Supporting Information

Partially Oxidized Iridium Clusters Within Dendrimers: Size-Controlled Synthesis and Selective Hydrogenation of 2-Nitrobenzaldehyde

Tatsuya Higaki,[a] Hirokazu Kitazawa,[ab] Seiji Yamazoe,[ab] and Tatsuya Tsukuda*[ab]

[a] *Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033*

[b] *Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Katsura, Kyoto 615-8520*

1. Preparation of Ir15:G6, Ir30:G6 and Ir60:G6 supported on SiO_2

Ir15:G6 was synthesized through the following procedure. First, a mixture of G6-OH aqueous solution (1801.6 mg, 9.06 wt%, 2.8 μmol) and K_2IrCl_6 aqueous solution (2.1 mM, 20 mL, 42 μmol, 15 eq to dendrimer) was diluted to 25 mL with water and stirred for 100 min. Next, $NaBH_4$ aqueous solution (0.42 M, 10 mL, 100 eq to Ir ions) was rapidly added to the solution kept at 60°C with vigorous stirring (about 1150 rpm). After 250 min, the reaction vessel was cooled down to 0°C in an ice bath to prevent aerobic re-oxidation. The reaction mixture was deionized by centrifugation using membrane filters with a cut-off filter under 10 kDa. After deionization three times, the retentate was diluted to 20 mL. As-prepared solution was immediately supported on pretreated SiO_2 for catalytic usage and lyophilized for XRD measurement using a freeze dryer (FDU-2200, EYELA). Following a similar synthesis procedure, Ir30:G6 and Ir60:G6 were prepared using 903.0 mg and 450.6 mg of G6-OH, respectively. As-prepared clusters were loaded to SiO_2 using the following method. A total of 7 g of SiO_2 was ground with an agate mortar for as long as 40 min. After 100-mesh sieving, SiO_2 powder was stirred in 400 mL of deionized water at 80°C until completely dry. The SiO_2 powder was then desiccated at 80°C for 12 h. The dried powder was calcined at 500°C for 4 h in a crucible. SiO_2 samples (JRC-SIO-11) used in this study were supplied by the Catalysis Society of Japan. A total of 750 mg of thus pre-treated SiO_2 was added to 150 mL of deionized water. After sonication for 60 min, 15 mL of as-prepared Ir:G6 was added

dropwise to the solution (10 mL/h). After stirring for 24 h, a supported Ir cluster was collected by membrane filtration and desiccated *in vacuo* overnight.

2. Catalytic test

Catalytic hydrogenation of 2-nitrobenzaldehyde was performed using IrX:G6/SiO_2 (X=15, 30, 60) as catalysts. 2-Nitrobenzaldehyde (105 μmol, 15.9 mg) and IrX:G6/SiO_2 (54.6 mg, 2.1 μmol as Ir atoms) were added to toluene (2 mL) and the mixture was stirred (ca. 1140 rpm) under H_2 (0.1MPa) at 30°C in an auto clave reactor. After 1 h, the reaction products were analyzed by gas chromatograph (Shimadzu GC-2025) equipped with a column (GC Sciences Inc. InertCap Pure-WAX) and a flame ionization detector (FID).

The leaching test was conducted as follows. After the catlytic reaction by Ir15:G6/SiO_2 was completed, the catalyts were removed by filtration. To this solution, 2-nitrobenzaldehyde (105 μmol) and biphenyl as an internal standard (52.5 μmol) were added and the mixed solution was stirred under H_2 (0.1MPa) at 30°C. After 1h, the products were analyzed by GC.

3. Characterization

A. UV-Vis spectroscopy

Ultraviolet-visible (UV-Vis) spectra were recorded on UV-Vis spectrometers (V-630 or V-670, JASCO). The concentration of the samples was 0.7 mM for Ir:G6.

B. Transmission electron microscopy (TEM)

A total of 10 μL of as-prepared Ir:G6 solution was diluted 100 times for the measurement. Hydrophilic treatment was applied to a hydrophobic-film-coated TEM grid using an ion bombarder for 2 min in soft mode. A drop of the diluted solution was placed on the pretreated TEM grid. The solvent was dried naturally for 1 h and then was dried *in vacuo* overnight. A transmission electron microscope (JEM-2100F, JEOL) operated at 200 kV was used to study the morphology.

C. Powder X-ray diffraction (PXRD)

The lyophilized samples were placed on an Si plate (zero diffraction plate). Powder X-ray diffraction (PXRD) profiles of the solid samples were measured using a diffractometer (SmartLab 3, Rigaku) with a radiation source of Cu Kα (1.5405 Å) operated at 60 kV and 60 mA.

