

Zeolite-encapsulated Cu(II)-salen complex as a catalyst for oxidation of cyclohexanol

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Cu (salen) complex encapsulated in zeolite Y is characterized by elemental analysis, IR, UV-vis and ESR spectroscopy and is shown to be a catalyst for the selective oxidation of cyclohexanol to cyclohexanone in the presence of H₂O₂ under much milder conditions (80°C) than those in current practice.

Zeolites have been used as interactive supports for metal clusters¹ and the ionic attachment of metal complexes². Recently strategies have been evolved for the entrapment of metal complexes in zeolite matrices using the flexible ligand and template synthesis approach³⁻⁵. Such encapsulated metal complexes offer several advantages in catalytic reactions due to their ruggedness, protection against deactivation by dimer and cluster formation during catalysis and ease of separation from the reaction products.

For example, mono and polynuclear carbonyl compounds of Rh and Ir have been entrapped in Y-zeolite for vapour phase carbonylation of methanol and aromatic compounds as well as for hydroformylation reactions⁶⁻¹⁰. The Pd(salen) complex encapsulated in X or Y zeolite has been found to be an active catalyst for the selective hydrogenation of hex-1-ene in the presence of cyclohexane¹¹. Similarly VO(salen)-Y zeolite complex is reported to be active in the oxidation of toluene with H₂O₂ to give benzaldehyde, benzyl alcohol, *p*-cresol and *o*-cresol respectively¹². Recently zeolite-encapsulated Mn(II)-bipyridyl complexes have been found to catalyse selective epoxidation of alkenes without complications from competing processes such as self oxidation or catalase activity¹³. In the present communication we report on the catalytic activity of [Cu(salen)] complex encapsulated in the supercages of zeolite Y for the selective oxidation of cyclohexanol to cyclohexanone using H₂O₂ as the oxidant.

Synthesis of [Cu(salen)] encaged in zeolite Na-Y was performed by a stepwise method described in the case of Mn(salen) complexes by Bowers and Dutta¹⁴. Cu-Y zeolite was prepared by ion-exchange of Na-Y with 0.01 M aqueous solution of Cu(CH₃COO)₂. The resulting solid was washed with deionized hot water till filtrate was colourless and then filtered and dried at 155°C under vacuum. For the encapsulation of the complex the salen ligand was refluxed with the Cu-Y at 240°C for 24 h in a closed system, then soxhlet extracted with CH₂Cl₂ to remove the unreacted ligand. Uncomplexed Cu ions remaining in the zeolite are removed by back exchange of the zeolite with 0.1 M NaCl solution for 12 h. It was then washed with hot water to remove chloride ions and finally dried at 120°C.

Thermogravimetric and chemical analysis performed on [Cu(salen)]-Y showed that after extraction an average number of one salen ligand per supercage and per Cu²⁺ ion remains in the sample. This ratio corresponds to the proposed stoichiometry of the complex¹⁵. The thermal degradation pattern for Cu-salen-Y shows a two-stage loss, the first corresponding to the loss of 4 intrazeolite water molecules¹⁶⁻¹⁸ and the second ascribable to the decomposition of the chelate moiety (Fig. 1). Compared to the free chelate (275°C) the accelerated decomposition of the zeolite-encapsulated chelate structure occurs at higher temperature (425°C) as anticipated^{19,20}.

The FT-IR profile of the encapsulated compound is essentially similar to the published data on the free chelate²⁰ except for the dominating hydroxyl absorptions in the region 906-1282 cm⁻¹ which is generally considered as the physico-chemical evidence for the encapsulation of salen compounds⁴. The UV-vis spectra of the compound shows a weak *d-d* absorption band around 740 nm and an enhancement of the L→M charge transfer bands at 355 nm indicative of the complex formation of salen ligand within the zeolite matrix²¹. ESR spectra of Cu-Y at 25°C a broad symmetric signal at *g*= 2.15 characteristic of Cu²⁺ ions at site I (ref. 22) which is slightly narrowed upon complexation with small superimposed nitrogen hyperfines typical of tetrahedrally distorted square planar geometry (supplementary material)^{15,23}. The distortion has been thought to arise from the constraints imposed by the zeolite cavity and its participation in coordination sphere²⁴.

