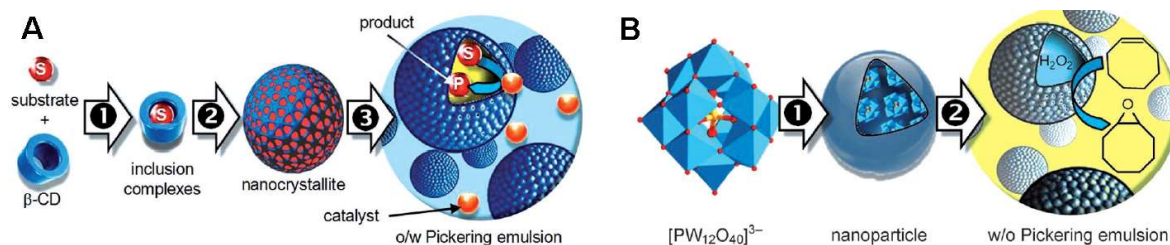


Self-assembly of 1-Decanol/ β -Cyclodextrin/Polyoxometalate in Colloidal Structures: a new lightning to understand POM catalysis in Pickering Emulsions

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Cyclodextrins (CDs) have a unique structure with a hydrophobic cavity and a hydrophilic surface allowing the formation of inclusion complexes with a wide variety of hydrophobic guests. While complexation of hydrophilic guests is considered to be unlikely, it has been recently shown that the complexation of polyoxometalate (POM) by γ - and β -CDs is possible giving respectively 1:2 and 1:1 inclusion complexes.¹ Our group has recently reported eco-friendly Pickering emulsions based on substrate/CD complexes for the oxidation of alkenes, organosulfurs and alcohols.² These highly efficient reaction media were based on the $[\text{Na}]_3[\text{PW}_{12}\text{O}_{40}]/\text{H}_2\text{O}_2$ catalytic system and were thus classified as Pickering assisted catalysis (PAC), as the catalyst was supposed to lie in the aqueous phase (Fig. 1A) contrary to the other systems based on self-assembled POM catalytic nanoparticles in which we have a Pickering interfacial catalysis (PIC) (Fig. 1B).



A. Principle of CD/substrate combination to perform interfacial catalysis in a O/W emulsion with a catalyst in aqueous phase (PAC). B. Principle of epoxidation in a W/O emulsion stabilized by catalytic nanoparticles formed by a POM and alkylammonium cations (PIC).³

However, and surprisingly, the PAC system exhibits a similar efficacy as the PIC system, which, in addition, requires an acidic co-catalyst.^{2,4} Face with this finding, a deeper investigation of the PAC system was undertaken by resorting to ¹H NMR, DLS, conductimetry, zetametry, TEM, and molecular dynamic experiments. It was thus shown this system can be described as core-shell structure consisting of a CD/1-decanol inclusion complexes core coated with a POM shell. These systems, based on colloidal tectonics concepts,⁵ which constitute a new class of nanostructured materials, can play important roles in various catalytic processes and offer sustainable eco-friendly solutions.

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