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“New Developments in Catalysis using Biomass as Support, Earth Abundant Metals and Plasmonic Activation”

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New Developments in Catalysis using Biomass as Support, Earth Abundant Metals and Plasmonic Activation

Cellulose nanocrystals (CNCs) are rod-shaped nanomaterials readily obtained from cellulose via sulphuric acid hydrolysis and now commercially available. We have explored the possibility of using these CNCs as supports for Pd, Ru and Ag nanocatalysts. Using Pd nanoparticles (NPs) deposited onto CNCs,¹ the hydrogenation of prochiral ketones at room temperature and 4 bars H₂ was performed and afforded unprecedentedly high ees for a system relying only on cellulose as chiral inducer.² High resolution transmission electron microscopy and tomography were used to better characterize the catalyst and shed light onto the chiral transfer mechanism. Ru NPs were also deposited onto CNCs, and successfully used as a biphasic and recyclable arene hydrogenation catalyst under 4 bar of H₂ and room temperature.³ At last, a CNC suspension was used to synthetically harvest Ag NPs directly from silver metal rods, which were used as catalysts for the hydrogenation of aldehydes.⁴

Besides we have explored a number of strategies to reduce the reliance on precious metals. For instance to studied the reduction of carbonyls in the solid phase, exploiting mechanical energy and using a cheap and air-stable silane, polymethylhydrosiloxane (PMHS) and a catalytic amounts of fluorides.⁵ While looking into the Cu(I) catalyzed A³-coupling reaction, we designed a support allowing the controlled release of catalytically active species as well as its scavenging after reaction. This system achieved excellent catalytic performance, superior to the reaction under homogeneous conditions, suggesting an interesting confinement effect.⁶

Besides, we have employed silver nanocubes for hydrogen activation and hydrogenation of ketones and aldehydes via irradiation at 405 nm, corresponding to the position of the plasmon band of the nanocubes.⁷ Exposure to other wavelengths, or absence of light failed to provide activity thus proving the plasmonic effect. Compared to other catalytic systems, the plasmonically activated catalyst provides access to primary and secondary alcohols using milder conditions, in a highly atom economical fashion.

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