluster complex for 1 h at 298 K in argon, followed by the removal of the solvent by evaporation. The dried incipient catalyst was charged in a reactor. Prior to the reaction with $SO_2$, each sample, except $TiO_2$-supported $Ru_3(CO)_{12}$ (*vide infra*), was heated under vacuum to 573 K, slowly increasing the temperature in 40 min from ambient temperature and then held at that temperature for 50 min. A slow stream of $H_2$ was then introduced while maintaining the temperature at 573 K for 90 min. The $H_2$ stream was maintained until the sample was cooled down slowly to a certain reaction temperature for the next reaction with $SO_2$ and $H_2$. The $Ru_3(CO)_{12}/TiO_2$ sample was gradually heated under vacuum raising the temperature from ambient to 313 K in 5 min, held at 313 K for 30 min,

heated up to 573 K in 20 min, and finally held at 573 K for 50 min. The reduction of the catalyst by $H_2$ was carried out as described previously. Metal particles supported on $Al_2O_3$ or $TiO_2$ were also prepared from metal salts as precursors: $RuCl_3 \cdot 3H_2O$ (Furuya Metals Co., Ltd.), $Co(NO_3)_2 \cdot 6H_2O$ (Junsei Chemical Co., Ltd.), $NiCl_2 \cdot 6H_2O$ (Kanto Chemical Co., Inc.), and $Fe(NO_3)_3 \cdot 9H_2O$ (Kanto Chemical Co., Inc.). $Al_2O_3$ or $TiO_2$ was impregnated with methanol solution of metal salt at 298 K for 1 h under argon atmosphere followed by the removal of the solvent under reduced pressure. The impregnated catalyst was charged in a gas reactor. Prior to the reaction with $SO_2$, all impregnated metal salts, except $RuCl_3 \cdot 3H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$, were heated under argon from ambient temperature to 673 K, raising the temperature in 40 min, then sulfided with a flow of $H_2S$-containing gas (10 vol% $H_2S$ in $H_2$) at 673 K for 120 min, and finally cooled down to a certain reaction temperature to begin the successive $SO_2$-reduction process. The pretreatment of supported $RuCl_3 \cdot 3H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ was similar to that for the supported cluster complexes previously described. Throughout the present study, the loading of each precursor on the support was 1.5 wt% based on the metal, unless otherwise stated.

### Sulfur Dioxide Reduction by Hydrogen

The catalytic reaction was carried out in a fixed-bed flow reactor made of a 500-mm-long Pyrex-glass tube, 15 mm in diameter, which was heated externally using an electric furnace or tube mantle heater. Four hundred milligrams of an impregnated support was placed in the vertical reactor with fine quartz wool supporting the [catalyst/support] powder. After the pretreatment, as described in the preceding section, the feed gas was introduced from the top of the reactor at a constant flow rate using mass flow controllers (STEC, SEC-4400MO $SO_2$, and SEC-400MK3 $H_2$) and passed through the catalyst bed. The temperature was measured by a sheathed E-type thermocouple placed in the reaction tube, at the external position of the catalyst bed, and was controlled within 1 K by a programmable temperature controller using a PID regulator. The reacting gases, $SO_2$ and $H_2$, were introduced at the rates of 20 and 40 $cm^3$ $min^{-1}$, respectively (total space velocity 9000 $cm^3$ $g^{-1}$ $h^{-1}$) under atmospheric pressure. The used gases, $SO_2$, $H_2S$, and $H_2$, had purities higher than 99.9%. An ice-bath trap connected to the outlet of the reactor was used to collect the elemental sulfur and water produced. The trapped sulfur was extracted from carbon tetrachloride, dried, and weighed to measure the yield. An online gas chromatograph (Shimazu, GC-14B) connected to the outlet of the ice-bath trap was used to analyze gaseous products. The GC had two columns, Uniport B and Shimalite TPA, and one thermal conductivity detector (TCD) for the detection of $H_2S$, $SO_2$, and $H_2$.

