

XAFS studies on the formation of atomic Pd active in the Suzuki coupling reactions

Cross-coupling reactions, such as Suzuki, Negishi and Heck reactions, are very important in the field of organic synthesis and are utilized for the production of pharmaceuticals, organic electroluminescent devices, and liquid crystals. These reactions attract much attention these days; as a matter of fact, the 2010 Nobel Prize in Chemistry was awarded to the discoverers of these reactions. In the Suzuki coupling reactions, selective formation of C-C bond occurs through the reaction between halogenated aromatics and derivatives of phenylboronic acids. On the other hand, C=C bond formation occurs between halogenated aromatics and olefins with high selectivity and yield in Heck reactions. To date, numerous Pd complexes, such as palladacycles and *N*-heterocyclic carbenes, have been developed as catalysts for use in these reactions. However, these Pd(0) or Pd(II) complexes cause difficulties in the synthesis and purification of the final product. Another class of catalysts for these reactions, namely, heterogeneous catalysts, are easy to prepare and readily separated from the products. Therefore, heterogeneous catalysts that show high activity are more beneficial than homogeneous ones from the viewpoint of environmental friendliness and low energy consumption. Among these supported catalysts, there are several reports on supported Pd catalysts that are nearly as active as the best homogeneous ones. These highly active heterogeneous catalysts have been realized when well-dispersed active sites with a homogeneous structure are fabricated on supports. Moreover, well-dispersed metals having surface atoms with a low coordination number are anticipated to exhibit high activity; this behavior is different from that of a bulk-type catalyst.

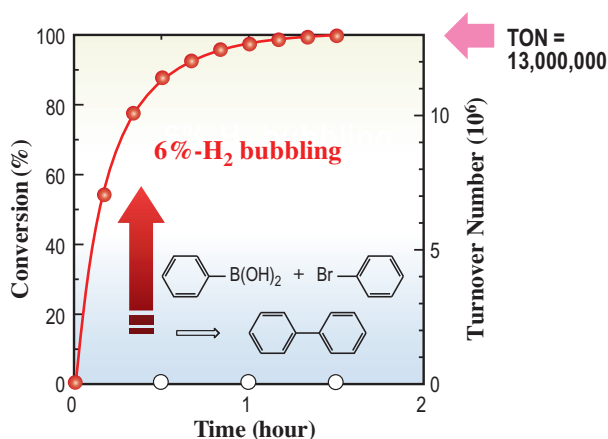


Fig. 1. Time course of the conversion of bromobenzene over 0.4 wt% Pd/USY with or without 6% H₂ bubbling.

Zeolites have a large surface area and uniform micropores, which can accommodate dispersed metal clusters, leading to a high surface-to-volume ratio. Using zeolites as supports for Pd is therefore expected to lead to high catalytic activity. Among the various zeolites, faujasite-type zeolites are the most promising for use as a support for Pd because they have a large supercage with diameters of *ca.* 1.3 nm. Indeed, we found that Pd loaded on ultra-stable Y (USY) zeolites exhibited excellent catalytic activity in a Suzuki reaction when H₂ was bubbled through the system prior to the reaction [1]. Evolution of the extremely high activity was found only when *o*-xylene and Pd ammine complexes were used as the solvent and the Pd precursor, respectively. The catalytic activity was improved significantly by continuously bubbling H₂ through the system during the reaction, as shown in Fig. 1 [2]. A similar enhancement of the catalytic activity by H₂ was also found in Heck reactions [3]. To reveal the reason for the evolution of such high catalytic activity, we have tried to analyze the structure and valence of active Pd species generated by H₂ bubbling in *o*-xylene using extended X-ray absorption fine structure (EXAFS) analysis under *in situ* conditions.

EXAFS experiments were performed at beamlines BL14B2 and BL01B1. Figure 2 illustrates the equipment for *in situ* measurements of Pd/USY immersed in *o*-xylene. The Pd/USY catalyst and *o*-xylene were mounted in the plastic cell connected to the condenser. The 6% H₂ diluted with He was introduced to the Pd/USY while the solution was stirred with a magnetic stirrer. The Pd *K*-edge EXAFS

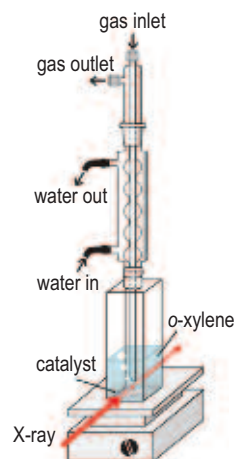


Fig. 2. Equipment for *in situ* XAFS measurements of Pd/USY in *o*-xylene with H₂ bubbling.