D. X-ray photoelectron spectroscopy (XPS)

The powdered sample was placed on a 1-in sample holder using carbon conductive tape. The XP spectra were obtained by using a spectrometer (PHI 5000 VersaProbe, ULVAC-PHI) with an energy resolution of 0.5 eV.

E. X-ray absorption fine structure (XAFS)

Ir L_3 edge XAFS measurements were carried out at the BL01B1 beam line at the SPring-8 facility of the Japan Synchrotron Radiation Research Institute (Proposal Nos. 2015B1308, 2015A1590, 2014B1430). An Si(311) double-crystal monochromator was used for the incident beam. X-ray absorption (XA) spectra for Ir bulk and K_2IrCl_6 were recorded in transmission mode, and ionization chambers were used for the I_0 and I detectors. XA spectra for IrX:G6/SiO_2 (X = 15, 30, 60) were recorded in fluorescence mode, and ionization chambers and 19-element SSD were used for the I_0 and I detectors, respectively. Energy calibration was carried out using Au foil. Data analysis was carried out using the program REX2000 Ver.2.5.9 (Rigaku Co.). The XANES and EXAFS data were analyzed by subtraction of the atomic absorption background from the χ spectra using a cubic spline and normalization to the edge height. The k^3-weighted χ spectra were Fourier transformed into r-space, using the Fourier transformation range 3.0–15 $Å^{-1}$. Curve-fitting analysis was performed for the Ir–Ir and Ir–O bonds. The curve-fitting range was 1.1–2.9 Å for IrX:G6/SiO_2 and 2.0–2.9 Å for Ir bulk. The phase shift and backscattering amplitude functions of Ir–Ir, Ir–Cl, and Ir–O bonds were extracted from Ir metal (Space group: Fm3m, ICSD#: 41524), $IrCl_3$ (Space group: C2/m, ICSD#: 23171), and IrO_2 (Space group: P42/mnm, ICSD#: 56009), respectively, by calculation using FEFF8 [1]. The results are summarized in Table S1.

4. Results

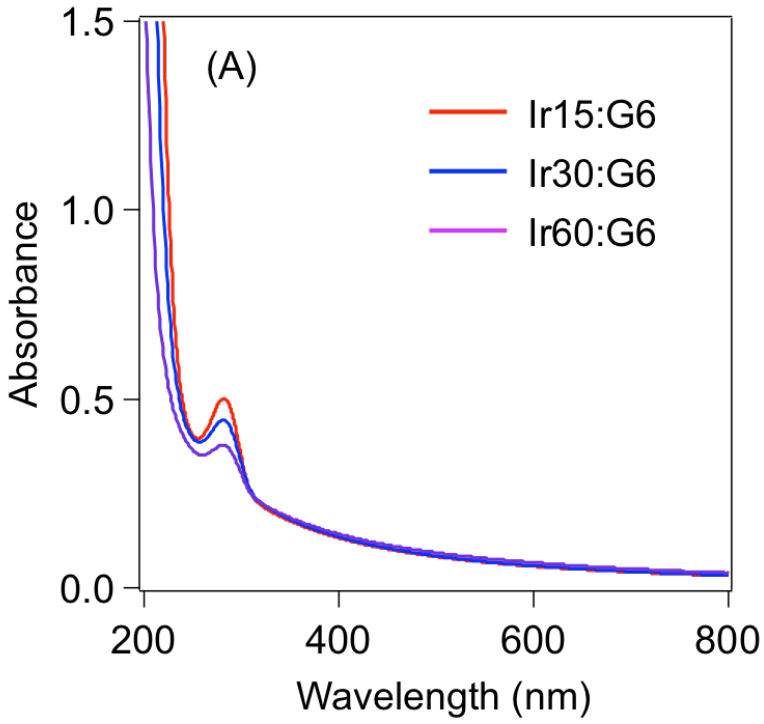

Figure S1. UV-Vis spectra for Ir:G6 clusters.

Table S1. Curve-fitting results for Ir–Ir and Ir–O bonds of Ir:G6/SiO_2 and Ir metal.

