

Zeolite Encapsulated Metal Complexes and Their Catalytic Activities: An Overview

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Abstract: *The heterogenization of homogeneous catalysts can be achieved by immobilization, grafting, anchoring or encapsulating them in an inert solid like organic polymer or inorganic support. Transition metal complexes having good catalytic properties are immobilized through encapsulation in the super cages of zeolites is called zeolite encapsulated metal complexes (ZEMC) or ship-in-the-bottle complexes. Zeolite encapsulated metal complexes enjoy the advantageous features of homo- as well as heterogeneous catalysts, these materials have provided opportunities to develop catalytic processes for various reactions such as oxidation alkylation, cyclization, acylation, isomerisation and hydrogenation etc.*

Keywords: *zeolite encapsulated metal complexes (ZEMC); catalyst*

1. INTRODUCTION

Important properties of the industrial catalysts are the substantial working life and the retention of their effectiveness while environmental issues stress on the development of such catalytic processes that are beneficial from industrial as well as environmental point of view. Amongst the variety of catalytically active species known, the transition metal complexes catalyze a wide range of chemical reactions such as oxidation, hydrogenation, polymerization etc. However, these homogeneous catalysts produce a large amount of undesired products that may cause serious problem to the environment. There is, therefore, a need to find more efficient catalytic system, especially for fine chemicals industry and also to meet the environmental challenges. Many efforts have been directed in past two decades towards the development of heterogeneous processes and the heterogenization of known active as well as new homogeneous catalysts [1]. The heterogenization of homogeneous catalysts can be achieved by immobilization, grafting, anchoring or encapsulating them in an inert solid like organic polymer or inorganic support. Their polymerization may also provide heterogenized catalysts.

All kinds of materials that are thermally stable and chemically inert can be used as support for catalyst. The functionalized polymers (cross-linked as well as non-cross-linked) have widely been used as support for homogeneous catalysts through covalent bonding. Amongst various inorganic supports, alumina and silica are the most common. One of the oldest methods to prepare supported catalysts is the co-precipitation of the catalytically active component and the support to give a mixture which is subsequently dried, calcined and reduced to give a porous material with a high surface area. Another but most preferred method is loading pre-existing support materials in the form of shaped bodies with the catalytic active phase by means of impregnation or precipitation from solution [2].

Transition metal complexes having good catalytic properties have also been immobilized through encapsulation in the super cages of zeolites in order to prepare heterogeneous catalysts with the desired structure and function [3, 4]. This new class of catalysts is called zeolite encapsulated metal complexes (ZEMC) or ship-in-the-bottle complexes. As zeolite encapsulated metal complexes enjoy the advantageous features of homo- as well as heterogeneous catalysts, these materials have provided opportunities to develop catalytic processes for various reactions such as oxidation alkylation, cyclization, acylation, isomerisation and hydrogenation etc.

2. ZEOLITE ENCAPSULATED METAL COMPLEXES AND THEIR CATALYTIC ACTIVITIES

As zeolite encapsulated metal complexes enjoy the advantageous features of homo- as well as heterogeneous catalysts, these materials have provided opportunities to develop catalytic processes for various reactions such as hydrogenation, oxidation, alkylation, cyclization, acylation and isomerisation etc. Bedioui has suggested basically three general approaches to the preparation of zeolite encapsulated metal complexes. These are: flexible ligand method, template synthesis method and zeolite synthesis method. In addition to these, other two approaches, such as, ion exchange method and adsorption method may also be considered [3, 5]. A review dealing with selected complexes encapsulated in the cavity of zeolite and their catalytic activity has been presented here.

3. CHIRAL COMPLEXES

The catalytic activity of chiral complexes has become a powerful tool in modern synthetic organic chemistry. Jacobson *et al.* have used chiral Mn-salen complexes for the asymmetric epoxidation of a series of unfunctionalized alkenes with high stereo control [6]. Alcón *et al.* have reported encapsulation of manganese (II) and Cu (II) complexes of chiral ligands in zeolite-Y. Encapsulation was affected by flexible ligand method. These encapsulated complexes catalyze the oxidation of methyl phenyl sulfide and (2-ethylbutyl) phenyl sulfide. Conversions of these substrates vary in the range 73 – 100 %. The greater stability of these encapsulated complexes over homogeneous analogues has been attributed to the suppression of dimeric or polymeric species formation [7, 8].

The [Co(salophen)]-Y (H_2 salophen = Schiff base derived from 3,5-di-*tert*-butylsalicylaldehyde and *o*-phenylenediamine) also been studied as oxygenating agents in the palladium-hydroquinone catalysed aerobic oxidation of 1,3-dienes. It is also active for the aerobic oxidation of 1,3-cyclohexadiene to 1,4-diacetoxy-2-cyclohexene at room temperature. Interestingly these catalysts are reusable [9].

