

Supported ruthenium carbido-cluster catalysts for the catalytic removal of nitrogen monoxide and sulfur dioxide: the preparation process monitored by sulfur K-edge X-ray absorption near-edge structure

Yasuo Izumi,^a Taketoshi Minato,^a Ken-ichi Aika,^a Atsushi Ishiguro,^b Takayuki Nakajima,^b and Yasuo Wakatsuki^b

^aDepartment of Environmental Chemistry and Engineering, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan

^bInstitute of Physical and Chemical Research, 2-1, Hirosawa, Wako, Saitama 351-0198, Japan

The preparation process of ruthenium carbido-cluster catalysts for the reduction of sulfur dioxide was traced by means of sulfur K-edge X-ray absorption near-edge structure (XANES). During the activation process, a pair of peaks at 2472.5 – 2472.8 and 2482.7 – 2482.8 eV appeared. The pair was ascribed to the RuS_x phase. Once the catalysts were activated at 503 – 573 K, another pair of peaks at 2474.2 and 2479.2 eV appeared. The pair was assigned to the π* and σ* transition peaks, respectively, of adsorbed SO₂ molecules on the catalyst surface.

1. INTRODUCTION

Catalytic removal of nitrogen oxides [1] and sulfur oxides [2] is one of the most important issues in environmental problems. We have investigated supported ruthenium carbido-cluster catalysts derived from [Ru₆C(CO)₁₆]²⁻ crystal. The supported cluster was

found to be good catalyst for sulfur dioxide reduction to elemental sulfur by hydrogen gas [3, 4] and nitric oxide reduction by carbon monoxide [5].

The difference in catalytic activity between supported cluster catalysts and conventional impregnated catalysts is interpreted on the basis of the metal site structure (coordination and particle size), the structural/electronic effects of support materials to the metal site, and the kinds of adsorbed/intermediate species on the surface [6–8]. In the cases of SO_2 and NO reduction, the former two factors were recently investigated by ruthenium K-edge extended X-ray absorption fine structure (EXAFS) [4,5,9].

In this manuscript, the third factor was studied by sulfur K-edge X-ray absorption near-edge structure (XANES). Infrared absorption spectroscopy is often used to monitor the adsorbed/intermediate species on the surface. However, by infrared absorption, the atoms dissociated from reactant molecules that are buried into the catalysts are often inaccessible, e.g. sulfur atom of SO_2 dissociated and reacted to form the RuS_x phase. The major objective of this paper is to monitor both adsorbed and buried sulfur atoms by S K-edge XANES in the preparation process of supported ruthenium catalysts.

2. EXPERIMENTAL SECTION

The crystal of $[(\text{Ph}_3\text{P})_2\text{N}]_2[\text{Ru}_6\text{C}(\text{CO})_{16}]$ (**1**) was reacted in purified THF in argon atmosphere with titania. The support material was fixed to TiO_2 because the cluster on TiO_2 exhibited higher activity for the SO_2 reduction than the cases supported on other inorganic oxides. As a reference, a conventional Ru catalyst was impregnated with aqueous $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ solution. Ru content was 1.5 wt% in both cases. These catalysts are denoted as $[\text{Ru}_6\text{C}]/\text{TiO}_2$ and conv-Ru/ TiO_2 , respectively.

The incipient catalysts were heated in vacuum for 1.5h and then reduced for 3h with hydrogen both at 573 K. The catalysts were reacted in a gas flow system (flow rate $60 \text{ cm}^3 \text{ min}^{-1}$) of SO_2 (33.8 kPa) + H_2 (67.5 kPa) at 443 – 573 K. Produced elemental sulfur was flushed in the argon flow at each reaction temperature for 2h to be separated from the catalyst, and the catalyst sample was transferred to *in-situ* glass cell and sealed by fire. The cell is made of Pyrex glass with the $12.5 \mu\text{m}$ -Kapton (Toray-Dupont) films on both sides.

