

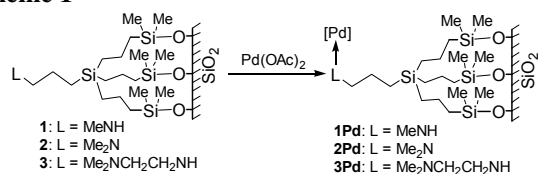
EXAFS study of palladium complex catalysts immobilized on silica via a tripodal linker unit with amino groups

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Introduction

Immobilization of molecular catalysts via linkers on inorganic oxide supports is a promising strategy for facilitating the separation of catalysts from reaction mixtures and for assisting the catalyst recycling process. We have recently found that the amino palladium catalysts immobilized on a silica support via a tripodal linker unit (**1Pd–3Pd**) show high catalytic performance for the Suzuki-Miyaura coupling reaction (Scheme 1). In this study, Pd *K*-edge EXAFS measurements were performed to explore the local structure of palladium of **1Pd–3Pd**.

Scheme 1



Experimental

Pd *K*-edge extended X-ray absorption fine structure (EXAFS) measurements were carried out at the NW10A beamline at the Photon Factory Advanced Ring (PF-AR) in the IMSS-KEK. All spectra were measured using a Si(311) double-crystal monochromator in transmission mode at room temperature. Analysis of EXAFS data was conducted using the commercially available analytical program REX2000 (Rigaku Co.).

Results and Discussion

Figure 1 shows the Fourier transforms (FT) of the k^3 -weighted EXAFS spectra for the catalysts and the reference materials, including [Pd(NH₃)₄]Cl₂, Pd(OAc)₂, and Pd foil. A peak around 2.5 Å in the spectrum of the Pd foil, assigned to scattering from the nearest neighbor palladium atoms in a metallic palladium cluster, was not observed in the spectra of **1Pd**. The FT profiles of these samples were similar to those of [Pd(NH₃)₄]Cl₂ and Pd(OAc)₂ consisting of an isolated palladium atom with a square planar PdE₄ (E = N or O) structure locating Pd–E at the distance of 2.02 or 2.03 Å, respectively [1,2]. Because the parameters associated with the phase shift function and backscattering amplitude of Pd–N are similar to those of Pd–O, curve-fitting analysis of the EXAFS spectra cannot distinguish between nitrogen and oxygen coordinated to palladium. Curve-fitting analysis

of the first shell in the FT of EXAFS for the catalysts **1Pd–3Pd** was carried out using parameters for Pd–N scattering extracted from [Pd(NH₃)₄]Cl₂ (Table 1). The optimum fitting results for **1Pd–3Pd** were 3.6–3.7 for the coordination numbers (CN) and around 2.02 Å for the distance (*r*). These results indicated that palladium was most likely surrounded by four nitrogen and/or oxygen atoms, in other words, the palladium was loaded onto the amino-functionalized silica surfaces **1–3** as palladium complexes, without aggregating to form palladium particles.

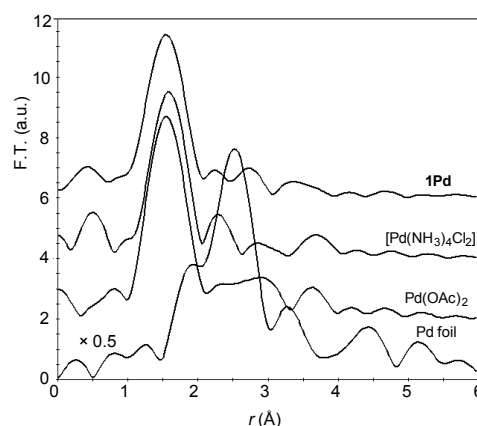


Figure 1: Fourier transforms of the k^3 -weighted Pd *K*-edge EXAFS spectra for the **1Pd** and [Pd(NH₃)₄]Cl₂, Pd(OAc)₂, and Pd foil, as reference materials.

Table 1: Curve-fitting results of Pd *K*-edge EXAFS spectra for the catalysts **1Pd–3Pd**^a.

| Catalyst | CN ^b | <i>r</i> (Å) ^c | ΔE (eV) ^d | R (%) ^e |
|------------|-----------------|---------------------------|----------------------|--------------------|
| 1Pd | 3.6 ± 0.6 | 2.03 ± 0.02 | −5.4 ± 3.0 | 0.6 |
| 2Pd | 3.7 ± 0.9 | 2.02 ± 0.02 | −6.5 ± 3.0 | 1.7 |
| 3Pd | 3.7 ± 0.5 | 2.01 ± 0.02 | −0.4 ± 3.5 | 0.9 |

^a The Debye–Waller factor was fixed at 0.03 Å² for all analyses. ^b Coordination number of Pd–E (E = N or O). ^c Radial distance of E from Pd. ^d Difference in the edge energy between a reference compound and the catalyst. ^e R = $\sum(k^3\chi_{obs} - k^3\chi_{cal})^2 / \sum(k^3\chi_{obs})^2 \times 100$.

References

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- [2] S. D. Kirik, R. F. Mulagaleev, A. I. Blokhin, *Acta Crystallogr., Sect. C*, C60, m449 (2004).

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