

# Chiral Ni-Schiff Base Complexes inside Zeolite-Y and Their Application in Asymmetric Henry Reaction: Effect of Initial Activation with Microwave Irradiation

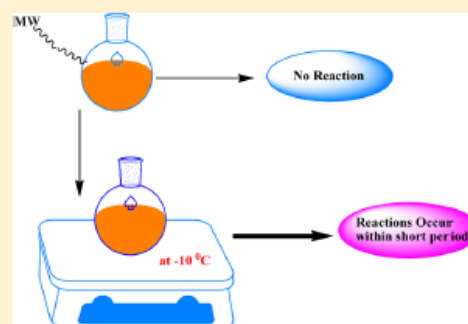
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## Supporting Information

**ABSTRACT:** Chiral Ni(II)-Schiff base complexes synthesized inside the cavity of zeolite-Y were used as heterogeneous chiral catalyst for asymmetric Henry reaction. Synthesized catalysts were characterized using various spectrochemical and physicochemical techniques. Solid state NMR analysis has been used to confirm the internal location of the metal complexes. To the best of our knowledge MAS NMR has not been used to characterize chiral diamagnetic Ni<sup>2+</sup>-Schiff base complex inside zeolite-Y. The catalytic activities of the materials were dependent on temperature, solvent, and amount of catalyst. High catalytic transformation of aldehydes with nitromethane to nitro-aldol product (92% yield and 83% ee, *S*-isomer) was achieved at -10 °C. Initial activation of the reaction with microwave irradiation for 15 min leads to a substantial decrease in the reaction time in comparison to normal stirring. Heterogeneous catalysts were found to be advantageous over the homogeneous counterparts in terms of recyclability of the catalyst. Most importantly, product selectivity, percentage yield, and enantioselectivity were found to be high with the heterogeneous catalyst. The catalytic activities of the metal complexes were influenced by the structural modification of the Schiff base ligands. Calculation of the energy barrier using density functional theory (DFT) suggests that the activation barrier is less in the case of the encapsulated complexes.



## INTRODUCTION

Asymmetric Henry reaction or nitro-aldol condensation reaction has been considered as an important class of organic transformations due to the application of the aldol product in various natural product syntheses.<sup>1–5</sup> Different homogeneous and heterogeneous chiral catalysts are implemented to achieve such asymmetric transformation.<sup>6–10</sup> Although various chiral homogeneous catalysts so far reported have been found to show good catalytic activity, but they fail in terms of recyclability, and in many cases homogeneous catalysts suffer from loss of catalytic activity.<sup>11–14</sup> Nowadays, many researchers use different techniques, such as use of ionic liquids, supercritical liquids, etc., to recover the homogeneous chiral catalyst.<sup>15</sup> However, besides these methodologies, heterogenization of homogeneous catalyst via encapsulation or immobilization into solid support has been found to be advantageous over various other techniques.<sup>16–18</sup> Zeolites, MCM-41, etc. and such inorganic mantles are nowadays found to be excellent supports for heterogenization of homogeneous catalysts.<sup>19–22</sup> Out of the various Si-based materials, zeolite-Y, a crystalline aluminosilicate with pore dimension of 7.4 Å and supercage of 13 Å, has been found to be the most effective host for encapsulation of transition metal complexes. Starting from the

pioneering work of Herron,<sup>23</sup> quite a good number of works have been reported on encapsulation of transition metal complexes inside the cavity of zeolite-Y. From our group we have reported design of various metal complexes with 1,10 phenanthroline, with picolates, and with chiral and achiral Schiff base complexes inside zeolite-Y.<sup>24–28</sup> Although a significant number of metal catalyst has been synthesized inside the zeolite-Y cavity, significantly fewer reports are available on designing of chiral catalyst inside zeolite-Y. Recently, we have reported the synthesis of a chiral vanadium Schiff base complex inside zeolite-Y<sup>29</sup> and also a Cu-Cinchonidine complex supported on zeolite-Y.<sup>30</sup> Vanadium Schiff base complexes were found to be efficient catalysts for oxidation of 2-naphthol and styrene. Looking into the advantages of zeolite-Y encapsulated chiral metal Schiff base complexes, in this study we report the synthesis and characterization of the Ni<sup>2+</sup>-Schiff base complexes inside zeolite-Y and their application in asymmetric Henry reaction.

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