S K-edge XANES data were measured in fluorescence excitation mode at KEK-PF (Tsukuba, Japan) using beamline 9A with a Ni/Rh coated harmonic rejection mirror and a fully-tuned Si(111) double crystal monochromator under ring conditions of 2.5 GeV and 390 – 270 mA. The entire path of the X-rays beam was in a He atmosphere. The samples were at room temperature. The detection gas was nitrogen for ion chamber to collect the X-ray fluorescence originated from the sample [10]. The photon energy was calibrated by assigning the maximum of the first pre-edge feature in the XANES spectrum of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ to 2472.02 eV [11].

3. RESULTS

The sulfur K-edge XANES spectra of ruthenium catalysts are shown in Fig. 1A. The $[\text{Ru}_6\text{C}]/\text{TiO}_2$ samples were reacted in $\text{SO}_2 + \text{H}_2$ at 443 (a) and 503 K (b). The conv-Ru/ TiO_2 samples were reacted in $\text{SO}_2 + \text{H}_2$ at 473 (e) and 573 K (f). Both catalysts were inactive at 443 K, and became active when elevated to 468 and 503 K, respectively, for the reaction to catalytically produce elemental sulfur. These spectra in the process of active catalyst preparation are compared to spectra of amorphous RuS_x ($x = 2, 3, 6$) species prepared from the mixture of H_2S (10.1 kPa) and H_2 (91.2 kPa) gas at 573 K [9] (c), SO_2 (101.3 kPa) adsorption at 290 K (d) both over $[\text{Ru}_6\text{C}]/\text{TiO}_2$ catalysts, and standard inorganic and organometallic compounds (Fig. 1B) for elemental sulfur S_8 (g), bulk RuS_x ($x = 2, 3, 6$; the mixture of these, but 2 may be major) (h), the crystal of $\text{Ru}_3(\text{CO})_9(\mu_2\text{-H})_2(\mu_3\text{-S})$ (i), $\text{Ru}_6\text{C}(\text{CO})_{15}(\mu_3\text{-SO})$ (j), and $[(\text{Ph}_3\text{P})_2\text{N}]_2[\text{Ru}_6\text{C}(\text{CO})_{15}(\mu_2\text{-SO}_2)]$ (k) [12].

Two typical strong peaks were observed at 2474.2 and 2479.2 eV for activated $[\text{Ru}_6\text{C}]/\text{TiO}_2$ catalyst (Fig. 1b). The two peaks were also observed at the same energy positions for activated conv-Ru/ TiO_2 catalyst (f). These two peaks are denoted as Pair A. Compared to these activated catalysts, two strong peaks were observed at 2472.8 and 2482.7 eV for inactive $[\text{Ru}_6\text{C}]/\text{TiO}_2$ catalyst (a) and at essentially the same energy positions for inactive conv-Ru/ TiO_2 (e). These two peaks are denoted as Pair B. The trend of peak intensity increase/decrease was followed by progressive augmentation of the reaction temperature: 443 (Figure 1a), 473 (not shown), and 503 K (b) for the $[\text{Ru}_6\text{C}]/\text{TiO}_2$ catalyst and at 473 (e), 523 (not shown), and 573 K (f) for the conv-Ru/ TiO_2 catalyst. The ratio of peak intensity

did not change in each Pair A and B, strongly suggesting that two peaks in a pair were derived from the common kind of sulfur site.

Two strong peaks appeared at similar energies (2475.6 and 2479.3 eV) to Pair A for $[\text{Ru}_6\text{C}(\text{CO})_{15}(\mu_2\text{-SO}_2)]^{2-}$ (Figure 1k). The differences from the corresponding peak in Pair A (Figure 1b, f) were 0.1 – 1.4 eV. When SO_2 gas was adsorbed on the $[\text{Ru}_6\text{C}]/\text{TiO}_2$ at 290 K (d), two strong peaks appeared exactly at the same energies as (b). Thus, Pair A was ascribed to adsorbed SO_2 molecules on the $[\text{Ru}_6\text{C}]/\text{TiO}_2$ catalyst. Two peaks at 2474.2 and 2479.2 eV are ascribed to the transitions to π^* and σ^* , respectively [13].

