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Local Coordination Structures of γ-Al$_2$O$_3$-Supported Ir Dimer for Surface-Assisted Transfer Hydrogenation Catalysis

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Introduction

A novel oxide-supported Ir dimer, which was found to be active for transfer hydrogenation of aromatic ketones, was prepared on a γ-Al$_2$O$_3$ surface. Detail characterization of the supported Ir dimer revealed the surface-assisted transfer hydrogenation catalysis on the supported Ir dimer catalyst. Local coordination structures of the supported Ir dimers were investigated by Ir L$_{III}$-edge XAFS.

Experimental

An Ir dimer $[\mathrm{Ir_2}\{\eta^5\text{-}\mathrm{C_5(CH_3)_5}\}_2(\mu\text{-}\mathrm{CH_2})_2]$ (**Ir$_2$**) was impregnated on several oxide supports (γ-Al$_2$O$_3$, SiO$_2$, and MgO) and reacted with surface hydroxyl groups on these surfaces at 473 K for 2 h (**Ir$_2$/ γ-Al$_2$O$_3$**, **Ir$_2$/SiO$_2$**, and **Ir$_2$/MgO**). Hydride intermediate Ir dimer was prepared by the reaction of the supported Ir dimer on γ-Al$_2$O$_3$ and isopropanol at 343 K (**Ir$_2$-H$_2$/γ-Al$_2$O$_3$**), and subsequent reaction with acetopheone was performed in toluene at 343 K (**Ir$_2$-Rxn1/γ-Al$_2$O$_3$**).

Ru K-edge XAFS was measured at BL9C and BL12C stations with Si(111) double crystal monochrometer. Ionization chambers filled with pure N$_2$ and Ar gases were used to monitor the incident and transmitted X-rays, respectively. EXAFS spectra were analyzed using REX2000, Ver. 2.3.3, Rigaku. Curve-fitting analysis was carried out in k-space and k^3-weighted EXAFS oscillations were Fourier transformed into R-space. The fitting parameters were coordination number (CN), interatomic distance (R), Debye–Waller factor (σ^2; mean-square-displacement), and the correction-of-edge energy (ΔE_0). Phase shifts and backscattering amplitudes for Ir–Ir and Ir–C (C$_5$(CH$_3$)$_5$) were calculated by using FEFF8 code.

Results and Discussion

The local coordination structure of **Ir$_2$/γ-Al$_2$O$_3$** was investigated by the curve-fitting analysis of Ir L$_{III}$-edge EXAFS data using the results of quantitative analysis of the coordinating ligands (Table 1). The precursor **Ir$_2$**, whose coordination structure was determined by X-ray diffraction, was successfully fitted and the EXAFS oscillation of **Ir$_2$/γ-Al$_2$O$_3$** was fitted well with four contributions: Ir–Ir at 0.269 ± 0.001 nm (CN = 1.2 ± 0.2), Ir–C (C$_5$(CH$_3$)$_5$) at 0.245 ± 0.001 nm (CN = 5.0 ± 0.7), Ir–O at 0.212 ± 0.001 nm (CN = 3.2 ± 0.2), and Ir···Al at 0.319 ± 0.001 nm (CN = 1.9 ± 0.2). The Ir–Ir bond distance at 0.269 ± 0.001 nm indicates that the Ir=Ir bond of **Ir$_2$** was stretched to a single Ir–Ir bond on the γ-Al$_2$O$_3$ surface. The CN of Ir···Al (1.9 ± 0.2) at 0.319 ± 0.001 nm suggested that there were two O(Al) species coordinated to the Ir center. The CN of Ir–O/C was estimated to be 3.2 ± 0.2, where the oxygen and carbon contributions cannot be discriminated by EXAFS curve fitting. The quantitative analysis by GC indicated that one μ-CH$_2$ ligand remained on the Ir dimer (the CN of Ir–C (μ-CH$_2$) = 1), and hence the CN of Ir–O was estimated to be 2, which was similar to that of Ir···Al (1.9 ± 0.2).

Ir L$_{III}$-edge EXAFS revealed that **Ir$_2$-H$_2$/γ-Al$_2$O$_3$** maintained its original dimeric structure with the Ir–Ir bond at 0.267 ± 0.001 nm (CN = 0.9 ± 0.1). It is to be noted that the CN of Ir···Al dropped from 1.9 ± 0.2 at 0.319 ± 0.001 nm to 1.2 ± 0.2 at 0.321 ± 0.001 nm. The CN of Ir–O/C was also reduced from 3.2 ± 0.2 (0.212 ± 0.001 nm) to 2.3 ± 0.2 (0.212 ± 0.001 nm), indicating that the CN of Ir–O(Al) was reduced from 2 to 1 under the consideration of the Ir–C (μ-CH$_2$) contribution (CN = 1). These results suggest that the bridged Ir–(OAl)$_2$–Ir bonds in the **Ir$_2$/γ-Al$_2$O$_3$** became a monodentate Ir–O(Al) bond in each Ir center to form **Ir$_2$-H$_2$/γ-Al$_2$O$_3$**. It was proposed that the interfacial bond transformation between the Ir dimer (**Ir$_2$/γ-Al$_2$O$_3$**) and the γ-Al$_2$O$_3$ surface promoted the formation of the dihydride Ir complex on γ-Al$_2$O$_3$ as an intermediate in the transfer hydrogenation.

Table 1 Structural Parameters Determined by Curve-Fitting Analysis of Ir L$_{III}$-edge EXAFS for **Ir$_2$/γ-Al$_2$O$_3$**, **Ir$_2$-H$_2$/γ-Al$_2$O$_3$**, and **Ir$_2$-Rxn1/γ-Al$_2$O$_3$**

Shell	CN	Distance /nm	ΔE_0 /eV	σ^2 /10^{-5} nm^2
Ir$_2$/γ-Al$_2$O$_3$ (R_f =0.15%)				
Ir–Ir	1.2 ± 0.2	0.269 ± 0.001	-1	6
Ir–C (C$_5$(CH$_3$)$_5$)	5.0 ± 0.7	0.245 ± 0.001	-6	9
Ir–O	3.2 ± 0.2	0.212 ± 0.001	17	5
Ir···Al	1.9 ± 0.2	0.319 ± 0.001	20	3
Ir$_2$-H$_2$/γ-Al$_2$O$_3$ (R_f =0.51%)				
Ir–Ir	0.9 ± 0.1	0.267 ± 0.001	-2	4
Ir–C (C$_5$(CH$_3$)$_5$)	4.9 ± 0.7	0.246 ± 0.001	-10	8
Ir–O	2.3 ± 0.2	0.212 ± 0.001	17	4
Ir···Al	1.2 ± 0.2	0.321 ± 0.001	21	4
Ir$_2$-Rxn1/γ-Al$_2$O$_3$ (R_f =0.13%)				
Ir–Ir	1.1 ± 0.1	0.268 ± 0.001	0	5
Ir–C (C$_5$(CH$_3$)$_5$)	4.9 ± 0.7	0.242 ± 0.001	-9	8
Ir–O	3.2 ± 0.2	0.213 ± 0.001	16	6
Ir···Al	2.2 ± 0.3	0.319 ± 0.001	20	5

Measured at 20 K. k = 30 – 150 nm^{-1}, R = 0.14 – 0.31 nm.

Reference

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