## RESULTS AND DISCUSSION

As detailed under Methods, each precursor was converted to fine metal particles dispersed on various supports (1.5 wt% loading), and the *in situ* prepared metal on an oxide support was then reacted with a mixture of $SO_2$ and $H_2$. It is very likely that the metal particles are immediately converted to metal sulfide particles, since this reaction produces active sulfur on the metal surfaces. Indeed, presulfidation of the dispersed metal derived from $RuCl_3$ with $H_2S/H_2$ gave catalyst species that also showed high activity (Table 2). The characterization of the initial supported metal particles and the particles recovered after the reaction of $SO_2$ with $H_2$ were described elsewhere (33).

### Ruthenium Catalysts Supported on Various Metal Oxides

Two precursors, cluster complex **1** and $RuCl_3$, at three different reaction temperatures were used to examine whether the oxide support had an effect on the catalytic activity (Table 1). The metal oxides used may be classified as basic oxide (MgO), amphoteric oxide ($TiO_2$, $ZrO_2$, $HfO_2$), and acidic oxide ($SiO_2$, $VO_2$, $Al_2O_3$). As is obvious from Table 1, acidity and basicity of the support are not an important factors. By comparing the conversion at 573 K, one

**TABLE 1**

**Conversion Percentage of SO₂ to S₈ by Reduction with H₂ Performed over Ruthenium Catalysts on Various Supports[a]**

| Support | [PPN]₂[Ru₆C(CO)₁₆] Reaction temperature/K | | | RuCl₃ · 3H₂O Reaction temperature/K | | |
|---|---|---|---|---|---|---|
| | 523 | 548 | 573 | 523 (Cn[b]) [Cnm[c]] | 548 | 573 |
| MgO | 1.5 | 4.7 | 6.0 | 0.5 (0.5) [0.04] | 7.1 | 8.8 |
| TiO₂ (a)[d] | 87.1 | 87.2 | 90.2 | 86.8 (88.4) [4.5] | 88.6 | 89.3 |
| TiO₂ (b)[e] | 77.5 | 77.6 | 87.4 | 84.7 (88.8) [3.2] | 85.6 | 85.7 |
| TiO₂ (c)[f] | 83.4 | 83.9 | 85.3 | 82.6 (82.6) [5.4] | 83.2 | 83.6 |
| ZrO₂ | 2.0 | 86.4 | 87.0 | 1.5 (2.7) [0.1] | 34.6 | 39.6 |
| HfO₂ | 3.3 | 3.7 | 69.1 | 1.3 | 3.7 | 58.5 |
| VO₂ | — | — | 3.5 | — | — | 3.0 |
| V₂O₅ | — | — | 13.7 | — | — | 7.6 |
| Al₂O₃ | 1.8 | 8.7 | 9.4 | 1.6 (2.0) [0.05] | 5.1 | 6.6 |
| Active C | — | — | 8.7 | — | — | 7.4 |
| SiO₂ | 1.0 | 4.5 | 4.6 | 0.4 (72.1) [0.8] | 75.9 | 76.8 |

[a] Conversion data were collected after the reaction time of 5 h. Loading of metal was 1.5 wt% unless otherwise stated. The total amount of supported catalyst was fixed at 400 mg.

[b] Conversion (Cn) obtained from area-normalized experiment taking $TiO_2(c)$ as the standard: metal/support area was fixed at 1.02 mg/m² by changing the amount of metal loading.

[c] Cnm = Cn/(mg Ru): Cn is normalized with the amount of metal used.

[d] About a 7/3 mixture of anatase and rutile.

[e] Anatase.

[f] Rutile.

