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XAFS study of Ru/K-Al_2O_3 catalyst functionalized by NHC ligands for selective hydrogenation

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1 Introduction

N-heterocyclic carbenes (NHCs) were directly grafted on the K-doped Al_2O_3-supported Ru nanoparticle catalyst (Ru/K-Al_2O_3)[1] that was highly active for the hydrogenation reaction.[2] The oxidation state and local coordination structures of NHC-modified Ru catalysts were investigated by Ru K-edge XAFS. The switchover of selectivity on the hydrogenation of phenylacetylene was observed together with the amount of NHC that was directly coordinated to Ru nanoparticle.[2]

2 Experiment

Ru/K-Al_2O_3 (Ru: 4 wt%, K: 4 wt%) were prepared according to the literature.[1] The solution of NHC (1,3-dicyclohexylimidazolium; ICy (**1**), 1,3-bis(2,4,6-trimethylphenyl)imidazolium; IMes (**2**)) was impregnated to Ru/K-Al_2O_3. 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 were analysed with IFEFFIT (Athena and Arthemis) ver. 1.2.11. k^3-Weighted EXAFS oscillations were Fourier transformed into R-space, and curve-fitting analysis was carried out in R-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 were calculated by the FEFF8 code.

3 Results and Discussion

The local coordination structures of catalysts were investigated by Ru K-edge EXAFS analysis, and structural parameters are listed in Table 1. The ICy-attached Ru/K-Al_2O_3 (Low ICy loading: **1**@Ru/K-Al_2O_3, the actual NHC loading was estimated by TGA) had Ru-Ru interaction at 0.266 ± 0.001 nm (Coordination number (CN): 3.9 ± 0.8), and Ru-O/C interaction at 0.201 ± 0.002 nm (CN: 2.8 ± 0.7). These values were similar to those of Ru/K-Al_2O_3 without NHC functionalization (Table 1), suggested that the modification of ICy did not change the Ru nanocluster catalyst itself, although the only the direct Ru-ICy bond was estimated by ^{13}C SS-NMR spectra. The little influence on Ru/K-Al_2O_3 after the attachment of ICy to Ru nanoparticle was also observed by Ru K-edge XANES and TEM. The increase in the amount of attached ICy on Ru/K-Al_2O_3 (**1**@Ru/K-Al_2O_3-HL), and the usage of different NHC (**2**) (**2**@Ru/K-Al_2O_3, **2**@Ru/K-Al_2O_3-HL) did not also affect the structure of Ru nanoparticle on Ru/K-Al_2O_3 (Table 1). The attached structure was different on the type of NHCs. Almost all of **1** was selectively coordinated on the surface of Ru nanoparticles irrespective of the loading of **1**. The attachment of **2** on Ru/K-Al_2O_3 suggested the two different coordinated structures on Ru nanoparticle with a small amount of **2** attached on the K-Al_2O_3.

The catalytic hydrogenation performance of phenylacetylene was dependent on the loading of **1**/**2**. For **1**@Ru/K-Al_2O_3 and **2**@Ru/K-Al_2O_3, fully hydrogenated product (ethylcyclohexane) was the major product (57% for **1**@Ru/K-Al_2O_3 and 92% for **2**@Ru/K-Al_2O_3); however, for **1**@Ru/K-Al_2O_3-HLand **2**@Ru/K-Al_2O_3-HL, partially hydrogenated product (ethylbenzene) was the major product. These results indicate that the type and loading of the NHC on Ru/K-Al_2O_3 can finely tune the chemoselective hydrogenation.

Table 1 Curve-fitting results of Ru K-edge EXAFS Fourier transforms of the Ru nanoparticle catalysts on K-Al_2O_3 (Ru: 4 wt%) [a]

Shell	CN	R /nm	ΔE_0 /eV	σ^2 /× 10^{-5} nm^2
Ru/K-Al_2O_3 (R_f= 2.3%)				
Ru–Ru	3.9 ± 1.0	0.266 ± 0.001	2 ± 2	10 ± 1
Ru–O	2.6 ± 0.8	0.200 ± 0.002	11 ± 4	6 ± 2
1@Ru/K-Al_2O_3 (R_f= 1.7%)				
Ru–Ru	3.9 ± 0.8	0.266 ± 0.001	3 ± 2	9 ± 1
Ru–O/C	2.8 ± 0.7	0.201 ± 0.002	11 ± 4	6 ± 2
1@Ru/K-Al_2O_3-HL (R_f= 1.0%)				
Ru–Ru	4.2 ± 0.6	0.267 ± 0.001	3 ± 1	9 ± 1
Ru–O/C	2.5 ± 0.6	0.201 ± 0.001	11 ± 3	6 ± 2
2@Ru/K-Al_2O_3 (R_f= 1.0%)				
Ru–Ru	4.2 ± 0.7	0.266 ± 0.001	2 ± 1	9 ± 1
Ru–O/C	2.6 ± 0.6	0.201 ± 0.002	10 ± 3	6 ± 2
2@Ru/K-Al_2O_3-HL (R_f= 1.8%)				
Ru–Ru	3.9 ± 0.9	0.266 ± 0.001	2 ± 2	10 ± 1
Ru–O/C	2.8 ± 0.7	0.201 ± 0.002	11 ± 4	6 ± 2

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

References

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