Sample	Bond	*CN* [a]	*r* / Å [b]	σ^2 [c]	R factor (%) [d]
Ir15:G6/SiO_2	Ir–O	3.5(0.5)	2.01(1)	0.09(2)	9.0
	Ir–Ir	3.0(0.5)	2.656(7)	0.080(9)	
Ir30:G6/SiO_2	Ir–O	4.1(7)	2.030(6)	0.010 (1)	6.5
	Ir–Cl	0.4(4)	2.42(2)	0.0085(5)	
	Ir–Ir	4.9(1.0)	2.675(3)	0.0038(34)	
Ir60:G6/SiO_2	Ir–O	3.6(5)	2.048(5)	0.0074(26)	9.5
	Ir–Cl	0.6(1)	2.425(8)	0.003(12)	
	Ir–Ir	6.4(1.0)	2.689(4)	0.011(2)	
Ir bulk	Ir–Ir	11.8(1.7)	2.705(2)	0.038(11)	2.0

R fitting range is 1.1–2.9 Å and *k* fitting range is 3–15 $Å^{-1}$. a: Coordination number; b: Bond length; c: Debye-Waller factor: σ^2; d: R factor: $[\Sigma(\chi^{data} - \chi^{fit})^2/\Sigma(\chi^{data})^2]^{1/2}$.

Table S2. Curve-fitting* results for X-ray photoelectron spectra of IrX:G6/SiO_2

Sample	Species		*BE* (eV)	Peak area	Population (%)	χ^2
Ir15:G6/SiO_2	Ir^0	$4f_{7/2}$	60.1	136	48	2.0
		$4f_{5/2}$	63.1	102		
	IrO_2	$4f_{7/2}$	61.3	148	52	
		$4f_{5/2}$	64.2	111		
Ir30:G6/SiO_2	Ir^0	$4f_{7/2}$	60.1	163	43	3.3
		$4f_{5/2}$	63.2	122		
	IrO_2	$4f_{7/2}$	61.4	216	57	
		$4f_{5/2}$	64.6	162		
Ir60:G6/SiO_2	Ir^0	$4f_{7/2}$	60.1	336	44	4.9
		$4f_{5/2}$	63.2	252		
	IrO_2	$4f_{7/2}$	61.4	423	56	
		$4f_{5/2}$	64.4	317		

*Background curve was calculated by the iterated Shirley method (×5) [2]. Curve fitting was performed using Voigt functions and FWHM was fixed to 1.77 and 2.47 for Ir^0 and IrO_2 bands, respectively. Area ratio between $4f_{7/2}$ and $4f_{5/2}$ was kept constant (4:3). Each peak position was calibrated referring to the binding energy of carbon 1s bands.

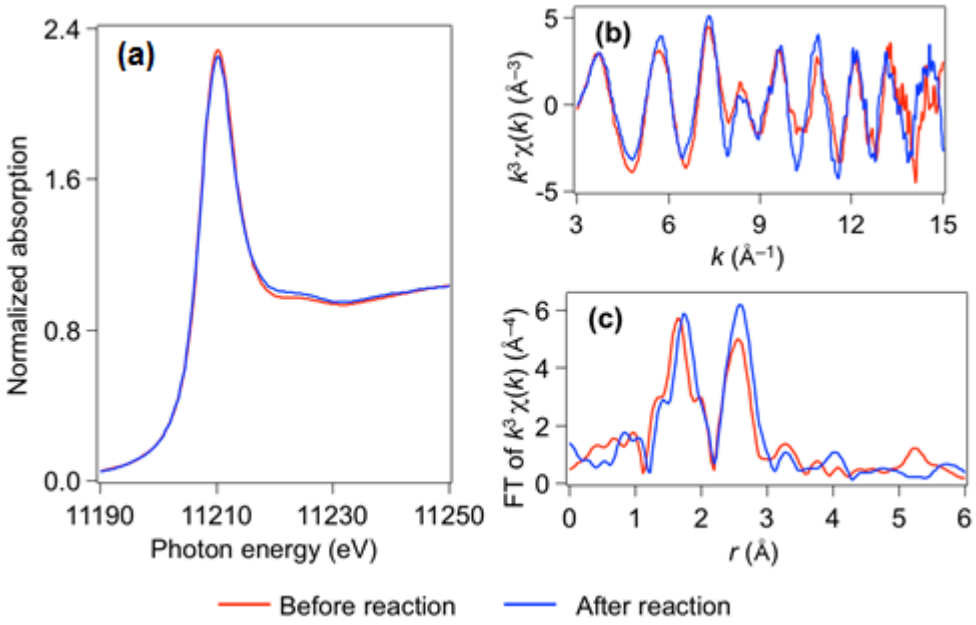

Figure S2. (a) XANES, (b) EXAFS and (c) FT-EXAFS of Ir15:G6/SiO_2 before and after reaction.

5. References

[1] A. L. Ankudinov, B. Ravel, J. J. Rehr, S. D. Conradson, *Phys. Rev. B* **1998**, *58*, 7565.

[2] A. Proctor, P. M. Sherwood, *Anal. Chem.* **1982**, *54*, 13.