Abstract

This study draws attention towards supporting materials, such as carbon materials and polymers, and their unique properties that lead to a rational design of heterogeneous nanocatalysts, especially for chemical reactions that are of high value in pharmaceuticals, pesticides, biological and fine chemicals industry. With the increasing demand of chiral products, a number of efficient asymmetric heterogeneous catalysts based on transition metal loaded support with chiral modifiers have been developed for a wide range of organic transformations. The major part of asymmetric catalysis is homogeneous catalysis because it facilitates molecular reactions in an efficient manner with high chirality transfer. Despite these merits, separation and purification of products, as well as recycling of the catalysts, make it less environmentally benign and more costly. The immobilization of asymmetric homogeneous catalysts on the support is a viable option to overcome such issues and to make them recyclable and economical.

Out of various studies on asymmetric heterogeneous catalysis, asymmetric hydrogenation of α-ketoester is one of the key reactions with wide application in pharmaceutical industries. Metal nanoparticles loaded carbon composite systems are of great interest as they blend the exclusive properties of carbon materials with metal nanoparticles. In the current research work, carbon materials, loaded with highly platinum dispersed nanoparticles, were synthesized for hydrogenation of methyl pyruvate using a natural chiral modifier. Out of various carbon supported metals, the Pt/MWCNTs was found to be most efficient system and provides high enantioselectivity (ee > 99%) due to the high absorption of cinchona and substrate on atomically dispersed Pt nanoparticles that maximize metal utilization. One to one Substrate-modifier interaction was examined by NMR. During this study, the excellent activity of Pt (111) plane was observed due to higher packing density, stability and cohesive energy than other crystal planes, leading to significant chemisorptions of a variety of chemical entities. For that, a strategy was developed that involves preparation of Pt (111) from phase transfer reagent Tw20, followed by mixing of functionalized carbon materials to obtain heterogeneous Pt (111) hexagonal nanocrystal loaded carbon catalyst, by simple thermolytic reduction in air, which were tested for asymmetric hydrogenation of α-ketoester at ambient reaction conditions, using cinchonine as modifier. Chiral polymers were also prepared and used as supports, because they are tuneable based on the monomer used and synthetically viable. In this study, it was found that the chirality could be transferred from the support to substrate with an ease in case of hydrogenation of carbonyl groups. In a distinct study, the F-CD-BF_4/Pt/MWCNTs were screened for stereoselective allylation of imine and aldehydes.