4. MODEL COMPLEXES FOR ENZYME MIMIC

Zeolite-encapsulated metal complexes have been used to mimic enzymatic systems. Metalloporphyrins, metallophthalocyanines and metal-Schiff base complexes model active sites of enzymes especially monooxygenase enzymes of cytochrome P-450 family. The replacement of the protein skeleton of neutral enzymes by a size and shape selective framework of zeolite may provide the best arrangement for the catalytically active centres. Because of these properties zeolite-encapsulated metal complexes are also called inorganic enzymes.

Bedioui has reviewed such oxidation catalysts and oxygen carriers [4]. Zeolite encapsulated iron phthalocyanines have been used for biomimetic oxidation of hydrocarbon [10]. Vanadium complexes have been considered as biomimetic models of the active site of haloperoxidases. In presence of oxidant like H_2O_2 , they form electrophilic peroxo complexes that selectively transfer an oxygen atom to the organic substrates. Even peroxovanadium(V) complexes catalyze such reaction very well [11].

5. SCHIFF BASE COMPLEXES

Oxovanadium(IV) complexes of ligands H_2 salen, H_2 sal-1,2-pn, H_2 sal-1,3-pn, H_2 saldien and Hehybe have been encapsulated in the cavity of zeolite-Y. These complexes catalyze the oxidation of phenol [12]. The [VO(salen)]-Y has been used as active catalyst in the oxidation of toluene by H_2O_2 to produce benzaldehyde, benzylalcohol, *o*-cresol and *p*-cresol [13]. Oxidation of cyclohexane has also been carried out by similar complexes [14, 15].

Zeolite encapsulated metal complexes prepared from other tetradentate Schiff base ligands also catalysed the oxidation of phenol using different oxidants. Thus, Cu(X-salen) [16], Mn(X-salen) [17] (X = H, Cl, Br or NO_2), have been used as catalysts. The oxidation products are mainly catechol and hydroquinone. In no cases the formation of 1,4-benzoquinone was detected.

Poltowicz *et al.* have encapsulated whole range of metallosalen complexes (e.g. [Fe (salen)], [Mn(salen)], [Cu(salen)] and Co(salen)]) in Na-X zeolite to study catalytic activity for the oxidation of cyclooctane [18].

Ratnasamy *et al.* have isolated copper (II) and manganese (III) complexes of salen derivatives encapsulated in the cavity of zeolite-X and zeolite-Y by zeolite synthesis method. The oxidation of styrene under aerobic conditions using *tert*-butylhydroperoxide gave benzaldehyde, styrene and phenylacetaldehyde. The catalytic efficiency of these encapsulated complexes were much higher than that of the neat complexes. Electron withdrawing substituents such as -Cl, -Br, - NO_2 on the aromatic ring enhances the rate of oxidation [19, 20].

These complexes also catalyse the oxidation of phenol and p-xylene. The aerobic oxidation of p-xylene in the absence of added hydrogen promoters and using *tert*-butyl hydroperoxide as the initiator and $\text{Mn}(\text{X-sal-1,3-pn})\text{Cl}-\text{X}$ and $[\text{Mn}(\text{sal-dach})\text{Cl}]-\text{X}$ ($\text{H}_2\text{sal-dach}$ = Schiff derived from salicylaldehyde and 1,2-diaminocyclohexane) at low temperature showed as high as 60 % conversion. Again conversion increased in presence of electron withdrawing group on the aromatic ring [21, 22].

Manganese (III) and nickel (II) complexes of H_2salen have also been used as catalyst for the epoxidation of cyclohexene, cyclooctene and 1-hexene using NaOCl and KHSO_5 as terminal oxidants. Selectivity in the epoxidation of linear olefins is possibly the result of small pore size of the zeolite host which governs the molecular sieving and orientation properties [23].

Complex, $[\text{Mn}(\text{salen})]^+$ encapsulated in zeolite-Y has been used for the asymmetric epoxidation of *cis*- β -methylstyrene with sodium hypochlorite [74]. Other similar complexes have also been used for the epoxidation of various types of alkenes, arenes and cycloalkenes [25-27]. The $[\text{Mn}(\text{salen})]^+-\text{Y}$ has been reported to be stereospecific in the epoxidation of *trans* stilbene as well as active for the epoxidation of *cis*-substituted aryl alkenes [28, 29].

Complexes $\text{NH}_4[\text{VO}_2(\text{sal-inh})(\text{H}_2\text{O})]-\text{Y}$ ($\text{H}_2\text{sal-inh}$ = Schiff base derived from salicylaldehyde and iso nicotinic acid hydrazide) and $\text{NH}_4[\text{VO}_2(\text{sal-oap})(\text{H}_2\text{O})]-\text{Y}$ ($\text{H}_2\text{sal-inh}$ = Schiff base derived from salicylaldehyde and *o*-aminophenol) encapsulated in zeolite-Y catalyze the oxidative bromination of salicylaldehyde to give 5-bromosalicylaldehyde with 90 % selectivity. These complexes have been encapsulated by reacting pre-exchanged ammonium vanadate with zeolite-Y with sodium salt of ligand in aqueous solution followed by adjusting pH to ca. 7.5 [30]. Complexes $\text{NH}_4[\text{VO}_2(\text{sal-inh})(\text{H}_2\text{O})]-\text{Y}$ and $\text{NH}_4[\text{VO}_2(\text{sal-oap})(\text{H}_2\text{O})]-\text{Y}$ also catalyze the oxidation of phenol to give catechol and hydroquinone with good selectivity towards catechol [31]. Dioxomolybdenum(VI) complex of similar ligand $\text{H}_2\text{sal-shz}$ catalyze aerial oxidation of cyclooctene [32].