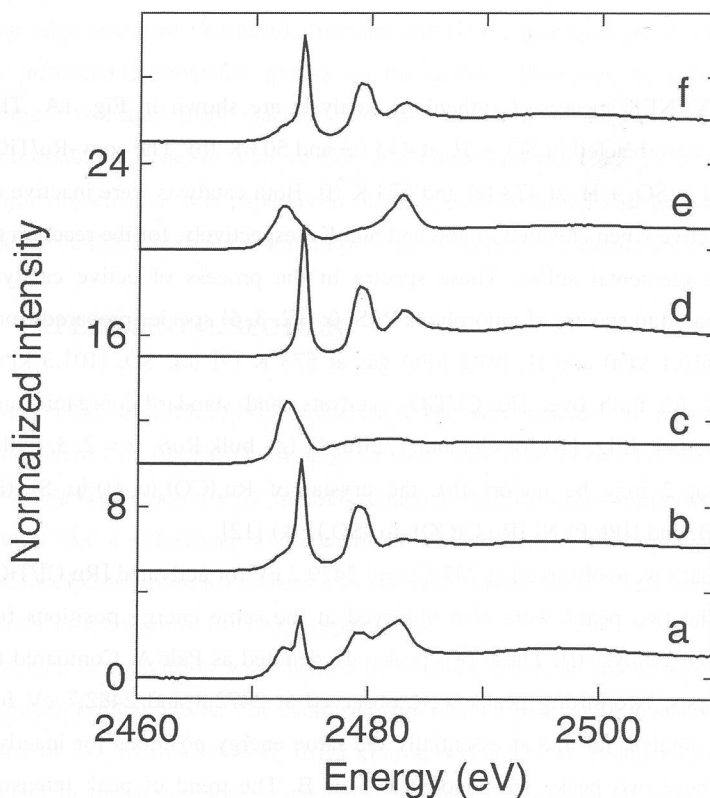


Figure 1. (A) S K-edge spectra for the $[\text{Ru}_6\text{C}]/\text{TiO}_2$ catalysts in $\text{SO}_2 + \text{H}_2$ at 443 (a), 503 K (b), in $\text{H}_2\text{S} + \text{H}_2$ at 573 K (c), and in SO_2 at 290 K (d), and conv-Ru/TiO₂ catalysts in $\text{SO}_2 + \text{H}_2$ at 473 (e) and 573 K (f).