**TABLE 2**

**Conversion (%) of SO₂ to S₈ by Supported Catalysts Derived from Metal Salts[a]**

| Catalyst precursor | Presupport[b] | Sulfidation[c] | Reaction temperature/K 573 | 623 | 673 |
|---|---|---|---|---|---|
| Co(NO₃)₂ · 6H₂O | Al₂O₃ | Yes | 15.6 | 44.0 | 76.1 |
| NiCl₂ · 6H₂O | Al₂O₃ | Yes | 2.3 | 12.7 | 18.8 |
| Fe(NO₃)₃ · 9H₂O | Al₂O₃ | Yes | 0.2 | 1.3 | 2.9 |
| RuCl₃ · 3H₂O | Al₂O₃ | Yes | 8.7 | — | — |
| RuCl₃ · 3H₂O | Al₂O₃ | No | 6.6 | — | — |
| Co–Mo | Al₂O₃[d] | Yes | 84.4 | — | — |
| Co–Mo | Al₂O₃ | Yes | 4.2 | — | — |
| Co(NO₃)₂ · 6H₂O | TiO₂ | Yes | 41.2 | — | — |
| NiCl₂ · 6H₂O | TiO₂ | Yes | 4.4 | — | — |
| Fe(NO₃)₃ · 9H₂O | TiO₂ | Yes | 0.2 | — | — |
| RuCl₃ · 3H₂O | TiO₂ | Yes | 75.8 | — | — |
| RuCl₃ · 3H₂O | TiO₂ | No | 89.3 | — | — |

[a] Each conversion was determined after 5 h reaction time.

[b] Loading of precursor: 1.5 wt% based on metal.

[c] Presulfided by 10 vol% $H_2S$ in $H_2$ at 673 K.

[d] Alloy loaded on $Al_2O_3$ by 16.6 wt%.

notices that group IV metal oxides are good carriers. As the reaction temperature was lowered to 548 K and further down to 523 K, a difference in the catalytic activity among the group IV triad was observed, decreasing in the order Ti > Zr ≫ Hf. To address whether metal dispersity has a serious influence on the catalytic activity, the conversions (Cn) at 523 K using the $RuCl_3$ precursor were also measured with a 1.02 mg/m² fixed metal versus surface area, i.e., using $TiO_2(c)$ as the standard (Table 1). The normalized values Cnm again indicate that $TiO_2$ is far better than the other metal oxides.

Table 1 compares two crystal phases of $TiO_2$ (*a*, mixture of anatase 70% + rutile 30%, *b*, anatase 100%, *c*, rutile 100%). Though the surface areas of the three $TiO_2$ metal oxides examined were not exactly the same (see Methods), we concluded that the crystal form of $TiO_2$ had no important effect on the catalytic activity. Throughout the present work, $TiO_2(a)$ (7 : 3 mixture of anatase and rutile) was used.

Thus, $TiO_2$ as the partner of ruthenium, achieving nearly or over 80% conversions, appears to be a good choice for the reduction of $SO_2$ to sulfur by $H_2$. In the literature, $Ru/Al_2O_3$ (8, 17) and $Co/TiO_2$ (11) have been examined as catalysts of $SO_2$ reduction with $H_2$. To the best of our knowledge, however, the combination of Ru with $TiO_2$ has not been reported. To compare the present $Ru/TiO_2$ system to typically known metal catalysts (i.e., Co, Ni, and Fe) on either $Al_2O_3$ or $TiO_2$ supports, we examined all of these systems using the same reaction conditions. With the exception of the $RuTiO_2$ combination taken from Table 1, these precursors were sulfided *in situ* with $H_2S/H_2$ before testing the catalytic reaction. As shown in Table 2, the Co–Mo alloy

with 16 wt% loading showed a high conversion at 84%, in agreement with the data reported in the literature (9). However, the same alloy showed poor reactivity when diluted to the 1.5 wt% loading employed in the present work for $Ru/TiO_2$.

The results summarized in Table 2 suggest that the activity of the metals decreased in the order $Co > Ru > Ni > Fe$ with the $Al_2O_3$ support, whereas when these were supported on $TiO_2$ and the reaction was tested at 573 K, the order was $Ru \gg Co \gg Ni > Fe$. Therefore, the combination of Ru and $TiO_2$ is specific and gives the best result under our rather mild reaction conditions, i.e., low temperature and low metal loading.