The manganese (III), iron (III) and cobalt (III) complexes of Schiff base derived from *m*-nitrobenzaldehyde and 2,6-diaminopyridine encapsulated in Na-Y zeolite. These catalysts have been used for the aerobic oxidation of 1-octene [33].

Not only oxidation, zeolite encapsulated complexes e.g. $[\text{Pd}(\text{salen})]$ and $[\text{Ni}(\text{salen})]$ encapsulated in zeolite X and Y have been used for the hydrogenation of olefins [86].

6. METALLOPHthalOCYANINES, METALLOPORPHYRINS AND MACROCYCLIC COMPLEXES

Metal phthalocyanines encapsulated in zeolite-X, zeolite-Y (MPC-Y) and ZSM-5 prepared by *in situ* ligand synthesis have been studied for the oxidation of phenol by H_2O_2 [87-92].

Raja and Ratnasamy [93] have reported the oxyhalogenations of benzene, toluene, phenol, aniline, anisole and resorcinol using phthalocyanines of Cu, Fe and Co encapsulated in zeolites X, Y and L.

Direct conversion of methane to a mixture of methanol and formaldehyde, and propane to a mixture of isopropanol and acetone have been achieved at ambient conditions with high activity and selectivity using phthalocyanines complexes of iron cobalt and nickel encapsulated in zeolites as catalysts and O_2 /*tert*-butyl hydroperoxide as oxidant [42, 43]. Metal phthalocyanines encapsulated in zeolite have also been used for the oxidation of hydrocarbons [44]. The oxidation of olefins like cyclohexene and 1-hexene were carried out with iodosylbenzene and *tert*-butyl hydroperoxide as oxidant in chloroform using CoPC-Y. It was observed that the encapsulated phthalocyanine was active even after 20 h of reaction [45].

7. COMPLEXES WITH OTHER TYPE OF LIGANDS

Binuclear copper (II), nickel (II) and cobalt (II) complexes of 3-formylsalicylic (H_2fsal) have been encapsulated in zeolite-Y for the oxidation of benzyl alcohol and ethylbenzene. Their catalytic potential vary in the order: $[\{\text{Cu}(\text{fsal})\}_2]-\text{Y} > [\{\text{Co}(\text{fsal})\}_2]-\text{Y} > [\{\text{Ni}(\text{fsal})\}_2]-\text{Y}$ [46]. Partial oxidation of these substrates has also been catalyzed by zeolite-Y encapsulated copper(II), nickel(II) and cobalt(II) complexes of dimethylglyoxime [47]. The catalytic reduction of oxygen (industrially known as deoxo reaction) by copper (II) complexes of embelin and 2-aminobenzimidazole encapsulated in the cavity of zeolite-Y was found to be enhanced with respect to that reported for simple complexes [48].

Jacobs *et al.* have reported *cis*-[Mn(bipy)₂]²⁺ encapsulated in zeolite X and Y and used them for the oxidation of a series of alkenes and cycloalkenes with H₂O₂ as oxidant. The catalytic epoxidation of cycloalkene is followed by acid-catalyzed ring opening. Thus, adipic acid from cyclohexene has also been obtained [49]. Similar iron(II) and manganese(II) complexes of 2,2'-dipyridyl have also been isolated by Niassary *et al.* for the oxidation of cyclic ethers, such as, tetrahydrofuran, tetrahydropyron, 2,3-dihydropyron and 1,4-dioxane using H₂O₂ and TBHP as oxidant. Mainly cyclic ether-2-ols and cyclic ether-2-ones have been obtained. Minor product, 2,3-dihydro cyclic ether has also been detected in some cases [50].

Oxovanadium(IV) picolinate, [VO(pic)₂] encapsulated in zeolite-Y has been studied for the oxidation of cyclohexane, isopropanol and benzene using H₂O₂ as an oxidant. Leaching of [VO(pic)₂] has, however, been noticed in the presence of H₂O₂ [51]. The monopero oxovanadium(V) monopicolinate complex has been isolated by the treatment of encapsulated complex with urea hydrogen peroxide in acetonitrile, the formation of which has been confirmed by UV-visible, Raman and XAFS studies. This novel catalyst retains the solution like activities in aliphatic and aromatic hydrocarbon oxidations as well as in alcohol oxidation [52].

8. CONCLUSIONS

It is evident from the review that zeolite encapsulated metal complexes have provided opportunities to develop catalytic system for various industrial processes. Particularly, oxidation reactions catalyzed by these specialized class of immobilized complexes are well documented.

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