



Digest paper

Bimetallic chiral nanoparticles as catalysts for asymmetric synthesis

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ABSTRACT

Chiral nanoparticles have become one of the most versatile catalyst for the effective construction of chiral organic moieties. Recently, bimetallic nanoparticles as catalysts have gained interest among the chemists. The presence of hetero metal–metal interactions has modified the surface of the catalyst both electronically and geometrically to show unique activities, selectivities and possess an improved stability than the corresponding monometallic catalyst. In this review, the newly emerging bimetallic chiral nanoparticle catalysts (Rh/Co, Cu/Fe, Pd/Fe, Pt/Fe, Pd/Au, Rh/Ag, etc.) and their application in asymmetric Pauson–Khand reactions, hydrosilylation, Suzuki–Miyaura coupling, α -arylation of tetralones, reduction of ketones, allylation of nitrobenzaldehyde, 1,4-addition reactions and arylation of aldimines have been discussed.

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Introduction

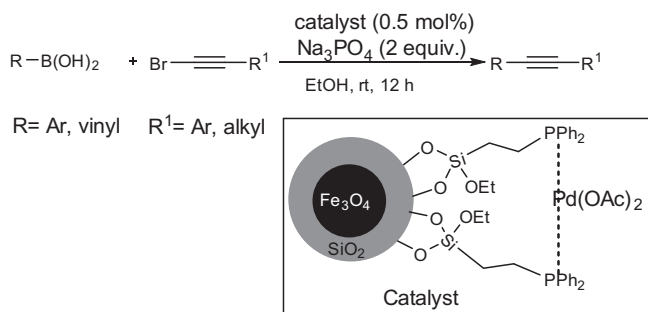
Catalyst plays an extraordinary role in organic transformations for the complete conversion of the reactants into the products under mild reaction condition. Generally, chemists are largely dependent on the homogeneous catalyst due to its high reactivity,

selectivity, and requirement of low catalyst loading.¹ Despite many advantages, poor reusability of the catalyst and metal contamination in the product are the common problems faced using homogeneous catalyst. Particularly in industries, where the reactions are carried out in larger scales, overall loss in economy is the major problem faced in using homogeneous catalysts due to the loss of precious metal catalyst as it cannot be easily recovered.^{2,3}

These drawbacks of the homogeneous catalysts led to the development of a process known as heterogenization.⁴ This

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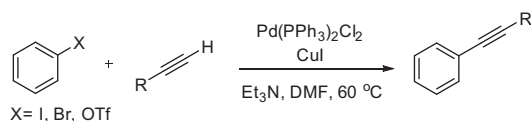
Scheme 1. Fe-magnetic nanoparticle immobilized palladium catalyst for the Suzuki coupling reaction.

heterogenization process involves grafting of the homogeneous catalyst to a solid support (polymers, silica, alumina, etc.) for its easy recovery.^{2a,5} However, the use of heterogenized catalyst are having serious limitations such as low reactivity, selectivity, non-robustness, leaching of metals from the catalyst, cost, and the tedious procedure involved in designing of the catalysts.^{2a,5b}

So, there is a need for a new catalytic system, which should be active like homogeneous catalysis, and easily recoverable like heterogeneous catalyst. Transition metal nanoparticles (also known as nanoclusters or colloids) can be considered as a bridge between homogeneous and heterogeneous catalysis (nanocatalysis).⁶ Since the size of NPs are very less generally from 1 to 100 nm (1 nm = 1×10^{-9} m), availability of the surface area is very high and hence there is an increased contact between the reactants and catalysts which results in dramatic increase in reactivity.⁷ Thus, the transition metal nanoparticles can combine the advantage of both the systems, and can offer unique activity as catalyst with high reactivity and selectivity.⁸

Further, the easy separation of the metal nanoparticles (MNPs) by the facile and efficient methods such as precipitation, centrifugation, nano filtration, magnetic decantation (in case of Fe, Co, Ni) and its reusability are the other salient features for its preferability. MNPs have also been reported to act merely as a solid support for many metal complexes and organocatalysts for effective separation and recyclization.⁹ Particularly, Fe nanoparticles in the form of its oxide Fe_2O_3 and Fe_3O_4 namely ferrite and magnetite respectively are widely used as a support for catalyst (Scheme 1). The magnetic nature of the support allows the simple separation of the catalyst using an external magnetic field, thus avoiding centrifugation and filtration.^{8b,10}

