

# XAFS Characterization of Dispersed Ru Nanoclusters Transformed from A Grafted Trinuclear Ru Complex on SiO<sub>2</sub> for Selective Alcohol Oxidation

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## Introduction

Ru nanoclusters (average diameter = 1.3 ± 0.3 nm) were successfully prepared by using a Ru<sub>3</sub> cluster Ru<sub>3</sub>O(CH<sub>3</sub>COO)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>·(CH<sub>3</sub>COO) grafted on a pyridine-functionalized SiO<sub>2</sub> surface. The local coordination structures of the prepared Ru nanoclusters, which were found to be efficient for the selective oxidation of alcohols, were investigated by Ru K-edge XAFS.

## Experimental

A SiO<sub>2</sub>-supported Ru<sub>3</sub> cluster (**2**) was prepared by the attachment of a Ru<sub>3</sub> trinuclear complex Ru<sub>3</sub>O(CH<sub>3</sub>COO)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>·(CH<sub>3</sub>COO) (**1**) on a SiO<sub>2</sub> surface functionalized with pyridine ligands. A SiO<sub>2</sub>-supported Ru nanocluster catalyst (**3**) was prepared by heating at 823 K for 2 h under the vacuum, following H<sub>2</sub> (40 kPa) reduction (823 K, 1 h). Catalyst (**4**) was prepared by heating at 823 K for 2 h under air, following H<sub>2</sub> (40 kPa) reduction (823 K, 1 h), and catalyst (**5**) was prepared by heating at 823 K for 2 h under air.

Ru K-edge XAFS was measured in a transmission mode at 20 K at the NW10A station with a Si(311) double-crystal monochromator. EXAFS spectra were analyzed using ATHENA and ARTEMIS programs. *k*<sup>3</sup>-Weighted EXAFS oscillations were Fourier transformed into *R*-space, and curve-fitting analysis was performed in *R*-space with coordination number (CN), interatomic distance (*R*), Debye-Waller factor ( $\sigma^2$ ), and correction-of-edge energy ( $\Delta E_0$ ). Phase shifts and backscattering amplitudes were calculated by the FEFF8 code using the crystal structures of Ru metal, RuO<sub>2</sub>, and **1**.

## Results and Discussion

The local coordination structures of the the SiO<sub>2</sub>-supported Ru<sub>3</sub> complex and Ru nanocluster were examined by Ru K-edge EXAFS analysis, whose structural parameters are listed in Table 1. The local coordination structure of the supported Ru<sub>3</sub> complex on **2** was similar to **1**, indicating the dispersed grafting of **1** on SiO<sub>2</sub> surface without decomposition. Ru K-edge EXAFS of **3** showed exhibited a new peak at 0.2-0.3 nm, together with a strong peak at 0.16 nm. They were curve-fitted to be a combination of Ru-Ru bonds at 0.266 ± 0.003 nm (CN = 2.0 ± 1.1), Ru···Ru contribution at 0.305 ± 0.003 nm (CN = 1.3 ± 0.8), and Ru-O at 0.202 ± 0.001 nm (CN = 3.9 ± 0.5). This result supported the formation of dispersed Ru nanoclusters (average diameter = 1.3 ± 0.3

nm from TEM analysis) and suggested the presence of both metallic and oxidized Ru species on **3**. **3** was significantly active for the selective oxidation of benzyl alcohol. The Turnover number (TON) was 91.4 with 90.4% of aldehyde selectivity after 6 h. For **4** and **5**, metallic Ru and RuO<sub>2</sub> particles were respectively observed, both of them showed low activity for the benzyl alcohol oxidation (TON was 3.1 and 5.2 for 6 h).

**Table 1** Structural Parameters Determined by Curve-Fitting Analysis of Ru K-edge EXAFS Measured at 20 K

Shell	CN	<i>R</i> /nm	$\Delta E_0$	$\sigma^2 / \times 10^5 \text{ nm}^2$
<b>1</b> [Ru <sub>3</sub> (μ <sub>3</sub> -O)(CH <sub>3</sub> COO) <sub>6</sub> (H <sub>2</sub> O) <sub>3</sub> ] CH <sub>3</sub> COO <sup>a</sup>				
Ru···Ru	2	0.331 ± 0.001	-2 ± 4	3 ± 1
Ru-O (μ <sub>3</sub> -O)	1	0.190 ± 0.003	0 ± 2	4 ± 1
Ru-O (ligands)	5	0.204 ± 0.001	0 ± 2	4 ± 1
Ru···C (CH <sub>3</sub> COO)	4	0.300 ± 0.003	0 ± 2	4 ± 1
Ru···O (CH <sub>3</sub> COO)	4	0.331 ± 0.004	0 ± 2	4 ± 1
<b>2</b> (Ru: 3 wt%) <sup>b</sup>				
Ru···Ru	1.9 ± 0.7	0.332 ± 0.001	-2 ± 4	3 ± 4
Ru-O (μ <sub>3</sub> -O)	0.9 ± 0.2	0.189 ± 0.003	1 ± 2	4 ± 1
Ru-O/N (ligands)	5.1 ± 0.7	0.204 ± 0.001	1 ± 2	4 ± 1
Ru···C (CH <sub>3</sub> COO)	3.7 ± 0.7	0.301 ± 0.003	1 ± 2	4 ± 1
Ru···O (CH <sub>3</sub> COO)	3.7 ± 0.7	0.331 ± 0.006	1 ± 2	4 ± 1
<b>3</b> (Ru: 3 wt%) <sup>c</sup>				
Ru-Ru	2.0 ± 1.1	0.266 ± 0.003	3 ± 4	10 ± 4
Ru···Ru	1.3 ± 0.8	0.305 ± 0.004	3 ± 4	10 ± 4
Ru-O	3.9 ± 0.5	0.202 ± 0.001	13 ± 2	8 ± 1
<b>4</b> (Ru: 3 wt%) <sup>d</sup>				
Ru-Ru	11.3 ± 0.6	0.268 ± 0.001	6 ± 1	3 ± 1
<b>5</b> (Ru: 3 wt%) <sup>e</sup>				
Ru···Ru	1.8 ± 0.3	0.312 ± 0.001	9 ± 1	2 ± 1
Ru···Ru	7.8 ± 0.7	0.356 ± 0.001	9 ± 1	2 ± 1
Ru-O	5.3 ± 1.2	0.198 ± 0.001	11 ± 3	3 ± 2

<sup>a</sup> *k* = 30–160 nm<sup>-1</sup>, *R* = 0.10–0.33 nm, *R*<sub>f</sub> = 1.6%. <sup>b</sup> *k* = 30–160 nm<sup>-1</sup>, *R* = 0.10–0.33 nm, *R*<sub>f</sub> = 1.7%. <sup>c</sup> *k* = 30–160 nm<sup>-1</sup>, *R* = 0.11–0.30 nm, *R*<sub>f</sub> = 1.7%. <sup>d</sup> *k* = 30–160 nm<sup>-1</sup>, *R* = 0.16–0.30 nm, *R*<sub>f</sub> = 0.2%. <sup>e</sup> *k* = 30–160 nm<sup>-1</sup>, *R* = 0.10–0.36 nm, *R*<sub>f</sub> = 1.7%.

## Reference

[1] S. Muratsugu, M. H. Lim, T. Itoh, W. Thymrongpatanaraks, M. Kondo, S. Masaoka, T. S. A. Hor, M. Tada, *Dalton Trans.* **2013**, in press.

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