

Formation of stable self-assembled multilayer palladium nanoparticles for ligand-free coupling reactions

Cross-coupling reactions with an organometallic catalyst, especially a palladium-based catalyst, are a key to the synthesis of functional molecules such as those used in pharmaceuticals, agricultural chemicals, solar cells, and organic electroluminescent displays. For the synthesis of functional molecules, carbon-nitrogen bond-forming reactions are frequently used, as well as carbon-carbon bond-forming reactions [1].

Metal cross-coupling reactions generally require the use of an excellent ligand [1]. Cross-coupling reactions of metals, including Pd-coupling reactions, have evolved with ligand development. The ligand has several important roles in cross-coupling reactions. For example, in the Buchwald-Hartwig reaction, the ligand inhibits metal aggregation, accelerates oxidative addition, and/or reduces elimination steps. The use of ligands is, however, associated with a problem of product purification. Separation of the product from the ligand is a costly and time-consuming process. Moreover, sophisticated ligands are generally expensive. Furthermore, inert reaction conditions are generally required as phosphorus ligands are oxidized easily.

To emancipate cross-coupling reactions from the restrictions imposed by ligands, the use of metal nanoparticles as catalysts has emerged as one of the most promising solutions. Transition-metal nanoparticles are usually 1–10 nm in diameter and have a narrow size dispersion, and their synthesis is reproducible with well-defined compositions and clean surfaces. To achieve a useful nanoparticle catalysis, the key technique in metal nanoparticle preparation is the stabilization of particles by a

protective agent to avoid the formation of bulk metal. Two types of stabilization can be achieved depending on the nature of the protecting agents: (a) electrostatic stabilization using ionic compounds as protecting agents and (b) steric stabilization using neutral molecules such as polymers or other bulky molecules [2]. On the other hand, the immobilization of nanoparticles on supports can increase the stability of metal dispersions to achieve catalytic systems with novel properties. In other words, combination of the advantages of heterogeneous and homogeneous catalysis is desirable. The development of systems of organometallic catalysts involving metallic nanoparticles is an active research field.

With this background, we recently developed a novel Pd nanoparticle catalyst, named sulfur-modified gold-supported palladium (SAPd, Fig. 1) [3]. SAPd can be easily prepared by the treatment of gold with Piranha solution, a mixture of sulfuric acid and hydrogen peroxide, and subsequent palladium absorption. In earlier investigations, SAPd was applied to a ligand-free Buchwald-Hartwig reaction [4], Suzuki-Miyaura couplings [3], and a carbon (sp^3 and sp^2)-hydrogen bond activation reaction, and exhibited superior performance to conventional Pd catalysis. SAPd is an environmentally sustainable ideal catalyst since SAPd can usually be used repeatedly and the amount of leached Pd in the whole reaction mixture is less than 1 ppm. SAPd is now commercially available and widely used for ligand-free Pd cross-coupling including liquid-phase combinatorial synthesis, medicinal library synthesis, and flow-reaction systems.

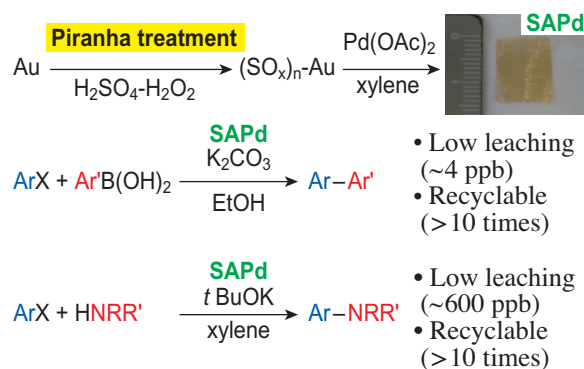


Fig. 1. Preparation of SAPd and its use in ligand-free Pd coupling.

We have also characterized the structural and chemical properties of SAPd by spectroscopic analytical techniques [5]. Extended X-ray absorption fine structure (EXAFS) experiments (Fig. 2) at beamlines BL14B2 and BL27SU and transmission electron microscopy (TEM) analyses were performed to clarify the geometrical properties of Pd catalysis in SAPd. X-ray absorption near-edge structure (XANES) analysis at the sulfur and carbon *K*-edges was used to determine the chemical states of sulfur and carbon in SAPd. As a result, we found that SAPd was constructed with about 10 layers of Pd(0) nanoparticles with a diameter of less than 5 nm (Fig. 3).

