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Transition Metal Complexes On Insoluble Support And Their Applications In Transformations Of Organic Reactions

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Abstract : In this review we present some important recent work on the catalytic action of some supported transition metal complexes. Different types of synthesized heterogeneous transition metal catalysts including anchoring transition metal complexes on polymer or silica and zeolite encapsulated complexes are discussed. An overview of their physicochemical characterization techniques are reported. The review is focused and devoted to the catalytic applications of these host-guest materials towards the transformations of some organic reactions e.g. oxidation, epoxidation, hydrolysis, ring-opening…….etc.

Key word: Supported transition metal complex catalysts; organic reactions.

Introduction

Heterogeneous catalytic processes are of great importance in industry. They are quite important in the refining of petroleum. About 70 % of all crude oil pass through such process.On the other hand, Adsorption and desorption phenomena occur frequently in all fields of our every days life as well as in many industrial and technical applications. This starts with simple glues and ends with the filters for pollutant gases in large power plants.

Transition metals can act as catalysts for two reasons. First, because they can have several different oxidation states. They can take part in electron transfer reactions. Second, transition metals and their ions can provide sites at which reactions can take place. They can bond to a wide range of atoms and molecules e.g. those with lone pair or π electrons forming complexes with different numbers of bonds. Not only they can form four and six numbers of bonds but also sometimes two, three and five. This feature give them a high probability to form the suitable intermediates required for proceeding the catalytic reactions. They can show catalytic behavior when dissolved in solutions or as solids i.e., homogeneous or heterogeneous catalysts.

Adsorption and desorption processes are also important elementary steps in the complicated chain of reactions that make up a typical mechanism in heterogeneous catalysis. Before the reaction can start at all, the

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reactant atoms or molecules must adsorb at the solid surface. Then they will diffuse along the surface, react with each other or with the surface to generate reaction intermediates, and eventually, in most cases after several reaction steps, the final products have to desorb from the surface.

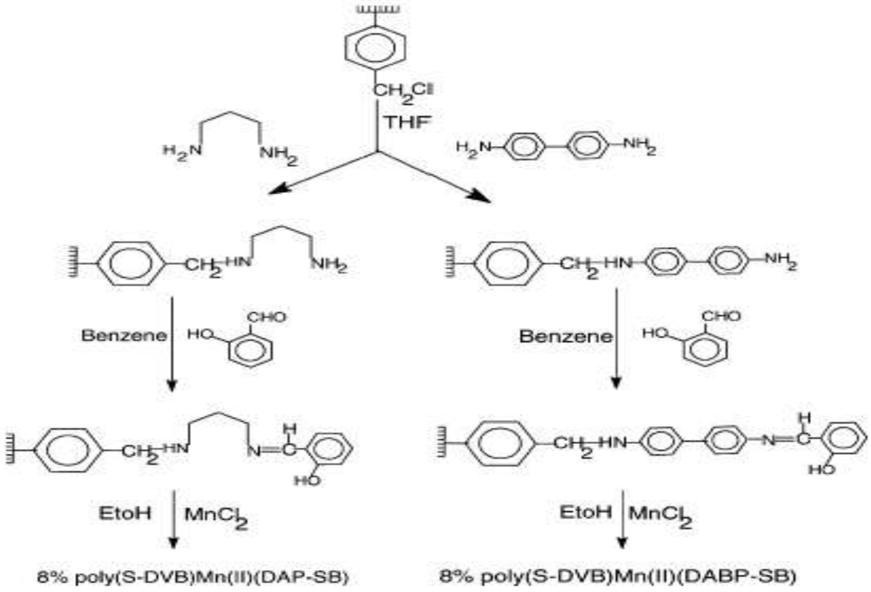
The texture of the surface of a catalyst, namely, the specific surface area and pore geometry are of prime importance in determining the activity, sometimes, also the selectivity of the solid catalyst. In fact Schwab and Schwab-Agallidis [1] reported that the activity and selectivity of a catalyst could be strongly influenced by the geometrical characteristics of its surface. They showed that the dehydrogenation reaction proceed on flat surface while dehydration took place in narrow pores. In general the activity of a given catalyst towards specific reaction is proportional to the concentration of the active surface sites which are dependent on the surface area.

