## Tetradentate Phosphine-Protected Au Nanoparticles Supported on Cs<sub>2</sub>CO<sub>3</sub> as Robust Oxidation Catalyst

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An essential issue in the development of metal nanoparticle (NP) catalysts is the stabilization of the NPs against aggregation while leaving the surface exposed. To overcome this problem, we have used linear polymers such as PVP to stabilize Au NPs, which are active in the aerobic oxidation of alcohols.<sup>1</sup> However, the PVP-stabilized Au NPs are not robust enough for catalysis under harsh conditions. In this work, we used bulky multidentate phosphine ligands to improve the stability of AuNPs with the expectation that part of the surface will be exposed due to steric hinderance between the bulky ligands (Figure 1a).

Au NPs protected by monodentate triphenylphosphine (TPP), bidentate 1,2-bis(diphenylphosphino)ethane (DPPE), and tetradentate tris(2-(diphenylphosphino)ethyl)phosphine (TDEP) were synthesized by reducing the Au-phosphine and AuSMeCl complexes in dichloromethane (Figure 1b). Transmission electron microscopy revealed that average particle sizes of Au:TPP, Au:DPPE and Au:TDEP were  $2.8 \pm 0.5$  nm,  $2.2 \pm 0.5$  nm, and  $2.2 \pm 0.6$  nm, respectively, which were consistent with the crystalline sizes estimated from powder X-ray diffraction patterns. The catalytic activity of these phosphine-protected Au NPs was compared using the aerobic oxidation of benzyl alcohol (BnOH) as a model reaction. During the catalytic reaction, the Au NPs were deposited on the powder of Cs<sub>2</sub>CO<sub>3</sub>, which acts as a base for the deprotonation of BnOH. Au:TDEP/Cs<sub>2</sub>CO<sub>3</sub> catalysts showed good activity and stability in benzyl alcohol (BnOH) oxidation.

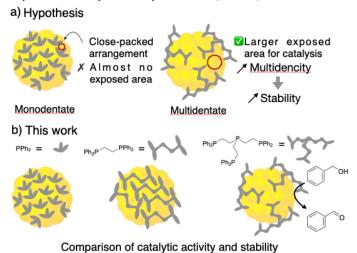


Figure 1. a) The hypothesis of using multidentate ligand. b). The main content of this work. 1) S. Hasegawa, S. Masuda, S. Takano, K. Harano, T. Tsukuda, *ACS. Catal.* **2022**, *12*, 6550.