XAFS Characterization of Oxide-Supported Ru Nanoparticle Catalysts for Selective Nitrile Hydrogenation

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1 Introduction

Several supported ruthenium nanoparticle catalysts were prepared by the attachment of $Ru_3(CO)_{12}$ on various oxide supports, and catalytic performance on hydrogenation of valeronitrile highly depended on the type of oxide supports of catalysts. It was found out that K-doped AluC-supported Ru nanoparticle catalyst (Ru_{3-CO}/K-AluC) exhibited the highest activity and selectivity to corresponding primary amine for the hydrogenation of valeronitrile among other oxide-supported Ru nanoparticles we prepared.[1] The local coordination structures of Ru catalysts after the catalytic reaction were investigated by Ru K-edge EXAFS analysis to obtain the structural change in Ru nanoparticles.[1]

2 Experiment

Catalysts were prepared by a wet impregnation method, and valeronitrile hydrogentaion reactions were conducted in *n*-heptane under 101.3 kPa of H_2 at 343 K. After the catalytic reaction, the samples were collected. 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 Arthemis) ver. 1.2.11. 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 RuO_2, respectively.

3 Results and Discussion

The local coordination structures of catalysts were examined by Ru K-edge EXAFS analysis, and structural parameters are listed in Table 1. The Ru_{3-CO}/K-AluC (Ru: 2 wt%, K: 4 wt%) before the hydrogenation reaction had Ru-Ru interaction at 0.265 ± 0.001 nm (Its coordination number (CN) was estimated to be 4.6 ± 0.6.), and Ru-O interaction at 0.200 ± 0.003 nm (Its CN was estimated to be 2.1 ± 0.8.). The Ru-O interaction disappeared after the hydrogenation reaction of high primary amine selectivity, and only Ru-Ru interaction was observed. The CN of Ru-Ru of Ru_{3-CO}/K-AluC after the reaction at 0.264 ± 0.001 nm was 5.3 ± 0.8, which was increased a little compared with the value before the reaction.

On the other hand, the Ru-O interaction was still observed on the Ru catalyst prepared on AluC without K-doping (Ru_{3-CO}/AluC (Ru: 2 wt%)) after the hydrogenation reaction. The CN of Ru-O at 0.204 ± 0.002 nm was 2.2 ± 0.6, and the CN of Ru-Ru at 0.262 ± 0.001 nm was 2.5 ± 0.4, which was smaller than that of Ru_{3-CO}/K-AluC. This result suggests that the oxidized Ru species still existed after the catalytic reaction, which might result in the low selectivity of the primary amine. When MgO was used as the support, the selectivity of primary amine on Ru_{3-CO}/MgO was also lower than that of Ru_{3-CO}/K-AluC. The local coordination analysis of Ru K-edge EXAFS of Ru_{3-CO}/MgO after the reaction exhibited the similar trends as Ru_{3-CO}/AluC.

Table 1 Curve-fitting results of Ru K-edge EXAFS Fourier transforms of the oxide-supported Ru nanoparticle catalysts (Ru: 2 wt%) [a]

Shell	CN	R /nm	ΔE_0 /eV	σ^2 /× 10^{-5} nm^2
Ru_{3-CO}/K-Alu C (R_f= 0.8%) **Before reaction**				
Ru-O	2.1 ± 0.8	0.200 ± 0.003	2 ± 5	8 ± 4
Ru-Ru	4.6 ± 0.6	0.265 ± 0.001	1 ± 1	9 ± 1
Ru_{3-CO}/K-Alu C (R_f= 1.9%) **After reaction**				
Ru-Ru	5.3 ± 0.8	0.264 ± 0.001	2 ± 2	7 ± 1
Ru_{3-CO}/MgO (R_f= 1.2%) **After reaction**				
Ru-O	2.4 ± 0.9	0.204 ± 0.003	5 ± 5	9 ± 4
Ru-Ru	4.0 ± 0.7	0.269 ± 0.001	5 ± 1	9 ± 1
Ru_{3-CO}/Alu C (R_f= 1.5%) **After reaction**				
Ru-O	2.2 ± 0.6	0.204 ± 0.002	6 ± 4	8 ± 3
Ru-Ru	2.5 ± 0.4	0.262 ± 0.001	1 ± 2	8 ± 1

[a] *k* range and *R* range were 30-150 nm^{-1} and 0.13-0.30 nm, respectively.

References

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