Smart Copolymer Modified Metal Nanoparticles for Improved Catalytic Performance

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ABSTRACT

Catalyst is an indispensable component of most chemical reactions and catalysis has gained considerable attention for academic research as well as industrial applications in recent years. Nanoparticles can be used as 'quasi-homogeneous' catalysts, which bridge the gap between homogeneous and heterogeneous catalysts. Despite several advantages, agglomeration is the major drawback of using nanoparticles. Amphiphilic smart polymers as capping agents play a vital role in preventing nanoparticle agglomeration. In this dissertation, different amphiphilic smart polymers were synthesized by RAFT polymerization method and used as a stabilizing agent on nanoparticles' surfaces. The catalytic performance of these polymer-stabilized nanoparticles was explored in reduction and oxidation reactions in various conditions.

A set of amphiphilic random polymers P[NVP-*r*-NVP butane] was synthesized and used as a stabilizer for gold nanoparticles. The catalytic efficiency of these polymer-stabilized nanoparticles was analyzed in terms of their hydrophilic and hydrophobic properties. The temperature-induced phase behavior of polymers can be utilized in the recovery of the catalysts.

Three amphiphilic poly[(NIPA)-*b*-(styrene-*r*-vinyl pyridine)] copolymers having different chain length was used to cap gold nanoparticles and gold nano rods and the catalytic efficiency of these polymer-GNP conjugates was evaluated for the reduction reaction in water. Thermo-sensitive conformational changes of these block copolymers in aqueous medium renders non-Arrhenius type temperature-dependent catalytic efficiency due to change in accessibility of GNP surface. The catalytic efficiency of GNPs was also influenced by the length of the coated polymers, shape of the gold nanoparticles and presence of salt or surfactant in the solution, which was also attributed to the altered accessibility of the reactants to the catalyst surface. Nearly no loss of catalytic activity and initial rate constant on recycling confirmed the stability of the polymer coating.

Various composition of pH switchable cationic block copolymers, P[NVP-*b*-DMAEMA], were synthesized with varying number of DMAEMA units. The size and shape of the synthesized gold nanoparticles were found to depend on the chain length of the polymers and the pH of the medium. Polymer chain length, pH, and temperature influenced the catalytic efficiency of the polymer stabilized gold nanoparticles in the reduction reaction.

Currently, green chemistry is gaining immense popularity in catalysis since it reduces the use of organic solvents and acids, harsh reaction conditions, etc. Smart polymers can be used to graft on non-noble metal oxide nanoparticles to make them useful catalysts. P[NIPA-*r*-NVP)-*b*-AA] was synthesized and used as a grafting agent on magnetic iron oxide nanoparticle surface. The polymer functionalized magnetic nanoparticles can be used as a potent, green catalyst in the styrene oxidation reaction. It is possible to conduct the reaction in an aqueous medium and at lower temperatures. The catalysts didn't leach in the reaction medium and were easily recycled and reused.

Keywords: Smart polymers; RAFT polymerization; N-vinylpyrrolidone; N-isopropyl acrylamide; Dimethyl aminoethyl methacrylate; gold nanoparticles; gold nanorods; Magnetic nanoparticles; Cloud point; 4-Nitrophenol reduction, Styrene oxidation.