# Catalytic properties of surface-exposed silver nanoclusters within a ring-shaped metal oxide

Noble-metal nanoclusters have attracted increasing interest in various fields owing to their unique properties that depend on their structures and electronic states. In addition, the exposed metal surfaces of metal nanoclusters provide a significant opportunity to impart unique catalytic properties. Silver (Ag) nanoclusters and nanoparticles supported on metal-oxide supports exhibit cooperative reactivity, leading to various catalytic molecular transformations [1]. However, the exposed reactive surfaces of metal nanoclusters can easily lead to undesirable agglomeration, hindering the development of structurally well-defined metal nanoclusters with exposed metal surfaces and/or interfaces.

Polyoxometalates (POMs) are anionic metal-oxide clusters with diverse structures and properties [2]. Recently, we developed a synthetic method for stable Ag nanoclusters using lacunary POMs, which acts as a stabilizing ligand owing to some deficient sites from the parent POM structure [3]. Due to the unique acidity/basicity, redox properties, and photochemical properties of POMs, POM-stabilized Ag nanoclusters have substantial potential in various applications that differ from those of nanoclusters stabilized by organic ligands or conventional metal-oxide supports. In this study, we utilized a rigid and bulky POM $[P_8W_{48}O_{184}]^{40-}$ (**P8W48**) with a cavity of ~1 nm in diameter for the sequential synthesis of surface-exposed Ag nanoclusters. This led to unprecedented catalytic properties owing to the exposed Ag surface and cooperative reactivity of Ag nanoclusters and POMs (Fig. 1) [4].

By reacting the tetra-*n*-butylammonium (TBA) salt of **P8W48** with silver acetate in acetone, 16 Ag$^+$ ions were accumulated within the cavity of **P8W48** to form **Ag16**. Then, we reacted **Ag16** with silver acetate in *N,N*-dimethylformamide as a solvent and a mild reducing reagent. The yellow reaction mixture turned brown, indicating the formation of Ag nanoclusters. X-ray crystallographic analysis was performed at SPring-8 **BL02B1** ($\lambda$ = 0.4132 Å, 100 K), which revealed the formation of a {Ag$_{30}$} nanocluster within the cavity of **P8W48** (**Ag30**), wherein 30 Ag atoms existed in a distorted body-centered cubic arrangement (Figs. 2(a,b)). Furthermore, by reacting **Ag30** with a reducing reagent (i.e., TBABH$_4$ or H$_2$ gas), another {Ag$_{30}$} nanocluster was successfully obtained within the cavity of **P8W48** (**Ag30'**), wherein 26 of the 30 Ag atoms were arranged in a face-centered cubic structure (Figs. 2(c,d)). Elemental analysis, acid–base titration, and X-ray photoelectron spectroscopy showed
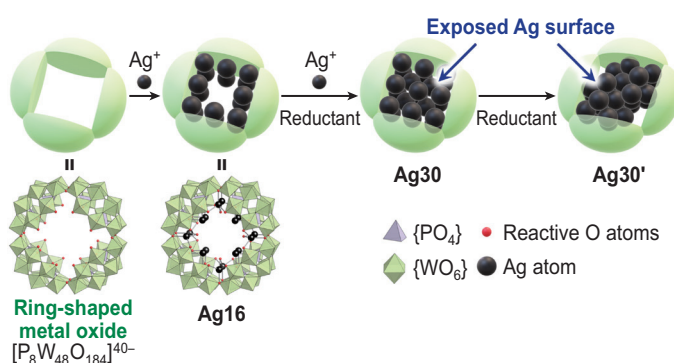


Fig. 1. Schematic of the sequential synthesis of surface-exposed Ag nanoclusters within ring-shaped POMs.

that the total charges of the {Ag$_{30}$} nanoclusters of **Ag30** and **Ag30'** were +22 {Ag$_{30}$}$^{22+}$ and +16 {Ag$_{30}$}$^{16+}$, respectively. These results showed that the reduction of the {Ag$_{30}$}$^{22+}$ nanoclusters of **Ag30** led to the structural transformation of **Ag30** and **Ag30'**. Notably, both **Ag30** and **Ag30'** possessed exposed Ag surfaces at the apertures of the ring-shaped {P$_8$W$_{48}$} framework, making them attractive molecular catalysts.

**Ag30'** exhibited excellent catalytic activity for the selective reduction of nitrobenzene to aniline using H$_2$ as a reductant under mild reaction conditions (60°C, 4 atm H$_2$ pressure) compared with the conditions using typical Ag catalysts on metal-oxide supports (>100°C, >10 atm H$_2$ pressure). However, the {Ag$_{27}$} nanocluster
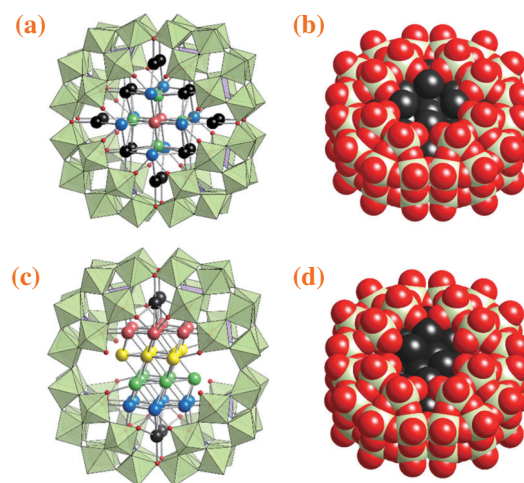


