

Iron-immobilized Periodic Mesoporous Organosilica as Active and Selective Catalyst for Amino Alcohol Synthesis

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Periodic mesoporous organosilica (PMO) is a heterogeneous solid material that has crystal-like mesoporous walls of 4 Å diameter and can be incorporated with organic linker molecules such as ligands for metal chelation [1-3]. In this study, one of such PMO embedded with 2,2'-bipyridine linker (BPy-PMO), was utilized for immobilization of environmentally benign and economically viable iron species. By utilization of the PMO-based solid ligand system, unique 1:1 (Fe:BPy) coordination (Figure 1) was realized without using any special bulky substitution strategy traditionally used in homogenous catalyst preparation. The iron-immobilized PMO (Fe-BPy-PMO) was characterized by IR, UV, XRF, XRD and XAS analyses. The analyses have shown relatively high metal loading, presumably due to high ligand density owing to the high surface area of the PMO structure. The mesoporous nature of the PMO has been retained with slightly lowered average pore diameter, suggesting the metal immobilization inside the mesopores, based on nitrogen adsorption desorption analysis.

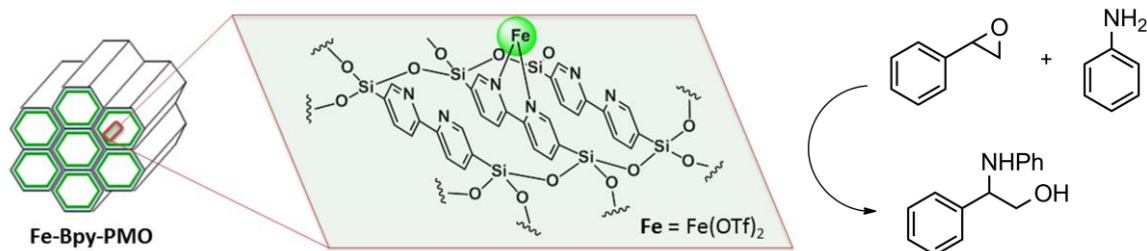


Figure 1 Structure and catalysis of Fe-BPy-PMO.

The iron-immobilized PMOs were then employed as catalysts in epoxide ring opening reactions with anilines. Terminal epoxides, such as styrene oxide, exclusively afforded the products from the nucleophilic attack at the C-2 position. The catalytic activities of conventional homogeneous Fe catalysts were found out to be much less active than Fe-BPy-PMOs, suggesting that immobilization of the iron species on the PMO brings preferable catalytic active sites for the ring-opening reaction. The catalyst was recyclable with slight loss of the catalytic activity. In the presence of both trans- and cis-stilbene oxides, conversion the trans-stilbene oxide to the corresponding ring-opened product was favored over that of cis-stilbene oxide. The yield of the reaction was found to be 68% with 85% trans-selectivity. The catalysts were recyclable at least for four times by simple washing with slight loss of the catalytic activity. The trans:cis selectivity was maintained during the recycle runs. The unique region-selectivity found in this study could be useful in natural product synthesis or drug synthesis due to the environmentally acceptable features of iron.

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