



Asymmetric reactions of chiral organo-magnetic nanoparticles



Venkatachalam Angamuthu, Dar-Fu Tai*

Department of Chemistry, National Dong-Hwa University, Hualien 974, Taiwan

ARTICLE INFO

Article history:

Received 1 August 2015

Received in revised form 4 September 2015

Accepted 5 September 2015

Available online 11 September 2015

Keywords:

Immobilization

Magnetic nanoparticles

Recyclable organocatalysis

Asymmetric reactions

Pseudo-homogeneous system

ABSTRACT

Magnetic nanoparticles (MNPs) have been widely used as a catalytic supports. MNPs have high surface-area that allows the design and setup of many catalytic sites. Their surfaces can be modified with chiral organocatalyst (COC) to become a sustainable catalytic material. This functionalized magnetite can be easily separated using an external magnet after reaction. We summarize the use of COC-MNPs which are robust and readily available for chiral transformation. The catalytic activity, recyclability, and immobilization method of COC-MNPs are described. The catalytic load, size of the particles, solvent system, ee values and de ratios are also evaluated on each asymmetric reaction.

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Contents

1. Introduction	254
2. Chiral organocatalysts supported on MNPs	255
2.1. L-Proline functionalized COC-MNPs	255
2.2. L-Prolinol functionalized COC-MNPs	256
2.3. Cinchona alkaloid modified COC-MNPs	257
2.4. Macmillan catalyst and cyclohexyl-1, 2-diamine coated on MNPs	257
2.5. Oligopeptide supported on MNPs for asymmetric reaction.....	259
3. Conclusions	259
Acknowledgements	259
References	259

1. Introduction

The development of an efficient and environmentally benign protocol for asymmetric synthesis was reached by the combined contribution of organo- and metal-ligand mediated asymmetric synthesis. Chiral organocatalysts (COC) have been chosen for this purpose [1–3]. The advantages of COC include their lack of sensitivity to moisture and oxygen, ready availability, low cost, and low toxicity when compared with (transition) metal catalysts. After conversion, homogeneous catalysts usually face out coming product purification, which is a tedious and problematic process; especially, when the transition metal complexes are involved. In particular, advanced methods for the removal of trace metal

contamination from products in regulatory industrial purification techniques have not been successful, because each methods has its own limitations of cost, efficiency, or waste disposal [4]. A sustainable and “green” catalyst for chiral organic transformation possess specific features including low preparation costs, high activity, great selectivity, high stability, efficient recovery and good recyclability [3–11]. A heterogeneous catalyst can facilitate recyclability and reuse, thereby minimizing waste generation in terms of environmental and economic concerns [12].

Magnetic nanoparticles (MNPs) have been developed as pseudo-heterogeneous supports for catalytic applications [13]. Their smaller size and high surface area lead to excellent loading and high catalytic activity. They can be as active as the homogeneous ones can [14,15]. This method avoids separation of the catalyst from a reaction mixture using centrifugation or tedious filtration. Its magnetic nature can simplify separation with an external magnet [14].

* Corresponding author. Fax: +886 3 863 3570.

E-mail address: dftai@mail.ndhu.edu.tw (D.-F. Tai).

The syntheses of MNPs have been reported using sol-gel techniques, co-precipitation, micro emulsion, laser pyrolysis, hydrothermal technique, microwave irradiation, sonolysis, and biological synthesis [16–21]. Magnetic metal nanoparticles (e.g., Fe, Co, and Ni), magnetic alloys and metal oxides (e.g., Fe₃O₄, CoFe₂O₄, MnFe₂O₄, and CuFe₂O₄) can be synthesized using these methods with the desired properties as catalysts or as catalyst supports [22]. Among all the MNPs, Fe₃O₄ has been widely explored [23,24] due to its simple use during synthesis as well as its toxicity, affordability, stability under harsh conditions, and polar surface. It can be easily immobilized with catalytic scaffolds and functionalization [25–31]. Synthesis of iron oxide nanoparticles (Fe₃O₄), protection, and functionalization as catalytic MNPs have been detailed discussed, reported and reviewed [32–34].

Recently, Dalpozzo [35] and NasirBaig et al. [36] described MNPs supported catalysis including metal complexes relevant to this scope. This review focuses on the recent application of COC supported on MNPs (COC-MNPs) in asymmetric synthesis.

2. Chiral organocatalysts supported on MNPs

Most COCs or biocatalysts (enzymes) are pure substance. However, MNPs are a composition of particles with various sizes. Immobilization of COC on MNPs results in the formation of a mix of materials. A random distribution of COCs on MNPs is inevitable in the formation process. The number of COC and their position on each particle is arbitrary. Self-aggregation, undesired covalent and noncovalent linkages could be coexisted. These COC-MNPs can only be considered as partially organized materials. A new phenomenon has evolved from the operation of these materials.

First, the length of the linker is critical for COC-MNPs. A linker between COC and MNPs is essential to minimize the steric repulsion between MNPs and their substrate. If the length of the linker was too long, aggregation of COC-MNPs will have occurred. Therefore, a medium size linker is the most appropriate for COC-MNPs.

