

XAFS Characterization of K-AluC-Supported Ru Cluster Catalysts for Selective Nitrile Hydrogenation

Fei WANG^{1,2}, Sutasinee KITAYAKARN¹, Nozomu ISHIGURO¹, Satoshi MURATSUGU^{1,2}, Mizuki TADA*^{1,2}

¹ Institute for Molecular Science, Myodaiji, Okazaki, Aichi 444-8585, Japan.

² Department of Chemistry, Graduate School of Science, Nagoya University, Furo, Chikusa, Aichi 464-8602, Japan.

Introduction

Supported ruthenium cluster catalysts were prepared by the attachment of Ru₃(CO)₁₂ on various oxide surfaces. Catalytic performance on hydrogenation of valeronitrile highly depended on the type of oxide supports of catalysts. Among all, K-doped AluC-supported Ru cluster catalyst (Ru/K-AluC) exhibited significant activity and high selectivity to corresponding primary amine for the hydrogenation of valeronitrile. The local coordination structures of active Ru catalysts were investigated by Ru K-edge EXAFS analysis.

Experimental

A 4 wt% Ru/K-AluC catalyst was prepared by a wet impregnation method, and valeronitrile hydrogenation reactions were conducted in *n*-heptane under 101.3 kPa of H₂ at 343 K. Ru K-edge XAFS was measured in transmission mode at 20 K at the NW10A station with a Si(311) double-crystal monochromator. The energy and current of electrons in the storage ring were 6.5 GeV and 60 mA, respectively. Ionization chambers filled with pure Ar and pure Kr were used to monitor incident and transmitted X-rays, respectively.

EXAFS spectra were analysed with IFEFFIT (Athena and Artemis) ver. 1.2.11^[1,2]. *k*³-Weighted EXAFS oscillations (30–150 nm⁻¹) were Fourier transformed into *R*-space, and curve-fitting analysis was carried out in *k*-space. Fitting parameters were coordination number (CN), interatomic distance (*R*), Debye-Waller factor (σ^2), and correction of edge energy (ΔE_0). Phase shifts and backscattering amplitudes for Ru-Ru and Ru-O were calculated by using Ru metal and RuO₂.

Results and Discussion

The valence states of Ru were investigated by Ru K-edge XANES as shown in Figure 1. The treatment of fresh Ru/K-AluC with *n*-heptane solvent under N₂ at 343 K for 20 min caused the shift of Ru edge energy from 22122 to 22117 eV, suggesting the reduction of Ru. After nitrile hydrogenation, it was unchanged at 22117 eV.

The local coordination structures of the Ru/K-AluC catalyst were examined by Ru K-edge EXAFS analysis, and structural parameters are listed in Table 1. The fresh catalyst had Ru-O interaction at 2.02 ± 0.01 Å, whose

coordination number (CN) was estimated to be 2.7 ± 0.4, and it disappeared after the treatment with *n*-heptane. The CN of Ru-Ru at 2.66 ± 0.01 Å, which was observed on the fresh catalyst (3.9 ± 0.9), increased to 5.7 ± 0.6 on the *n*-heptane-treated catalyst, suggesting that the clusterization of the supported Ru species proceeded. The CN of Ru-Ru of the catalyst after the nitrile hydrogenation was 6.1 ± 1.0, which was similar to that of the *n*-heptane-treated catalyst, indicated that the Ru cluster was efficient for the nitrile hydrogenation.

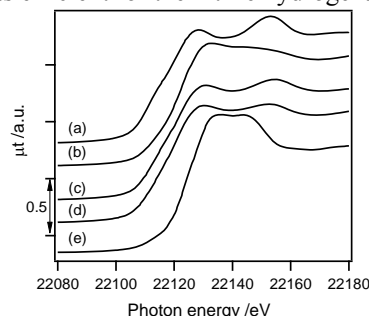


Figure 1 Ru K-edge XANES spectra of (a) Ru powder, (b) fresh Ru/K-AluC, (c) Ru/K-AluC treated with *n*-heptane, (d) Ru/K-AluC after the nitrile hydrogenation, and (e) RuO₂.

Table 1 Curve-fitting results of Ru K-edge EXAFS Fourier transforms of the K-AluC supported Ru cluster catalysts (Ru: 4 wt%)^a

Shell	CN	<i>R</i> / Å	ΔE_0 / eV	σ^2 / × 10 ⁻⁵ nm ²
as prepared <i>R</i> _f = 0.1 %				
Ru-O	2.7 ± 0.4	2.02 ± 0.01	8 ± 2	7 ± 1
Ru-Ru	3.7 ± 0.9	2.66 ± 0.01	6 ± 2	8 ± 1
Ru-Al	1.0 ± 0.5	2.85 ± 0.03	12 ± 5	2 ± 3
treated with <i>n</i>-heptane <i>R</i> _f = 1.0 %				
Ru-Ru	5.7 ± 0.6	2.66 ± 0.01	12 ± 5	7 ± 1
after hydrogenation for 12 h <i>R</i> _f = 1.8 %				
Ru-Ru	6.1 ± 1.0	2.65 ± 0.01	0 ± 2	7 ± 1

^a *k* range and *R* range were 3–15 Å⁻¹ and 1.3–3.0 Å, respectively.

References

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* mtada@chem.nagoya-u.ac.jp