XAFS Characterization of Molecularly Imprinted Pd-Complex Catalysts for Suzuki Cross Coupling Reaction

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Introduction

Molecularly imprinted Pd-complex catalysts were prepared on a SiO_2 surface by molecular imprinting of a SiO_2-supported Pd complex using SiO_2-matrix overlayers. The local coordination structures of the prepared molecularly imprinted Pd-complex catalysts, which exhibited fine shape selectivity for Suzuki cross coupling reactions, were investigated by Pd K-edge XAFS.

Experimental

A Pd precursor complex together with a template molecule, (dppe)Pd(temp) (**1**) (dppe = 1,2-ethanediylbis[bis[4-(1-methylethenyl)phenyl]-phosphine], temp = 5-(2-propen-1-ol)-[1,1'-biphenyl]-2,2'-diol) was attached on a SiO_2 surface functionalized with *p*-styryl moiety to prepare a SiO2-supproted Pd complex (**2**). SiO_2-matrix overlayers were stacked on the surface of **2** by chemical vapour deposition to prepare a molecularly-imprinted Pd complex on the SiO_2 surface (**3**).

Pd K-edge XAFS was measured in a transmission mode at 20 K at the NW10A station with a Si(311) double-crystal monochromator. Ionization chambers filled with pure Ar and pure Kr were used to monitor incident and transmitted X-rays, respectively. EXAFS spectra were analysed using ATHENA and ARTEMIS programs. k^3-Weighted EXAFS oscillations were Fourier transformed into *R*-space, and curve-fitting analysis was performed in *R*-space with 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.

Results and Discussion

The local coordination structures of the supported Pd complexes were examined by Pd K-edge EXAFS analysis, whose structural parameters are listed in Table 1. The (dppe)Pd(temp) complex precursor (**1**) with the template ligand had Pd-P bond at 0.223 ± 0.001 nm and Pd-O bond at 0.205 ± 0.001 nm, whose coordination numbers (CNs) were both fixed to be 2.0.

The bond distances of the Pd-P and Pd-O coordination in **2** were fitted as 0.223 ± 0.001 and 0.206 ± 0.002 nm, respectively. The CNs of the Pd-P and Pd-O bonds were fitted as 1.7 ± 0.1 and 2.0 ± 0.4, respectively. These results suggest that the local coordination structure of **1** with the template and the dppe ligand was maintained

after it was attached to the SiO_2 surface together with the results of ^{13}C NMR and UV/vis spectra.

The bond distances of the Pd-P and Pd-O coordination in **3** were fitted as 0.225 ± 0.001 and 0.203 ± 0.002 nm, respectively. The CNs of the Pd-P and Pd-O bonds were fitted as 1.6 ± 0.2 and 1.9 ± 0.4, respectively. These results also indicated the retention of the local coordination structure of the Pd complex in **3** after stacking of SiO_2-matrix overlayers. ^{13}C NMR and UV/vis spectra of **3** supported this result. Pd K-edge XANES of **1**, **2**, and **3** were almost identical, also supporting the structural and oxidation state similarities.

The SiO_2-supported Pd complex showed significant activity for the C-C coupling reaction, and different catalytic performances were observed for various combinations of aryl iodides and arylboronic acids on the molecularly-imprinted Pd complex catalyst **3**.

Table 1 Structural Parameters Determined by Curve-Fitting Analysis of Pd K-edge EXAFS Measured at 20 K

Shell	CN	R /nm	ΔE_0 /eV	$\sigma^2 / \times 10^5$ nm^2
		1 [a]		
Pd-P	2.0	0.223 ± 0.001	5.4 ± 0.9	2.4 ± 0.2
Pd-O	2.0	0.205 ± 0.001	6.2 ± 2.2	5.8 ± 0.8
		2 (Pd: 0.6 wt%) [b]		
Pd-P	1.7 ± 0.1	0.223 ± 0.001	5.4	2.4
Pd-O	2.0 ± 0.4	0.206 ± 0.002	6.2	5.8
		3 (Pd: 0.35 wt%) [c]		
Pd-P	1.6 ± 0.2	0.225 ± 0.001	5.4	2.4
Pd-O	1.9 ± 0.4	0.203 ± 0.002	6.2	5.8

[a] k = 30-160 nm^{-1}, R = 0.12-0.22 nm, R_f = 0.47%.
[b] k = 30-160 nm^{-1}, R = 0.12-0.22 nm, R_f = 1.0%.
[c] k = 30-140 nm^{-1}, R = 0.12-0.22 nm, R_f = 1.0%.

Reference

[1] N. Maity, S. Muratsugu, M. Tada, submitted.

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