

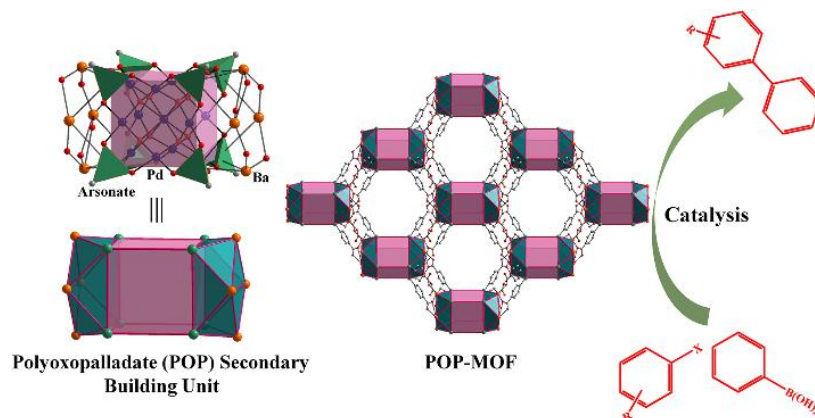
Noble Metal-Based Oxo-Clusters: From POMs to POPs and on to POP-MOFs

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Abstract

Polyoxometalates (POMs) based exclusively on Pd²⁺ addenda (polyoxopalladates, POPs) were discovered in 2008.^[1] The area of POP chemistry has developed rapidly ever since, due to the fundamentally novel structural and compositional features of POPs, resulting in unprecedented electronic, spectroscopic, magnetic, and catalytic properties.^[2] In terms of POP structural types, the symmetrical 12-palladate nanocube {MPd₁₂L₈} and the 15-palladate nanostar {MPd₁₅L₁₀} are the most abundant. Especially for the {MPd₁₂L₈} nanocube, many derivatives with various central guests including *d* and *f* block metal ions and various capping groups are known.^[2] We demonstrated the use of {MPd₁₂L₈} as discrete molecular precursors for the formation of supported palladium metal nanoparticles as hydrogenation catalysts, and we discovered an important dependence of the catalytic properties on the type of internal metal guest and external capping group.^[3] We also managed to construct 3D coordination networks using externally functionalized POPs, resulting in MOF-type assemblies (POP-MOFs) with interesting sorption and catalytic (C-C coupling) properties.^[4]



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