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Carbon-supported RhRu catalyst for arene C–H bond activation

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1 Introduction

It has been demonstrated that bimetallic nanoparticles and clusters exhibit novel catalysis derived from unique geometric and electronic structures.[1] Since the noble metal elements contained in bimetallic catalysts are generally zerovalent, little is known about the catalysis of bimetallic oxide nanoparticles and clusters based on noble metal elements.

In this study, it was found that carbon-supported RhRu catalyst showed remarkably high catalytic activity for the oxidative coupling of arenes and carboxylic acids using O_2 as the sole oxidant. Structural analysis by HAADF-STEM, EDS, and XAS revealed that the RhRu bimetallic oxide clusters ($RhRuO_x$) were the active species of the catalyst.

2 Experiment

Catalysts were prepared by the deposition of pre-formed metal colloids on activated carbon. The colloidal metal particles were synthesized by the ethylene glycol reduction of precursor metal ions in the presence of NaOH. Catalytic reactions were conducted by heating the stainless reactor containing a catalyst, benzene, acetic acid, and O_2 at 150 °C. X-ray absorption spectroscopy was carried out at the NW10A beamline in PF-AR of High Energy Accelerator Research Organization.

3 Results and Discussion

Monometallic and bimetallic catalysts were applied to the oxidative coupling of benzene and acetic acid (**Fig. 1**). Among the monometallic catalysts, Rh/C showed the highest yield of phenyl acetate (**3aa**). The **3aa** yields by the other monometallic catalysts were less than one-third that of Rh/C. Although the formation of biphenyl (**4a**) was also confirmed, Rh/C showed high selectivity for the C–O coupling reaction. In the case of bimetallic catalysts, RhRu/C showed the highest activity and the selectivity to **3aa** was also high. The yield of **3aa** by RhRu/C was more than two times higher than that by Rh/C, indicating the synergistic catalysis of Rh and Ru.

The metal particle size and element distribution of RhRu/C were analyzed by HAADF-STEM and EDS. The average particle size was calculated to be 1.2 ± 0.2 nm and elemental mapping indicated the coexistence of Rh and Ru in individual particles (**Fig. 2a–c**). According to the XANES of RhRu/C (**Fig. 2d,e**), Rh and Ru were oxidized. Therefore, the characterization results indicated that the RhRu bimetallic oxide cluster ($RhRuO_x$) with mean diameter of 1.2 nm was the active species of RhRu/C.

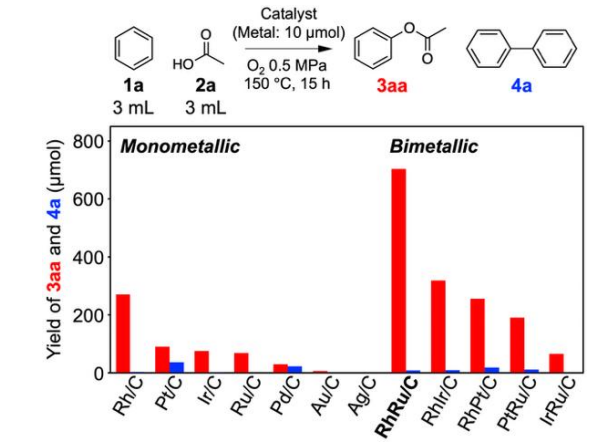

Fig. 1 Oxidative coupling of benzene and acetic acid with monometallic and bimetallic catalysts.

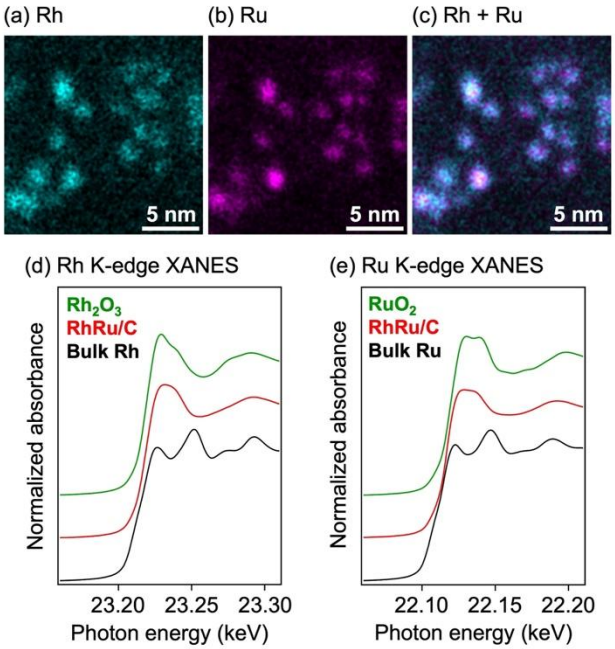

Fig. 2 EDS elemental maps and XANES of RhRu/C.

References

[1] Y. Nakaya, S. Furukawa, *Chem. Rev*. **2023**, *123*, 4855–4933.

Research Achievements

1. S. Hasegawa, K. Harano, K. Motokura, *J. Am. Chem. Soc.* **2024**, *146*, 19059–19069.

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