



Rhodium-calix[4]pyrrole and Rhodium-tetraphenyl porphyrin: Preparation, surface grafting and its catalytic application on nitrobenzene reduction

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Abstract: Rhodium containing macro molecules Calix[4]pyrrole (RhCP) and tetraphenyl Porphyrin (RhTPP) were prepared and grafted on the surface of functionalised molecular sieve materials. ¹H and ¹³C NMR, CHN analysis and Mass spectral analysis was used for structural elucidation of homogeneous organometallic complexes. ¹H NMR and CHNS analysis confirms the formation of Calix [4] pyrrole (CP) and Tetraphenyl porphyrin (TPP). The introduction of rhodium ion into the macromolecule is well evident from the disappearance of ¹H NMR signal characteristic of N-H bond (7.1ppm in CP and -2.74 ppm in TPP). Further the formation of RhCP and RhTPP complex is confirmed by CHNS and Mass spectral analysis, the data are in line with theoretically calculated value. The grafting of RhCP and RhTPP on diamino functionalised SBA-15 support was conformed through low angle XRD, ¹³C MAS-NMR and SEM-EDAX analysis. Both homogeneous and heterogeneous catalyst were utilized for nitrobenzene reduction. The RhCP and RhTPP heterogenized on SBA-15-F showed complete conversion of nitrobenzene with exclusive formation of aniline as a product. The catalytic activities were retained in both the systems even after several runs.

Introduction

Catalysis is the backbone of chemical processes involved in natural metabolic pathways and many industrial processes involved in day-to-day life.¹ About 80–90% of the chemical produced in industries are manufactured using catalysts, in which homogenous catalysts such as organometallic complexes containing transition metal ions play a major role.^{2–5} The major problems associated with homogenous catalysts are difficulty in catalyst recovery from reaction mixtures, product isolation, expensive precursor materials, and tedious procedures. Despite their limitations, industries prefer homogeneous catalysts owing to their high reactivity and selectivity. Development of heterogeneous catalysts or heterogenization of homogeneous catalysts overcomes the limitations of homogeneous catalysts and offers the advantages of both. This involves various approaches such as surface grafting through covalently connected organic moieties on a support, direct immobilization of homogenous catalysts on inorganic support, and ship-in-bottle methods.² Solid supports including microporous and mesoporous silica-based materials such as zeolites, MCM 41, SBA-16, SBA-15, and polymers have proved promising for

heterogenization of homogeneous catalysts.^{6–11} Particularly, mesoporous silica-based materials having uniform channels, large pore sizes, high surface areas, and thermal stability^{3c} offer great opportunities for grafting and encapsulation of various organometallic homogeneous catalysts. A variety of homogeneous catalysts such as Schiff-bases, cyclopentadienyl, and phosphine-based complexes have been heterogenized and demonstrated potential activity for various organic transformations.⁴ A lot of work has been carried out on homogeneous organometallic complexes derived from macromolecular ligands such as protoporphyrin's, calix[4]pyrrole (CP), and calix-arenes play an important role in catalysis and bio-catalysis. For example, a macrocyclic compound comprising four pyrrole subunits that are connected through α -carbon analogues to a heme unit can encapsulate various transition metal ions.⁵ In particular, lot of work has been focused on development of metallo-porphyrin based molecules and its applications on various fields such as hydration of alkenes and alkynes, oxidation of alcohols and oxygen reductions in fuel cell.⁶ The early work on these systems known as potential enzyme catalysts for several biological processes⁷ and was reported by Alder and Longo in 1964. Besides porphyrin, calix[4]pyrrole CP is an excellent macrocyclic molecule first synthesized by Baeyer in 1886 by acid condensation of pyrrole and acetone.⁸ These macrocyclic molecules play a vital role in catalysis, as well as medicinal, and analytical sciences, and in chemical sensors.⁹ The catalytic activities and stabilities of these macrocyclic materials are enhanced by encapsulating in inorganic solid supports. In 1983,

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