In summary, we discovered by performing XAFS and TEM analyses that SAPd, which catalyzes Pd cross-coupling in the absence of any ligand, has approximately 10 layers of self-assembled Pd(0) nanoparticles of less than 5 nm in diameter on a sulfur-modified gold surface. It is noteworthy that the Pd nanoparticles in SAPd are embedded in the high-density layers without condensation. The matrix

of SAPd, which comprises organic matter formed by the complexes of sulfate and xylene embedding the Pd nanoparticles in SAPd, prevents the aggregation of nanoparticles. These findings also clarify the ease and usefulness of the SAPd preparation method for constructing multilayers of highly reactive Pd nanoparticles on metal substrates and opens a new route for preparing other metal nanoparticles for organic synthesis. On the basis of these structural findings for SAPd, we very recently succeeded in making nickel, ruthenium, and iron nanoparticle catalysts for functional molecular syntheses.

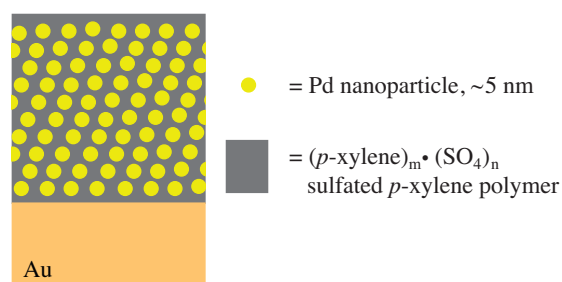


Fig. 3. Drawing of the SAPd structure.

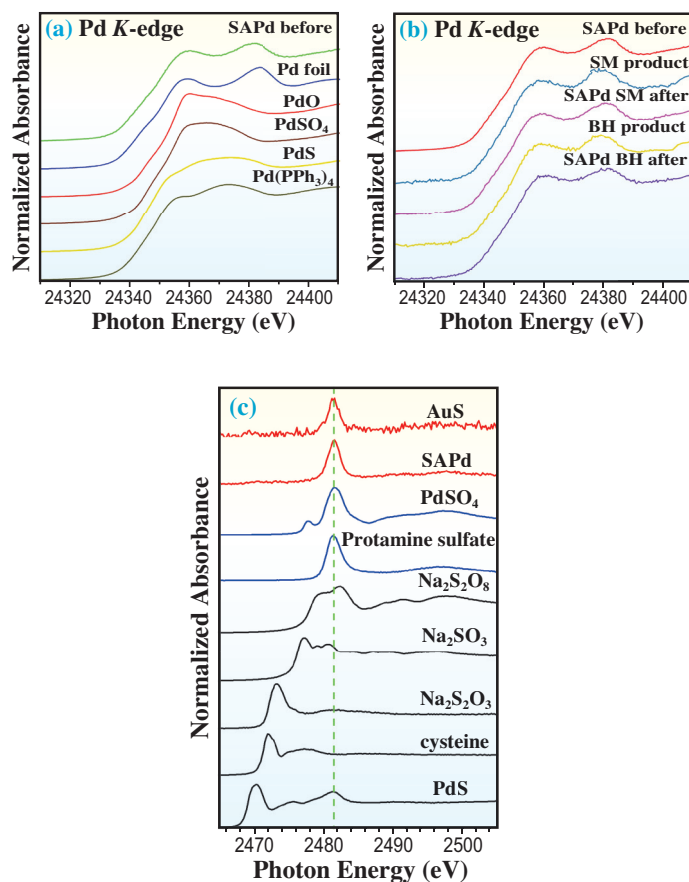


Fig. 2. Pd *K*-edge XANES spectra of (a) SAPd before: before cross-coupling reaction and standard materials, (b) SAPds. (c) S *K*-edge XANES spectra of SAPd before and standard materials.

Naoyuki Hoshiya^{a,b}, Satoshi Shuto^a
and Mitsuhiro Arisawa^{a,c,*}

^a Faculty of Pharmaceutical Sciences,
Hokkaido University

^b Kyoto Pharmaceutical University

^c Graduate School of Pharmaceutical Sciences,
Osaka University

*E-mail: arisaw@phs.osaka-u.ac.jp

References

- [1] J.F. Hartwig: Organotransition Metal Chemistry, University Science Books, 2010.
- [2] C. Deraedt, D. Astruc: Acc. Chem. Res. **47** (2014) 494.
- [3] N. Hoshiya *et al.*: J. Am. Chem. Soc. **132** (2010) 7270.
- [4] M. Al-Amin *et al.*: Adv. Synth. Catal. **354** (2012) 1061.
- [5] M. Arisawa, M. Al-Amin, T. Honma, Y. Tamenori, S. Arai, N. Hoshiya, T. Sato, M. Yokoyama, A. Ishii, M. Takeguchi, T. Miyazaki, M. Takeuchi, T. Maruko, S. Shuto: RSC Adv. **5** (2015) 676.