Fig. 2. Crystallographic structures of the anionic part of (**a,b**) **Ag30** (i.e., [{Ag$_{30}$}$^{22+}$(P$_8$W$_{48}$O$_{184}$)]$^{18-}$) and (**c,d**) **Ag30'** (i.e., [{Ag$_{30}$}$^{16+}$(P$_8$W$_{48}$O$_{184}$)]$^{24-}$) in the (**a,c**) polyhedral and (**b,d**) spacefill models. Green octahedron, {WO$_6$}; purple tetrahedron, {PO$_4$}; black, cyan, yellow, lime, and magenta balls, Ag atoms; red ball, oxygen atom.

completely covered by POMs[3] or polyvinylpyrrolidone (PVP)-coated Ag nanoparticles (Ag/PVP, 5 nm) hardly showed any catalytic activity. These results showed that the unique catalytic activity of **Ag30'** originated from its exposed Ag surface. Furthermore, this catalytic system could be applied to the selective reduction of various nitroarenes to their corresponding anilines (Fig. 3(b)). These results revealed the unique catalytic properties of **Ag30'**, which differ from those of typical Ag nanoparticle catalysts.

To further investigate the structure and electronic state of **Ag30'** after the catalytic reactions, we performed Ag $K$-edge X-ray absorption fine structure (XAFS) measurements at SPring-8 **BL01B1**. The $k$-space extended XAFS (EXAFS) oscillation pattern of **Ag30'** after the catalytic reaction showed no significant difference from that of **Ag30'** in the solid state, indicating that **Ag30'** maintained its structure during the catalytic reaction (Fig. 3(c)). Additionally, the X-ray absorption near-edge structure (XANES) spectrum of **Ag30'** after the catalytic reaction was compared with the XANES spectra of the original **Ag30'** and Ag foil, which showed that the {Ag$_{30}$} nanocluster was further reduced due to its reaction with H$_2$ (Fig. 3(d)). Deuteride (D$^-$) species were not observed in the $^2$H NMR study of the reaction solution of **Ag30'** and D$_2$ gas, revealing that a molecular H$_2$ dissociated into two protons and two electrons over **Ag30',** which were stored in the **P8W48** frameworks and {Ag$_{30}$} nanoclusters of **Ag30'**, respectively.

In conclusion, we synthesized atomically precise {Ag$_{30}$} nanoclusters within the cavity of a ring-shaped POM (i.e., [P$_8$W$_{48}$O$_{184}$]$^{40-}$), which possessed exposed Ag surfaces and interfaces with metal oxides. These {Ag$_{30}$} nanoclusters exhibited high stability despite their exposed Ag surfaces, showing notable catalytic activity for the selective reduction of organic substrates using H$_2$ as a reductant under mild reaction conditions. We envisage that this method can be applied to the synthesis of various surface-exposed metal nanoclusters, which will promote investigations into the unique properties and applications of metal nanoclusters.
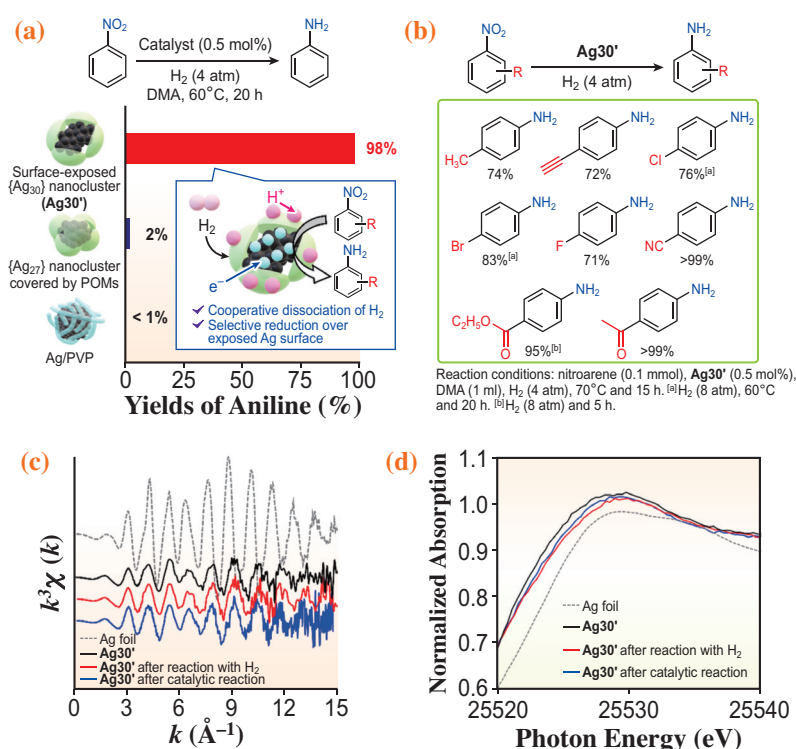


Fig. 3. (a) Catalytic activity and (b) substrate scope of the catalytic reduction of nitroarenes using **Ag30'**. (c) $k$-space EXAFS spectra and (d) XANES spectra of **Ag30'** before and after reacting with H$_2$ (4 atm, 60°C) in $N,N$-dimethylacetamide.

Kentaro Yonesato and Kosuke Suzuki*

Department of Applied Chemistry, The University of Tokyo

*Email: ksuzuki@appchem.t.u-tokyo.ac.jp

**References**

[1] X.-Y. Dong *et al*.: Catal. Sci. Technol. **5** (2015) 2554.
[2] M. T. Pope: Heteropoly and Isopoly Oxometalates (Springer, 1983).
[3] K. Yonesato *et al*.: J. Am. Chem. Soc. **141** (2019) 19550.
[4] *K. Yonesato, D. Yanai, S. Yamazoe, D. Yokogawa, T. Kikuchi, K. Yamaguchi, K. Suzuki: Nat. Chem. **15** (2023) 940.*