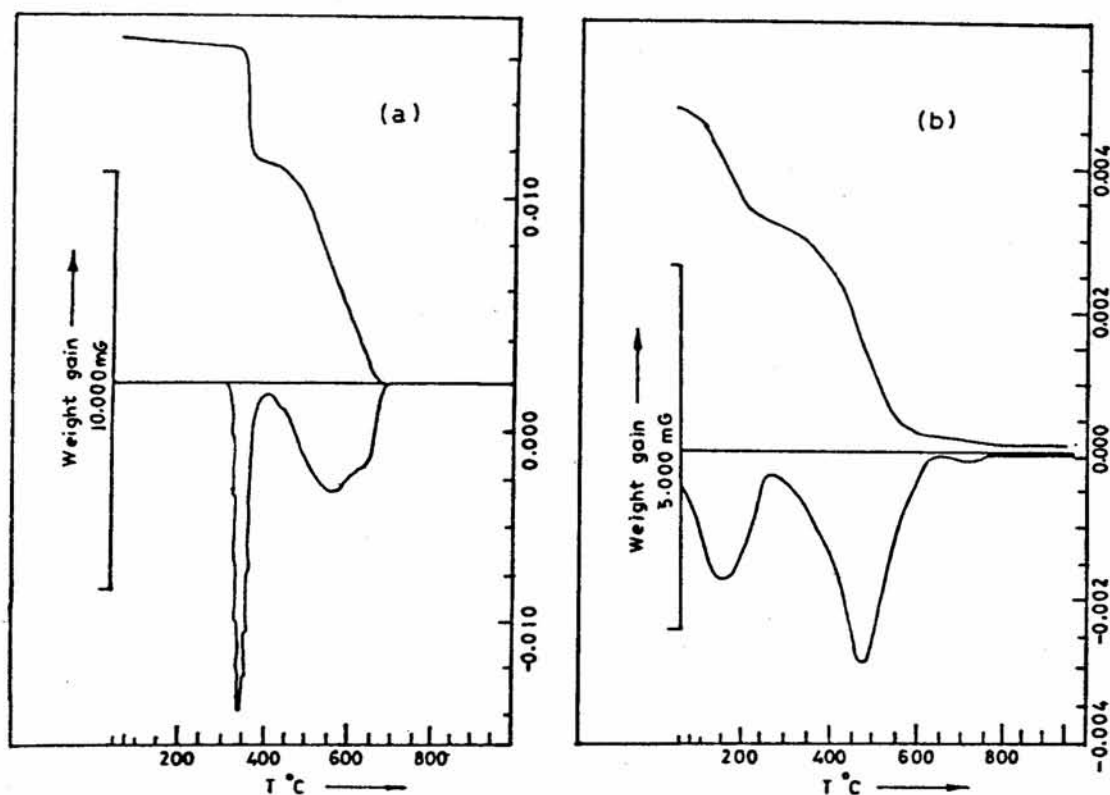


Fig. 1—TGA profiles of (a) Cu-salen, (b) Cu-salen-Y recorded on Mettler TA4000 system.

The catalytic activity of the Cu-salen-Y (0.1g) towards oxidation of cyclohexanol (1g) was carried out at 80°C. A mixture of 1 ml of 30 % aqueous H_2O_2 and 5 ml of water was the oxidant. The reaction was carried out for half an hour after which it was extracted with ether. Cyclohexanol and cyclohexanone were estimated by GC method (Schimadzu, Carbowax column). Under the experimental conditions the conversion of cyclohexanol was around 50 % with a selectivity of 98 % to cyclohexanone (Fig. 2). The present work has thus demonstrated a successful encapsulation of Cu-salen complex in zeolite Y. It has further shown that the essential structural features of the Cu-salen compound remain intact after encapsulation although with slight distortions due perhaps to be constraints of the cavity. The present commercial processes for the conversion of cyclohexanol to cyclohexanone involve passing the substrate over a Cu-SiO₂ catalyst at around 300°. Our encapsulated system provides a clean, one-step heterogeneous catalytic route for the conversion of cyclohexanol to cyclohexanone under much milder conditions (80°C) than those in current practise.

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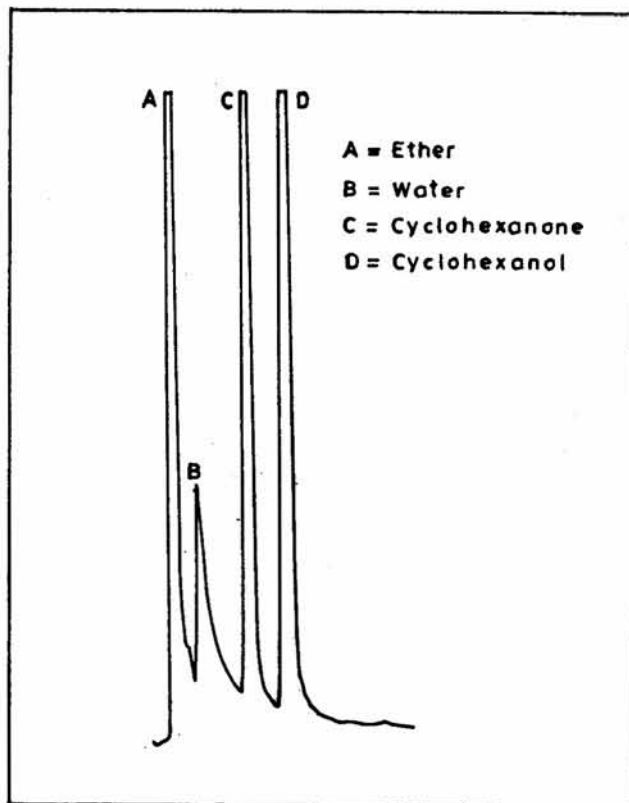


Fig. 2—GC trace of the products formed upon oxidation of cyclohexanol with catalyst [Cu (salen)].

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