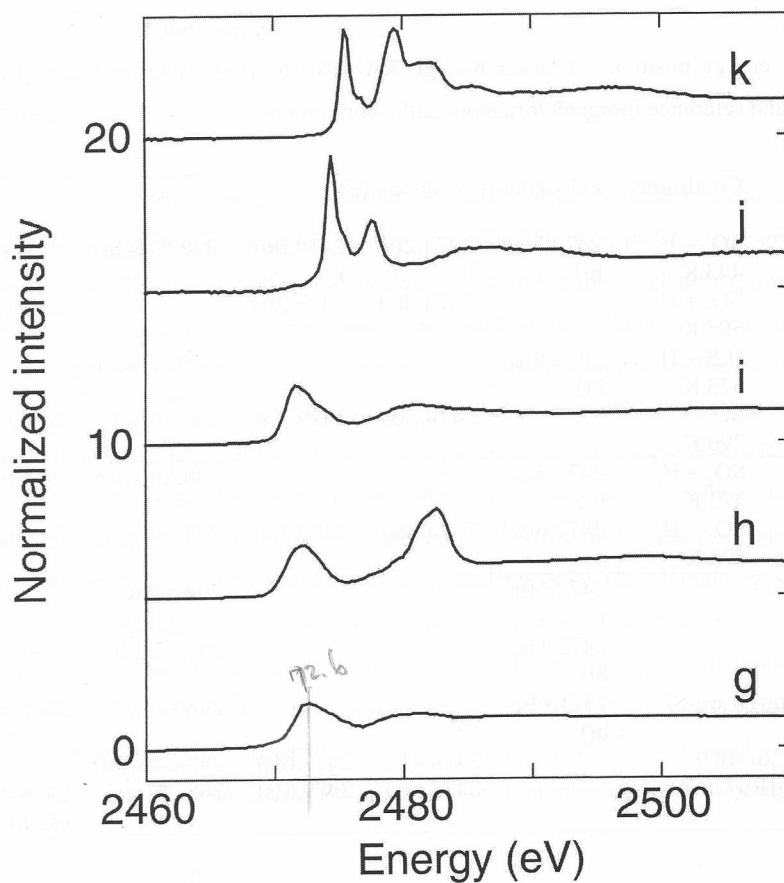


Figure 1. (B) S K-edge spectra for elemental sulfur S_8 (g), RuS_x ($x = 2, 3, 6$) (h), and the crystal of $Ru_3(CO)_9(\mu_2-H)_2(\mu_3-S)$ (i), $Ru_6C(CO)_{15}(\mu_3-SO)$ (j), and $[(Ph_3P)_2N]_2[Ru_6C(CO)_{15}(\mu_2-SO_2)]$ (k).

u_3
 Kim, Peden
 S
 2472.6
 2472
 Baso4 $Al_2(SO_4)_3$
 2482.4 2483.2
 2481.8 2482.6

Table 1.

The Peak energy positions of sulfur K-edge XANES for $[\text{Ru}_6\text{C}]/\text{TiO}_2$ and conv-Ru/ TiO_2 catalysts and reference inorganic/organometallic compounds

Catalyst/ Sample	Conditions	Peak energy positions (eV)				
$[\text{Ru}_6\text{C}]/\text{TiO}_2$	$\text{SO}_2 + \text{H}_2$ 443 K	2472.8(s, br)	2474.2(m)	2479.0(m)	2482.7(s,br)	2497(w,br)
	$\text{SO}_2 + \text{H}_2$ 503 K		2474.2(s)	2479.2(s)		2496.7(w,br)
	$\text{H}_2\text{S} + \text{H}_2$ 573 K	2472.9(s, br)			2480.7(w,br)	
	SO_2 290 K		2474.2(s)	2479.2(s)	2483.0(w)	2497(w,br)
Conv- Ru/ TiO_2	$\text{SO}_2 + \text{H}_2$ 473 K	2472.5(s, br)			2482.8(s,br)	2498(w,sh)
	$\text{SO}_2 + \text{H}_2$ 573 K	2472.6(w)	2474.2(s)	2479.2(s)	2483.0(w)	2496(w,sh)
S_8		2472.6(m)			2481.1(w)	
RuS_x		2472.1(s, br)			2482.5(s,br)	2498 (w,sh)
$\text{Ru}_3(\text{CO})_9(\mu_2\text{-H})_2(\mu_3\text{-S})$		2471.6(s, br)			2480.7(w,br)	2505(w,sh)
$\text{Ru}_6\text{C}(\text{CO})_{15}(\mu_3\text{-SO})$ [[$(\text{Ph}_3\text{P})_2\text{N}]_2[\text{Ru}_6\text{C}(\text{CO})_{15}(\mu_2\text{-SO}_2)]$]			2474.4(s)	2477.6(s)	2484.4(w,br)	
			2475.6(s)	2479.3(s)	2482.1(m)	2496.4 (w,sh)

The two peaks of Pair B (Figure 1a, e) were broader than those of Pair A. Relatively broad two peaks were observed at 2472.1 and 2482.5 eV for RuS_x (h). The differences from the corresponding peaks in Pair B were 0.2 – 0.7 eV. Two peaks were also observed at 2472.6 and 2481.1 eV for S_8 (g). The differences from the corresponding peaks in Pair B were 0.1 – 1.7 eV. Note that the peak intensity and the broadness of Figure 1g varied as the elemental sulfur sample was progressively diluted by boron nitride. Thus, Pair B is ascribed basically to sulfide, but the possibility that a part of produced elemental sulfur remained after the argon flush at the reaction temperature cannot be excluded. The first peak (2472.9 eV) in the spectrum for RuS_x species prepared from $\text{H}_2\text{S} + \text{H}_2$ on the $[\text{Ru}_6\text{C}]/\text{TiO}_2$ catalyst (Figure 1c) appeared at similar energy to that for RuS_x (2472.1 eV, h). However, the second peak at 2480.7 eV was very weak in (c) compared to that in (h). The

reason is unclear at the moment.