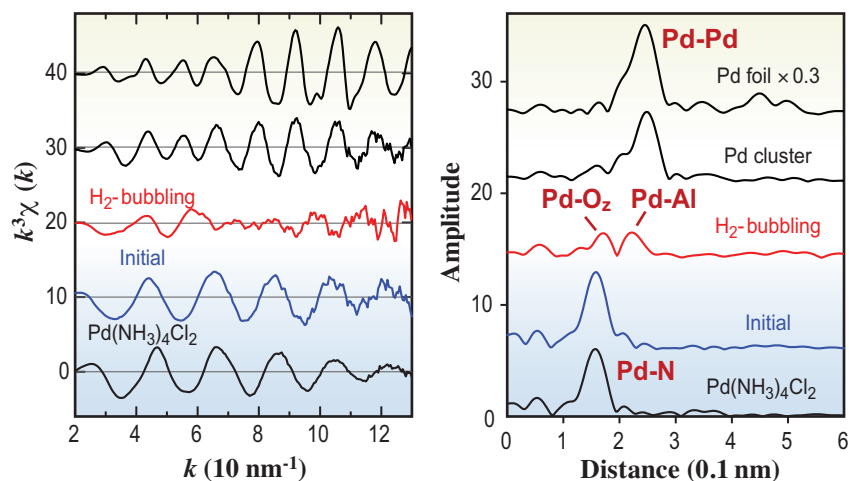


Fig. 3. Pd K-edge EXAFS $k^3\chi(k)$ and their Fourier transforms (FT) of Pd/USY measured after H₂ bubbling in *o*-xylene and reduction with H₂ in the gas phase, together with reference samples.

spectrum of Pd/USY measured in *o*-xylene using this *in situ* cell is given in Fig. 3. The spectrum showed Pd-O₂ and Pd-Al bonds arising from the framework of USY zeolites. The feature was much different from that of the Pd cluster where an intense Pd-Pd bond was observed. Pd L₃-edge XANES spectra measured at Rits-BL10 indicated that the valence of the Pd reduced with bubbling H₂ was +0.3. These facts indicate the formation of atomically dispersed Pd species with a slightly cationic character when Pd/USY was reduced with bubbling H₂ in *o*-xylene, which was considered to be the active species in Suzuki coupling reactions [4]. In addition to studying the active sites, it is important to obtain insights into the role of the support, taking into account that the catalytic performance of Pd varies significantly

depending on the type of support. For this purpose, the acid character of USY zeolites was analyzed by IRMS-TPD methods [5]. The detailed analysis of acid properties of USY zeolites in correlation with catalytic performance revealed that the strong acid sites characteristic of USY zeolites had a profound effect on the catalysis of Pd/USY [4]. On the basis of the catalytic activity, Pd K-edge and Pd L₃-edge XAFS analyses, and IRMS-TPD studies, the active species was proposed to be the atomic Pd with a partially cationic character, which was anchored to the strong acid sites induced by extra-framework Al species, as shown in Fig. 4.

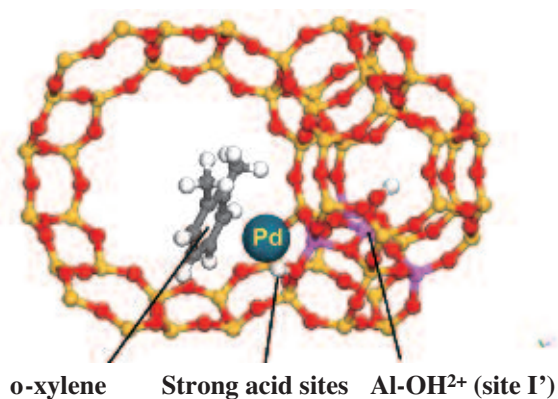


Fig. 4. Proposed structure of the atomic Pd generated in the supercage of USY zeolite.

Kazu Okumura

Department of Materials Science, Tottori University

E-mail: okmr@chem.tottori-u.ac.jp

References

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