## TiO₂-Supported Catalysts Derived from Various Ruthenium Precursors

The activities of the catalysts obtained from both cluster complex **1** and the $RuCl_3$ precursor are virtually similar when supported on $TiO_2$ with a reaction temperature higher than 523 K, as indicated in Table 1. However, the difference in reactivity of the catalysts derived from these two precursors became apparent when the reduction of $SO_2$ was carried out at lower temperature. Figure 1 plots the conversion of $SO_2$ to elemental sulfur as a function of reaction temperature. The light-off temperature observed for the $RuCl_3$-derived system is about 508 K, while the catalyst from cluster complex **1** maintains its high activity at 463 K.
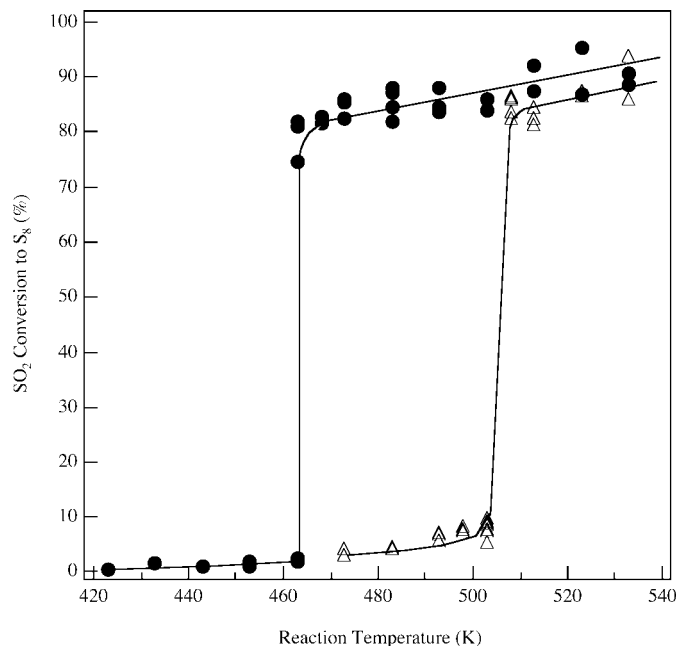
**FIG. 1.** Activity of the $TiO_2$-supported catalysts as a function of temperature. The catalysts were derived from cluster complex **1** (●) and $RuCl_3$ (△). Each spot was determined based on the yield of $S_8$ versus consumed $SO_2$ after 5 h reaction time.
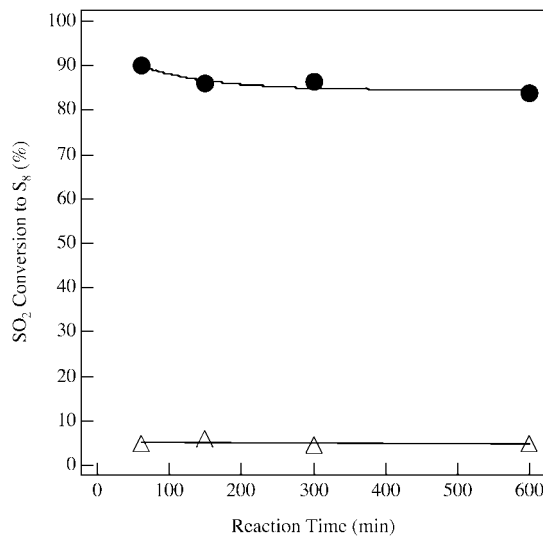
**FIG. 2.** Activity of the $TiO_2$-supported catalysts at 473 K as a function of time. The catalysts were derived from cluster complex **1** (●) and $RuCl_3$ (△). Each spot was determined by independent runs and based on the yield of $S_8$ versus consumed $SO_2$.

