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XAFS Study of Molecularly-Imprinted Pd Catalysts for Suzuki Coupling Reaction

Satoshi MURATSUGU*[1,3], Niladri MAITY[3], Hiroshi BABA[1], Masahiro TASAKI[1],
Mizuki TADA[1,2,3]

[1] Department of Chemistry, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8602, Japan.
[2] RCMS, Nagoya University, Furo-Cho, Chikusa-ku, Nagoya, 464-8602, Japan.
[3] Institute for Molecular Science, Myodaiji, Okazaki, Aichi 444-8585, Japan.

1 Introduction

Molecularly imprinted Pd-complex catalysts with different Pd loadings were prepared on a SiO_2 surface by molecular imprinting of a SiO_2-supported Pd complex with SiO_2-matrix overlayers.[1] The local coordination structures of the prepared molecularly imprinted Pd-complex catalysts were investigated by Pd K-edge XAFS. The catalytic performances of the molecularly imprinted Pd complex catalysts were very different for various combinations of aryl iodides and arylboronic acids, and reactants with bulky substituent groups were hindered on the imprinted Pd catalysts.[1]

2 Experimental

A Pd precursor complex (**1**) with a template molecule was attached on a SiO_2 surface functionalized with *p*-styryl moiety to prepare a SiO_2-supproted Pd complex (**A**). SiO_2-matrix overlayers of two different heights were stacked on the surface of **A** to prepare a molecularly-imprinted Pd complex on the SiO_2 surface (**B**, Pd: 0.35 wt%, low height; **C**, Pd: 0.23 wt%, high height).

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.

3 Results and Discussion

The local coordination structures of the supported Pd complexes were analyzed by Pd K-edge EXAFS (Table 1). **1** with the template ligand was curve-fitted by 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 **A** were curve-fitted as 0.223 ± 0.001 and 0.206 ± 0.002 nm, respectively, and the CNs of the Pd-P and Pd-O bonds were curve-fitted as 1.7 ± 0.1 and 2.0 ± 0.4, respectively. These results suggest that the local coordination structure of **1** was maintained after it was attached to the SiO_2 surface. This interpretation was supported with the results of ^{13}C SS NMR and UV/vis spectra.

The bond distances of the Pd-P and Pd-O coordination in **B** and **C** were both fitted as 0.225 ± 0.001 and 0.203 ± 0.002 nm, respectively, together with similar CN values (Table 1). These results also indicated the maintenance of the local coordination structure of the Pd complex in **B** and **C** after the stacking of SiO_2-matrix overlayers. The Pd K-edge XANES of **1**, **A**, **B**, and **C** were quite similar, supporting the similar structures and oxidation states.

The Suzuki cross-coupling performance of the SiO_2-supported Pd complex catalysts was investigated on the prepared molecularly-imprinted Pd catalysts, and the sensitivity of the cross-coupling activity was dependent on the height of the SiO_2-matrix overlayers. The cross-coupling reactions of bulky reactants were strongly suppressed on **B** and **C** compared with **A**, and the sensitivity was also dependent on the position of the substituent groups on the reactants.

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	σ^2 /× 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
A (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
B (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
C (Pd: 0.23 wt%) [d]				
Pd-P	1.5 ± 0.2	0.225 ± 0.001	5.4	2.4
Pd-O	1.6 ± 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%.
[d] k = 30-140 nm^{-1}, R = 0.12-0.22 nm, R_f = 1.3%.

Reference

[1] S. Muratsugu, N. Maity, H. Baba, M. Tasaki, M. Tada, *Dalton Trans.* **2017**, *46*, 3125-3134. (Selected as Inside Back Cover)

* smuratsugu@chem.nagoya-u.ac.jp