Colloidal Polymer Nanoparticles for Heterogeneous Asymmetric Organocatalysis and Transition Metal Catalysis

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Embedding catalytically active organic and organometallic functionalities into polymer nanoparticles is a promising strategy for the design of efficient and sustainable heterogeneous catalysts. Functional polymer supports can enhance catalytic performance by improving access to active sites while increasing structural stability. In this context, miniemulsion polymerization provides a versatile and efficient route to nanoparticles with well-controlled size, morphology, and high specific surface area, all of which are key parameters governing catalytic activity. [1].

In this work, polymer nanoparticles were synthesized via miniemulsion polymerization and subsequently functionalized with a range of catalytic ligands, including proline derivatives, Schiff-base metal complexes, and xanthene-based fluorophores. The synthetic approach is based on the copolymerization of a structural monomer (typically styrene or methyl methacrylate) with a catalytically active functional comonomer. For proline-based systems, tailor-made polymerizable comonomers bearing the catalytic moiety were synthesized and incorporated into the polymer matrix [2]. An analogous strategy was applied to Schiff-base systems, where the ligand was coordinated to Mn(III) prior to polymerization. In the case of xanthene-based catalysts, rhodamine B was functionalized with 2-hydroxyethyl methacrylate (HEMA) via Steglich esterification to obtain a polymerizable ester derivative. The corresponding nanoparticles were prepared from styrene, divinylbenzene, and the rhodamine-derived comonomer.

After synthesis and functionalization, the nanoparticles were assessed in a set of representative model reactions to determine their catalytic performance. Proline-functionalized nanoparticles showed high diastereoselectivity in the intermolecular aldol reaction between *p* -nitrobenzaldehyde and cyclohexanone in aqueous media. Schiff-base systems also displayed efficient catalytic activity in the asymmetric epoxidation of styrene and indene, with reaction kinetics followed by chiral chromatography. In all cases, substrate conversions exceeded 90%, while the more sterically hindered catalysts afforded the highest selectivity and yields above 99% after 24 h. Additionally, xanthene-containing nanoparticles proved highly effective as photocatalysts in the dehalogenation of meso-1,2-dibromo-1,2-diphenylene.

An important advantage of these colloidal catalytic systems is their easy separation and recyclability, which underscores their strong potential for sustainable catalytic applications.

Keywords:
miniemulsion, colloid, asymmetric catalysis, nanoparticle

References:

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