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An indirect approach for encapsulation of chiral cobalt catalyst in microporous Zeolite-Y

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ABSTRACT

Hierarchical structure in microporous zeolite-Y was introduced to overcome the diffusional restriction for direct encapsulation of chiral cobalt (II) Schiff base complexes. Mesopores with cylindrical channels of ~5 nm dimensions were formed on post modification of zeolite-Y and was evident from the transmission electron microscopy and surface area analysis. Two different chiral cobalt (II) Schiff base complexes with minor variation in the ligand structure were constructed inside the mesoporous zeolite-Y cavity. The formation of the metal complexes was ascertained from the decrease in surface area and mesoporous pore volume. The two synthesized heterogeneous chiral cobalt Schiff base complexes were used as catalysts for asymmetric Henry reaction. At -35 °C, more than 80% ee with S-major nitro-aldol product was achieved within 3h. Initial activation of the reaction mixture with microwave irradiation was found to have dramatic influence on the catalytic performance of the two catalysts.

1. Introduction

Over the last few decades transition metal complexes with different type of ligands has been synthesized inside the supercage of zeolite-Y cavity by “*ship in a bottle*” or “*flexible ligand method*” [1–20]. Flexible ligand method is mostly applicable to molecules or ligands with planar structure and size less than 7.5 Å [21]. Alternatively, the ligands with larger kinetic diameter are constructed within the supercage of zeolite-Y by diffusing the ligand precursor [18,19]. Schiff base ligands fall into those categories and hence are well constructed by diffusing a diamine and an aldehyde (say salicylaldehyde) inside the zeolite-Y cavity [11,21]. While the method is considered to be appropriate for successful encapsulation of metal Schiff base complexes but many a times the unreacted molecules or substrates limits the suitability of the technique [22]. Removal of such unwanted molecules becomes difficult and many often they block the pores and hampers the catalytic process [21,22]. Especially when it comes into the encapsulation of chiral metal catalysts, the *ship in a bottle* synthesis method turns out to be more painstaking [22]. The pore restriction is one of the major obstructers in diffusing the Schiff base ligand directly into the interior cavity of zeolite-Y [21,22]. It would have been better if the size of the ligand were matchable with the pore size of zeolite-Y. Unfortunately, the pore

opening of zeolite-Y (~0.74 nm) is smaller than the size of Schiff base ligands. Therefore, most of the synthesis processes are confined to the *ship in a bottle* method.

In situ generation of the mesoporous channel or an indirect method to create hierarchical structure in zeolite-Y could be an alternative route for direct penetration of those larger ligands sidestepping the smaller pores [23–27]. Recently, large numbers of approaches such as assembly methods or bottom-up methods, demetallization, top-down methods and mixed method have been adopted by various researchers to create such mesoporosity in microporous zeolites [22,23,26]. Besides this, the post-synthetic approach is another way of creating mesopores in zeolite-Y [21,23,28]. Garcia et al. and Chal et al. used such process to generate intracrystalline mesopores of narrow dimension [24,29–31]. Recently, Qin et al. also adopted the similar technique to create mesoporosity within zeolite-Y having low Si/Al ratio [25]. Zhao et al. very recently used hierarchical zeolite-Y as host for achiral Fe-Schiff base complexes and used as a catalyst for cycloalkane oxidation [27]. To the best of our knowledge reports on the encapsulation of chiral cobalt (II) Schiff base complex inside zeolite-Y via mesoporous channel creation is so far not available.

Chiral Schiff base ligands have been enticed as a suitable candidate for generating heterogeneous chiral catalyst for asymmetric Henry

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