Second, the best condition can be obtained by operating COC-MNPs as a pseudo-heterogeneous support in a pseudo-homogeneous system [34]. A linker with a large organic component will help to dissolve a higher portion of COC in the organic solvent. Its catalytic activity increases because of less phase barrier for substrate to overcome. On the other hand, polar linkers, such as ionic liquid (IL), raises the solubility and activity of COC-MNPs in an aqueous solution. Pseudo-homogenization [36] has emerged as an essential condition for COC-MNPs catalysis.

Third, the amount of COC in the system can serve as an indicator to define the effectiveness of COC-MNPs. Comparatively, the lower amount of COC-MNPs (mol%) indicates how much more effective it is. A loading with less than 5 mol% catalyst could be considered as near homogeneous (pseudo-homogenization). Leaches or poisoning over a period of time during asymmetric induction is a problem encountered by COC-MNPs.

Fourth, particle size can influence steric repulsion between COC and the substrate. As the size of COC-MNPs is larger, repulsion reduces the occurred aggregation. The chiral moiety on COC is exposed to the substrate for asymmetric induction. Otherwise, it will affect the yields and ee values. However, large MNPs particles decrease the chance of pseudo-homogenization.

2.1. L-Proline functionalized COC-MNPs

L-Proline has been lauded as the “simplest enzyme” due to its ability to catalyze reactions with high stereoselectivity [37]. Jacob et al. achieved better results from aldol reaction with L-proline immobilized on MNPs [38]. 4-Hydroxy-L-proline was used to link to the MNPs through a 4-ring position. Acrylates

and methacrylates derivatives of the 4-hydroxy proline and were subjected to polymerization with MNPs covered with acrylic acid or methacryloyl-containing phosphate. The obtained proline-functionalized MNPs (**Pro-1–4**) were subjected to a direct aldol reaction with aryl aldehydes and carbonyl compounds. The catalytic activity of these catalysts increased by sonication and addition of benzoic acid providing excellent yields of aldol products with good ee values but general diastereoselectivity (Table 1).

Comparatively, silica coated MNPs were formed by attaching 4-hydroxyproline with a triethoxysilylpropanecarbamate in toluene to provide **Pro-5** [39]. **Pro-5** was subjected to direct aldol reaction with aldehyde and cyclic ketones to provide good to moderate yield and enantiomeric excess (Table 1). The catalytic activities varied with the steric of substrates. The bulky substituent on the aldehyde decreases enantioselectivity and the larger alkyl groups on cyclic ketone dropped the yield. It is recyclable and can be reused for up to five cycles without any significant loss of activity.

In another approach, L-proline was linked through the carboxyl group by an amide bond on imidazolium-based IL-functionalized MNPs to afford a magnetically recoverable **Pro-6** [40]. For comparison, **IL-freePro-6** was prepared by attaching aminopropyltriethoxysilane to MNPs, followed by condensation with *N*-Boc-L-proline. These catalysts were employed for catalytic asymmetric aldol reaction in water. The enhanced catalytic efficiency was observed for **Pro-6** due to the imidazolium-based moiety. **Pro-6** favored the diffusion of reagents toward the catalytic site (pseudo-homogenization), which enhances the activity of the catalyst in an aqueous aldol reaction. The aldol products were obtained in good to moderated yields with high enantioselectivities (Table 1). The yields and enantioselectivities were lower for sterically hindered aldehydes.

A non-covalent approach has been developed using polyoxometalates functionalized MNPs. This was prepared via the well applied “acid-base” strategy and it can act as a catalyst support for chiral amines (**Pro-7**) [41]. **Pro-7** was tested in aldol reactions and the desired products were isolated in good yields, syn/anti ratios, and high ee values (Table 1). The reaction is more efficient with cyclic ketones than with acyclic ketones. It also has excellent reusability and maintained its catalytic activity even after 11 cycles.

Recently, Akceylan et al. reported *p*-*tert*-butylcalix[4]arene-based chiral organocatalysts (**Pro-8**) for a direct aldol reaction in water [42]. **Pro-8** was synthesized by tethering the calixarene moiety to MNPs with two proline moieties at the upper and lower rims of the calix[4]arene units. The catalytic activity of the **Pro-8** was tested on the asymmetric direct aldol reaction at room temperature between cyclohexanone and 4-nitrobenzaldehyde. An almost quantitative conversion of the corresponding product with good diastereoselectivity, and enantioselectivity was achieved in water (Table 1). It performed well and tolerated a variety of electron-withdrawing groups at the 4-position and 3-position of the phenyl ring except *p*-anisaldehyde. In some circumstance, the reaction with cyclic ketone other than cyclohexanone and *p*-nitrobenzaldehyde leads to opposite diastereoselectivity. The catalyst can be recycled five times without significant loss of its activity.

Pro-2 is the most efficient catalyst among these proline functionalized-MNPs (**Pro-1 to Pro-6**) for aldol reaction based on catalytic activity and recyclability with wide range of substrates. Although **Pro-7** is equally efficient as **Pro-2** with its activity and recyclability; however, it only showed good activity with cyclic ketones. **Pro-8** is also very efficient with varieties of aromatic aldehyde and cyclic ketones for aldol reaction. **Pro-8** is able to maintain high catalytic activity in aqueous medium based on the rigidity of calix[4]arene. **Pro-2 and Pro-7** performed best under solvent-free conditions. On the contrary, one should be aware that the diastereoselectivity of **Pro-8** decreased upon reducing the amount of water.

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