4. DISCUSSION

Pairs A and B were assigned to adsorbed SO_2 and sulfide bonded to ruthenium atoms, respectively. The activation of Ru catalysts was dependent on the heating temperature of catalysts. Pair B appeared when the catalysts were still inactive. Hence, ruthenium metal microparticles were first sulfided and then exhibited the catalytic reactivity to form elemental sulfur from SO_2 . The difference of sulfidation temperature for the $[\text{Ru}_6\text{C}]/\text{TiO}_2$ (503 K) and conv-Ru/ TiO_2 catalysts (573 K) may be originated from each Ru particle size. In general, smaller $[\text{Ru}_6]$ cluster is more reactive than larger Ru particles (10 – 50 Å) of conventional catalysts [14]. Pair A was exclusively observed in addition to the weak shoulder peaks of Pair B (Fig. 1A). Therefore, the surface during the catalysis of the $\text{SO}_2 + \text{H}_2$ reactions should be predominantly occupied by SO_2 . The elementary step of SO_2 dissociation to $\text{SO}(\text{ads})$ may be the rate-determining step of overall reaction.

The database to identify and evaluate the adsorbed, intermediate, and incorporated sulfur species was listed in Table 1 to investigate the SO_2 reduction and possibly also the desulfurization reaction. Further discussion of reaction mechanism of catalysis will need the combination of S K-edge XANES and pulse reaction measurements at beamline.

ACKNOWLEDGEMENT

The experiments were performed under the approval of the KEK-PF Program Review Committee (2000P018).

REFERENCES

1. M. Shelef, Chem. Rev., 95 (1995) 209.
2. S. C. Paik and J. S. Chung, Appl. Catal. B Environmental, 8 (1996) 267.
3. A. Ishiguro, Y. Liu, T. Nakajima and Y. Wakatsuki, J. Catal., in press.
4. Ishiguro, Y. Liu, T. Nakajima, T. Minato, F. Kiyotaki, Y. Izumi, K. Aika and Y.

- Wakatsuki, Syokubai (Catalysts), 43(6) (2001) 382.
5. T. Minato, A. Ishiguro, T. Nakajima, Y. Izumi, K. Aika and Y. Wakatsuki, in preparation.
 6. Y. Izumi and Y. Iwasawa, CHEMTECH, 24(7) (1994) 20.
 7. Y. Izumi and K. Aika, J. Phys. Chem., 99 (1995) 10336.
 8. Y. Izumi and K. Aika, J. Phys. Chem., 99 (1995) 10346.
 9. Ishiguro, T. Nakajima, T. Iwata, M. Fujita, T. Minato, F. Kiyotaki, Y. Izumi, K. Aika, M. Uchida, K. Kimoto, Y. Matsui and Y. Wakatsuki, Chem. Eur. J., submitted.
 10. F. W. Lytle, R. B. Gregor, D. R. Sandstrom, E. C. Marques, J. Wong, C. L. Spiro, G. P. Huffman and F. E. Huggins, Nucl. Instr. Meth. Phys. Res. 226 (1984) 542.
 11. Y. Izumi, T. Glaser, K. Rose, J. McMaster, P. Basu, J. H. Enemark, B. Hedman, K. O. Hodgson and E. I. Solomon, J. Am. Chem. Soc., 121 (1999) 10035.
 12. Y. Wakatsuki and T. Chihara, Bull. Chem. Soc. Jpn., 72 (1999) 2357.
 13. H. Sekiyama, N. Kosugi, H. Kuroda and T. Ohta, Bull. Chem. Soc. Jpn., 59 (1986) 575.
 14. Y. Izumi, Y. Iwata and K. Aika, J. Phys. Chem., 100 (1996) 9421.