The last few decades have seen immense growth in the field of asymmetric synthesis.¹¹ However, most of the successful enantioselective reactions are not utilized by chemical or pharmaceutical industries because high enantioselectivities are achieved with homogenous catalysts but separation and purification of the chiral metal catalysts after the reaction are becoming a tedious task. In the case of heterogenous catalysts though the purification/separation of catalyst is very easy, it suffers from poor selectivity due to reduced contacts between catalyst and substrates. Utilizing chiral metal nanoparticles as catalyst for asymmetric reactions is an effective remedy to the above-mentioned problems.



Scheme 2. Sonogashira coupling using catalytic amount of Pd and copper salts.

While the metal nanoparticles have been explored for a number of organic transformations,^{12–14} the development and application of chiral NPs for the synthesis of a number of asymmetric molecules have become the topic of recent research.¹⁵

Chiral nanoparticles are usually prepared by introducing a chiral environment *via* functionalization of the surface of the nanoparticles using chiral ligands,^{15j,16} chiral quaternary ammonium salts,¹⁷ or chiral macromolecules.^{15h,18} The different modes of chiral functionalization of the nanoparticles have been reviewed in the literature.^{16a,19}

To improve it further, the development of bimetallic nanoparticles is the emerging field of research.²⁰ The salient feature in the bimetallic NPs is that the presence of different types of two catalytically active metals, distributed closely to each other to give their combined effect to catalyze the reaction more effectively than their corresponding monometallic parent metals.²¹ This review will focus on the newly emerging, chiral bimetallic nanoparticle catalysts and its application in asymmetric synthesis.

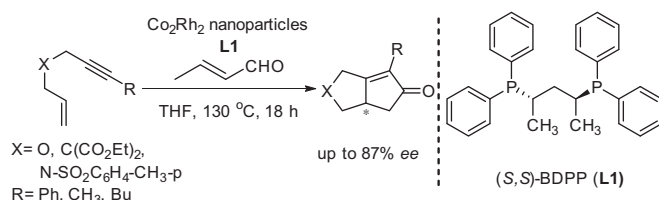
Bimetallic catalyst

The use of an external second metal as a catalyst in a number of transition metal catalyzed reactions are well known, e.g., Sonogashira cross coupling (Pd/Cu)²² (Scheme 2). In this reaction, the second metal acts as a co-catalyst either to activate the substrate or the main catalyst.²³ The use of two metal catalysts in a reaction in which one metal will tune the catalytic properties of the other have gained considerable interest due to the efficiency of the reaction in terms of reactivity and selectivity.²⁴

The continuous research in this field has led to the development of bimetallic catalyst in which two different metal components are present in the same entity. Though the two different metal components present in the catalyst can take various structures, alloy and core shell structures are the two major forms.²⁵

The nano sized bimetallic clusters were initially used in petroleum refineries for its better anti-knocking properties that replaced the usage of poisonous tetraethyl lead. In most of the cases, the bimetallic species used has been found to show improved activity than the mono metallic species.²⁶ The platinum/iridium bimetallic cluster when used in reformation of petroleum showed enhanced activity and prolongevity than the monometallic platinum.^{26b} Later, Pt/Ni bimetallic catalyst showed even better catalytic properties than the previous one.^{26d}

From then, the use of various bimetallic nanoparticles as catalysts have been developed and well explored in organic chemistry for a wide range of transformations.²⁷ Often unique reactivity, selectivity and modified catalytic activity from the corresponding monometallic species were witnessed from the bimetallic nanoparticle catalyzed reactions.^{20a,26c,28} The enhanced activity, often called as 'synergistic effect' arising from the combined properties of the two different metals present in the catalyst was resulted from the changes that occurred on the surface of the catalyst due to the presence of hetero metal–metal interactions. The addition of a second metal to the catalyst led to a change in



Scheme 3. Asymmetric Pauson–Khand reaction with Rh/Co bimetallic nanoparticles.

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