

XAFS Characterization of N-Heterocyclic Carbene-attached Cr and Rh-incorporated Ceria (NHC-*r*-Cr_{0.19}Rh_{0.06}CeO₂)

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1 Introduction

ICy-*r*-Cr_{0.19}Rh_{0.06}CeO₂ was newly prepared by the attachment of 1,3-dicyclohexylimidazol-2-ylidene (ICy) on H₂-reduced Cr_{0.19}Rh_{0.06}CeO₂ (*r*-Cr_{0.19}Rh_{0.06}CeO₂),^[1] and it showed catalytic activity for the 1,4-arylation of cyclohexenone with phenylboronic acid, whereas *r*-Cr_{0.19}Rh_{0.06}CeO₂ without ICy was inactive.^[2] We investigated the local coordination structures of ICy-*r*-Cr_{0.19}Rh_{0.06}CeO₂ and *r*-Cr_{0.19}Rh_{0.06}CeO₂ before and after the attachment of ICy.^[2]

2 Experimental

Rh K-edge XAFS of ICy-*r*-Cr_{0.19}Rh_{0.06}CeO₂ and *r*-Cr_{0.19}Rh_{0.06}CeO₂ were measured in a transmission mode at room temperature at the NW10A station with a Si(311) double-crystal monochromator. Samples were grounded and packed into a cell, and the cell was sealed with Kapton films under an Ar atmosphere so as not to be exposed to the air. EXAFS spectra were analyzed using ATHENA and ARTEMIS programs. *k*³-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 (σ^2), and correction-of-edge energy (ΔE_0). Phase shifts and backscattering amplitudes were calculated by the FEFF8.

3 Results and Discussion

Figure 1 shows Rh K-edge EXAFS Fourier transforms of ICy-*r*-Cr_{0.19}Rh_{0.06}CeO₂ and *r*-Cr_{0.19}Rh_{0.06}CeO₂, and curve-fitted structural parameters are summarized in Table 1. The curve-fitted CN and *R* for Rh-Rh bond of ICy-*r*-Cr_{0.19}Rh_{0.06}CeO₂ were 1.3 ± 0.2 and 0.207 ± 0.001 nm, respectively, and those of *r*-Cr_{0.19}Rh_{0.06}CeO₂ without ICy modification were also 1.3 ± 0.2 and 0.207 ± 0.001 nm, respectively. The curve-fitted CN and *R* for Rh-O bond (the interaction between Rh nanocluster and the surface of *r*-Cr_{0.19}Rh_{0.06}CeO₂) of ICy-*r*-Cr_{0.19}Rh_{0.06}CeO₂ were 2.8 ± 0.3 and 0.262 ±

0.001 nm, respectively, and those of *r*-Cr_{0.19}Rh_{0.06}CeO₂ without ICy modification were also 2.8 ± 0.4 and 0.261 ± 0.001 nm, respectively. The similar values indicated the maintenance of Rh nanocluster structure on the surface.

FT-IR, XPS, and photoluminescence spectroscopy showed that the ICy was existed as carbene species on the surface of *r*-Cr_{0.19}Rh_{0.06}CeO₂, and ICy-*r*-Cr_{0.19}Rh_{0.06}CeO₂ exhibited catalytic performances for 1,4-arylation of cyclohexenone (yield: >99%). On the other hand, Cr_{0.19}Rh_{0.06}CeO₂ (without ICy) did not show any catalytic activity for the 1,4-arylation, suggesting that the interaction of the ICy carbene ligand with the Rh nanocluster played a key role to induce the catalytic activity. DFT calculations suggested that ICy carbene ligand controlled the adsorption sites of the phenyl group on the Rh nanocluster to promote the C-C bond formation of the phenyl group and cyclohexenone.

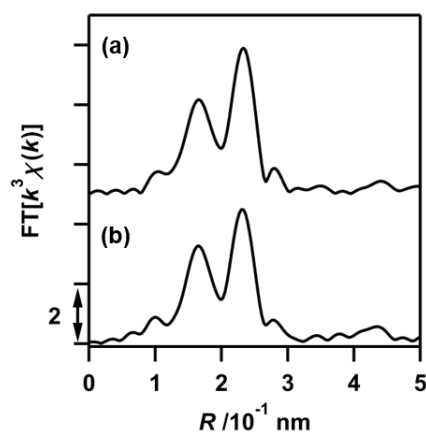


Figure 1. Rh K-edge EXAFS FTs of (a) ICy-*r*-Cr_{0.19}Rh_{0.06}CeO₂ and (b) *r*-Cr_{0.19}Rh_{0.06}CeO₂.

Table 1. Curve-fitting Results of Rh K-edge EXAFS Fourier Transforms of ICy-*r*-Cr_{0.19}Rh_{0.06}CeO_z and *r*-Cr_{0.19}Rh_{0.06}CeO_z^a

Shell	CN	<i>R</i> /nm	ΔE_0 /eV	$\sigma^2 / \times 10^{-5}$ nm ²
ICy- <i>r</i> -Cr _{0.19} Rh _{0.06} CeO _z				
Rh–O	1.3 ± 0.2	0.207 0.001	± 10 ± 2	5 ± 1
Rh–Rh	2.8 ± 0.3	0.262 0.001	± -2 ± 1	10 ± 1
<i>r</i> -Cr _{0.19} Rh _{0.06} CeO _z				
Rh–O	1.3 ± 0.2	0.207 0.001	± 9 ± 2	5 ± 1
Rh–Rh	2.8 ± 0.4	0.261 0.001	± -2 ± 1	10 ± 1

^a *k* range and *R* range were 30-140 nm⁻¹ and 0.12-0.27 nm, respectively.

References

- [1] S. Ikemoto *et al.*, *Phys. Chem. Chem. Phys.* **21**, 20868-20877 (2019).
 [2] S. Ikemoto *et al.*, *J. Am. Chem. Soc.* **145**, 1497-1504 (2023).

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