The change of catalytic activity versus reaction time at 473 K is depicted in Fig. 2, showing that the complex **1**-derived catalyst is robust and keeps its good constant activity at least up to 10 h reaction time. At this temperature, the activity of the $RuCl_3$-derived system remains low.

Other family members of the hexaruthenium cluster complexes **2–6** and mononuclear complex **7** were also used as precursors for the $TiO_2$-supported catalyst, and their catalytic activities at the 453–513 K temperature range are compared in Table 3. As shown in Table 3, the iron cluster analog **8** was completely inactive, and all the ruthenium precursors listed provide active catalysts at 513 K. Below this temperature, each complex shows its own light-off temperature, which may indicate their potential to produce active catalysts under mild conditions. The influence of the cationic portion is noteworthy, i.e., PPN in **1** and **4**, none in **3**, $PPh_4$ in **5**, and quaternary amine in **6**. The best cation among those examined is PPN, and the fact that PPN exists in close proximity to the $Ru_6$ unit is important. The mixture of [PPN]Cl and **3** was used for impregnation of $TiO_2$, which showed that the light-off temperature was similar to that of pure **3**. We tentatively assume that the cationic part has an influence on the formation steps of the catalyst particles (ruthenium sulfide) from the anionic cluster complex precursors, e.g., in their sizes and morphologies (33). The presence of an interstitial atom tends to give low-temperature active catalysts as is obvious by comparison of **2** to **1** and **4**. Mononuclear Ru(0) complex **7** produces a catalyst with an activity similar to that derived from $RuCl_3$; hence, our procedure in reducing $RuCl_3$ into Ru metal on $TiO_2$ may be appropriate, at least for the present $SO_2$ reduction system.

TABLE 3

Conversion of SO$_2$ to S$_8$ by TiO$_2$-Supported Catalysts Derived
from Cluster Complexes[a]

| Catalyst precursor | | Reaction temperature/K | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 453 | 463 | 473 | 483 | 493 | 503 | 508 | 513 |
| [PPN]$_2$[Ru$_6$C(CO)$_{16}$] | **1** | 2.8 | 81.9 | 84.3 | 84.7 | 85.1 | 86.1 | — | 90.1 |
| [PPN]$_2$[Ru$_6$(CO)$_{18}$] | **2** | — | — | 3.7 | 4.9 | 5.1 | 87.4 | — | 87.6 |
| Ru$_6$C(CO)$_{17}$ | **3** | — | — | 2.9 | 3.2 | 5.4 | 44.7 | — | 79.2 |
| [PPN][Ru$_6$H(CO)$_{18}$] | **4** | 2.3 | — | 83.5 | — | — | — | — | 88.3 |
| [PPh$_4$]$_2$[Ru$_6$C(CO)$_{16}$] | **5** | 1.8 | 2.0 | 3.1 | 78.6 | 88.8 | 90.4 | — | 92.3 |
| [Et$_3$NBz]$_2$[Ru$_6$C(CO)$_{16}$] | **6** | 1.5 | 2.8 | 3.3 | 3.8 | 6.4 | 86.2 | — | 90.1 |
| Ru(cod)(cot)[b] | **7** | — | — | — | — | — | 3.8 | 86.5 | 88.7 |
| RuCl$_3$ · 3H$_2$O | | 1.7 | 1.9 | 3.2 | 4.5 | 5.1 | 9.8 | 84.9 | 84.4 |
| [PPN]$_2$[Fe$_6$C(CO)$_{16}$] | **8** | — | — | — | — | — | — | — | 0.0 |

[a] Each conversion was determined after 5 h reaction time.

[b] cod = cyclooctadiene, cot = cyclooctatriene.

