

Zeolite Encapsulated Copper (II) Complexes of Pyridoxal Based Tetradentate Ligands for the Oxidation of Styrene, Cyclohexene and Methylphenylsulfide

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(Abstract)

Interaction of copper(II) exchanged zeolite-Y with N,N'-ethylenebis(pyridoxyliminato) (H₂pydx-en, **I**) and N,N'-propylenebis(pyridoxyliminato) (H₂pydx-1,3-pn, **II**) in refluxing methanol leads to the formation of corresponding complexes, abbreviated herein as [Cu(pydx-en)]-Y (**3**) and [Cu(pydx-1,3-pn)]-Y (**4**) in the super cages of the zeolite-Y. Neat complexes, [Cu(pydx-en)] (**1**) and [Cu(pydx-1,3-pn)] (**2**) have also been prepared with these ligands. Spectroscopic studies (IR, electronic and EPR), elemental analyses, thermal study, Field-Emission-Scanning Electron Micrographs (FE-SEM) and X-ray diffraction patterns have been used to characterize these complexes. The crystal and molecular structures of **1** and of **2**.CH₃OH, have been determined, confirming the ONNO binding mode of the ligands. The geometry around the metal ion is a very slightly distorted square planar in **1** and distorted square pyramid in **2**. The encapsulated complexes catalyse the oxidation, by H₂O₂ and *tert*-butylhydroperoxide, of styrene, cyclohexene and thioanisole efficiently. Under the optimized reaction conditions, the oxidation of styrene catalyzed by **3** and **4** gave 23.6 % and 28.0 % conversion, respectively using *tert*-butylhydroperoxide as oxidant where styrene oxide, benzaldehyde, benzoic acid, and phenylacetaldehyde are the major products. Better conversions have been obtained using H₂O₂ as oxidant. Oxidation of cyclohexene catalysed by these complexes gave cyclohexenepoxide, 2-cyclohexene-1-ol, cyclohexane-1,2-diol and 2-cyclohexene-1-one as major products. A maximum of 90.1% conversion of cyclohexene with **3** and 83.0% with **4** was obtained under optimized conditions. Similarly, a maximum of 80.3% conversion of methyl phenyl sulfide with **3** and 83.0 % with **4** was observed, where the selectivity of major product methyl phenyl sulfoxide was found to be ca. 60 %. Tests for the recycle ability and heterogeneity of the reactions have also been carried out and results indicate their recyclability. A possible reaction mechanism has been proposed by titrating methanolic solution of **1** and **2** with H₂O₂ to identify the possible intermediates.