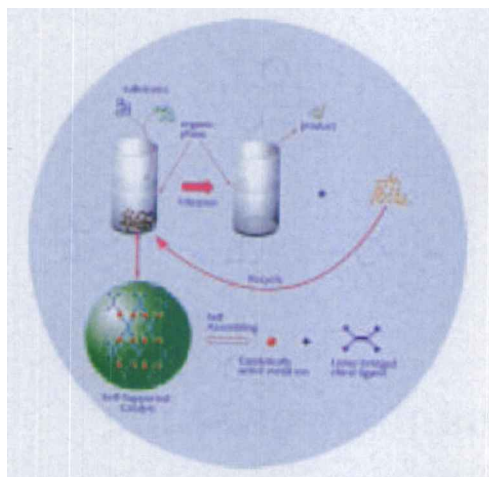


New Advances in Chiral Catalyst Immobilization



Self-supporting strategy for chiral catalyst immobilization.

Asymmetric catalysis of organic reactions is one of the most efficient ways to obtain optically pure chiral compounds, which are crucially important to the development of modern pharmaceutical and fine chemical industries, as well as material science. The development of chiral catalysts is of central significance to the success of practical application of asymmetric catalysis, which can be classified into homogeneous and heterogeneous catalysis according to the nature of the catalytic processes. Although homogeneous asymmetric catalysis has the advantages of high enantioselectivity and catalytic activity in various asymmetric transformations under mild reaction conditions, the difficulties associated with the recovery and reuse of expensive chiral catalysts severely hamper its practical applications. Furthermore, the potential contamination of the products caused by metal leaching from the homogeneous catalysts is particularly unacceptable for pharmaceutical production. One of the most promising ways to circumvent these difficulties is the immobilization of the homogeneous chiral catalysts using various strategies. So far many approaches have been developed for the immobilization of homogeneous catalysts, typically including the use of various supports (inorganic materials, organic polymers, dendrimers, or membranes), or employing special reaction medium such as ionic liquid or other biphasic systems. Despite the impressive successes

achieved in the catalyst recovery and recycle, the catalysts immobilized by using these traditional approaches are often flawed by the reduced enantioselectivity, diminished activity, and poor reproducibility in the catalysis and/or tedious catalyst synthesis in comparison with their homogeneous counterparts.

Recently, molecular recognition and self-assembly have been widely employed in the design and synthesis of novel functional materials based on supramolecular chemistry approach, which is emerging as a promising and rapidly growing research area in material sciences. With the financial supports from NSFC, CAS and 973 Programs of MOST, Prof. Ding Kuiling and his research group at CAS Shanghai Institute of Organic Chemistry (SIOC) successfully developed a conceptually new strategy for chiral catalyst immobilization in the field of heterogeneous asymmetric catalysis. On the basis of this strategy, the chiral multitopic ligands and metal ions are self-assembled into homochiral polymeric catalysts, which themselves by nature are usually insoluble in common organic solvents and thus provide an excellent platform to perform heterogeneous catalysis without using any supporting materials. The chiral multitopic ligand can spontaneously form chiral environment inside the cavities or on the surface of the solids for enantioselective control of the reaction, and the metal ions act as the catalytically active centers.

Prof. Ding and his coworkers at SIOC successfully applied this self-supporting strategy in the heterogenization of chiral catalysts for the catalysis of asymmetric carbonyl-ene, sulfoxidation, epoxidation and asymmetric hydrogenation reactions. In addition to the simple recovery and facile recycle, such kinds of self-supported chiral catalysts exhibit the advantages of facile preparation, robust chiral structures, and excellent enantioselectivities, and thus hold great promise for practical applications. Part of the results have been published on top international chemistry journals such as *J. Am. Chem. Soc.* (2004, 126, 10524; 2005, 127, 7694), *Angew. Chem. Int. Ed.* (2005, 44, 6362), *Chem. Eur. J.* (2005, 11, 4078), etc. Very recently, Prof. Ding and his

coworkers were invited to write a Concept article for *Chemistry: A European Journal* (Chem. Eur. J. 2006, 12, 5188) because of their significant contribution in this area. This new concept of self-supporting strategy for chiral catalyst immobilization has provided a promising approach to bridge the gap between homogeneous and heterogeneous asymmetric catalysis. Very recently, Prof. Ding and his coworkers reported the design and synthesis of a new type of polymeric chiral catalyst using both hydrogen bonding and coordination interactions. This new approach overcomes the difficulty of the somewhat tedious procedure for covalent multi topic ligand synthesis. The self-supported chiral catalyst generated by the aforementioned

approach demonstrates excellent asymmetric induction in the heterogeneous hydrogenation of dehydro-amino acid and enamide derivatives (91%—96% ee). Salient features of this catalyst, such as its simple preparation, facile recovery and reuse (“10 times”), as well as excellent stereo control performance, make it particularly interesting for practical asymmetric synthesis. The results of this work were published as the Hot Paper in *Angew. Chem. Int. Ed.* (2006, 45, 4108), and were highlighted by *Chemistry World* (July 2006, 14) (a magazine of Royal Society of Chemistry) with the title of “New Twists on Catalysis”

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