We also tested the trinuclear ruthenium carbonyl cluster Ru$_3$(CO)$_{12}$, since it was easily available and has been frequently used as a precursor for a supported Ru catalyst that hydrogenates unsaturated compounds (34–36). The Ru$_3$(CO)$_{12}$-derived catalyst, prepared as described under Methods, exhibited 85% conversion of SO$_2$ at the threshold temperature of 483 K; however, we cannot discuss this on a quantitative basis because Ru$_3$(CO)$_{12}$ easily sublimates from the TiO$_2$ bed during the initial vacuum treatment and contaminates the reaction system. One method is known that fixes Ru$_3$(CO)$_{12}$ on TiO$_2$ (37); however, in this procedure, the catalyst derived showed only low SO$_2$ conversion (5–10%) at the 473–523 K reaction temperature region.

### Selectivity of the Reaction by TiO$_2$-Supported Ruthenium Catalysis

In many cases, the reduction of SO$_2$ with H$_2$ over oxide-supported metal catalysts was suggested as proceeding via two independent steps occurring on two different sites. Hydrogenation of SO$_2$ to H$_2$S takes place on metal particles, and the successive Claus reaction (2H$_2$S + SO$_2$ ⇌ 3S + 2H$_2$O) completes the reduction on the support phase (9–12, 15, 17). Accordingly a small amount (≈5–10%) of toxic H$_2$S often results in being an inevitable by-product in reaction systems.

An advantage of the present Ru/TiO$_2$ system is that the outlet gas never contains H$_2$S as analyzed by the online GC. We confirmed that the Claus reaction could take place efficiently on TiO$_2$ at 523 K: when a mixture of H$_2$S and SO$_2$ was introduced over heated TiO$_2$, a good yield of S$_8$ was obtained. We believe, however, that the perfect selectivity of the present system to elemental sulfur basically originates from the feature of the Ru catalyst. When the hydrogenation of SO$_2$ was carried out with the Co/TiO$_2$ system at 573 K (see Table 2), a significant amount of H$_2$S was detected in the outlet gas. When the powder of unsupported RuS$_x$ ($x \approx 2$) was used as the catalyst for the hydrogenation at 523 and 623 K, *it converted* SO$_2$ to S$_8$ in yields of only 2 and 17%, respectively, while producing no appreciable amount of H$_2$S. Furthermore, all the reactions by Ru/support catalysts listed in Table 1 did not produce detectable amounts of H$_2$S whether either TiO$_2$ or other supports were used.

### CONCLUSIONS

The TiO$_2$-supported Ru metal, or Ru sulfide derived from Ru/TiO$_2$ during the reaction, is an excellent catalyst for reducing SO$_2$ to elemental sulfur by H$_2$, giving over 80% conversion with a calculated molar ratio (1 : 2) of the two reactant gases. The initial dispersion of Ru metal on TiO$_2$ was prepared from hexaruthenium carbonyl cluster complexes, as well as from ruthenium chloride, by an impregnation technique followed by the standard procedure of reduction to metal. In general, the catalyst systems based on the cluster complexes showed high activity at low reaction temperatures as compared to the catalyst derived conventionally from RuCl$_3$. Within the cluster complex-derived catalysts, the lowest temperature (threshold temperature) necessary to induce the catalytic reduction of SO$_2$ was dependent on the presence of an interstitial atom and a certain kind of cationic moiety, the best combination being complex **1**. The hexaruthenium carbido carbonyl complex **1** gave a catalyst that showed high activity at 463 K, while the catalyst obtained from RuCl$_3$ precursor did not show activity below 508 K.

Of the metal oxide supports examined, TiO$_2$ was the best one in terms of catalytic activity. Although the elucidation of its role must await future studies, TiO$_2$ may interact efficiently with ruthenium sulfide, inducing an enhanced catalytic reaction rate. Unlike the known systems for SO$_2$ hydrogenation, where reduction is achieved in two steps, i.e.,

reduction to H$_2$S on the supported metal sulfide phase and the successive reduction to sulfur on the support itself, the present system appears to give the final elemental sulfur on the metal sulfide phase. Thus the excellent selectivity for the production of elemental sulfur is primarily attributed to the feature of ruthenium. Further mechanistic study and characterization of the active catalyst are in progress.

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