2. Catalytic action of transition metal catalysts

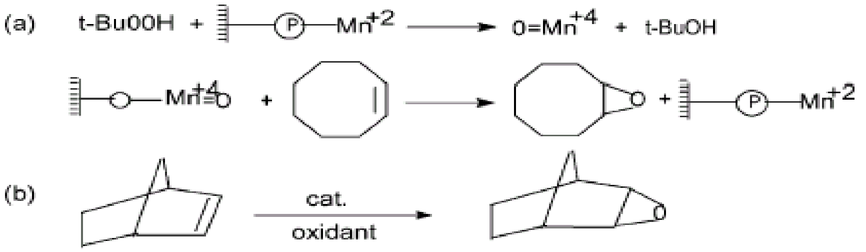
2.1. Anchoring transition metal complex catalysts

Immobilization of transition metal complexes on insoluble support (mainly organic polymer) appears to be a good way of heterogenising homogeneous catalytic systems [2]. Such type of heterogenised-homogeneous catalytic systems not only offer the combined advantages of homogeneous (mild conditions) and heterogeneous (easy separation), but also impose extreme shape selectivity in catalytic process. Moreover, Heterogenization of catalyst on inert support prolongs the life of the catalyst. The various advantages of supported catalysts have attracted organic and industrial chemists to develop heterogenized catalysts using suitable supports. The catalysts on cross-linked supports with pores of molecular dimension have shown significant increase in their selectivity and activity due to high concentration of active sites within the small pores. The efficiency of catalyst on inert support has been found to be high in comparison to unsupported state of catalyst because in unsupported state, the aggregation of catalyst reduces its efficiency. The insoluble cross-linked polymers are used widely as they are inert, non-toxic, thermally stable and easy to be recycled, whereas, linear soluble polymers are of limited value because their separation from reaction mixture is difficult. Similarly, linear insoluble polymer supports are also of limited use as they are not able to increase the turnover number in comparison to cross-linked polymers. Although various inorganic supports such as silica have been used for anchoring catalysts but polymer supports have been found to be more useful as they are able to provide preferential stereochemistry for catalysts and reactants [2] in presence of solvent in comparison to rigid inorganic supports. The unsupported metals and their oxides have shown poor catalytic efficiency in comparison to supported catalysts because in such catalysts only atoms at the surface participate in catalysis and other remain inactive.

Although the Schiff bases are one of the most versatile and thoroughly studied ligands, very few reports are available on the polymer anchored Schiff bases and their application in catalysis. These Schiff bases having multidentate coordination sites form complexes with transition metal ions readily. The polymer supported Mn(II) Schiff base complexes were prepared from crosslinked chloromethylated poly(styrene-divinyl benzene) copolymer beads by sequential modification into a Schiff base bearing ligand. These Schiff base bearing polymer on treatment with a solution of $MnCl_2.2H_2O$ gave the corresponding metal complexes (Scheme 1). The polymer supported Mn(II) complexes were characterised by elemental analysis, FT-IR, diffuse reflectance, SEM and thermogravimetric analysis. Physicochemical properties such as surface area, bulk density and swelling behaviour in different solvents were studied. The catalytic activity of the supported metal complexes were studied in the epoxidation of norbornene and *cis*-cyclooctene using tert-butylhydroperoxide (TBHP) as the terminal oxidant [3]. The two major mechanistic pathways for metal catalysed oxygen transfer are known to involve either peroxometal or oxometal species as the active intermediate. The peroxometal species are generally favoured with early transition metals, viz. Mo(VI), W(VI), V(V), etc. on the other hand, many first row transition metals including manganese follow that the metal oxocatalysed route. These mechanistic processes observed in homogeneous complex catalysis may be applicable in the polymer supported metal complexes. For Mn(II) supported polymeric catalysts, the probable mechanism is shown in Scheme 2.

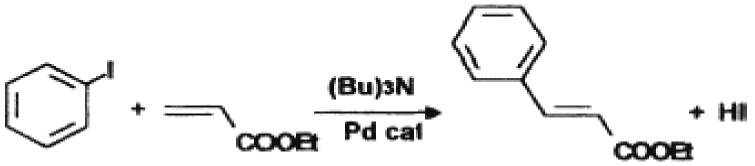


Scheme 1.

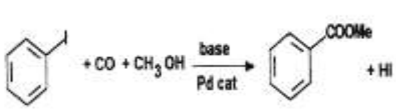


Scheme 2.

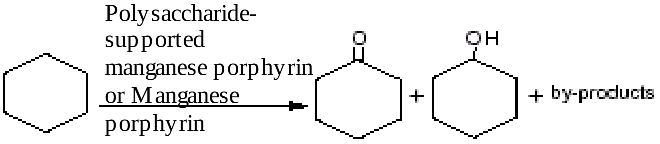
Pd-complexes of silica-anchored nitrogen containing chelating compounds were prepared by the following reactions: (a) synthesis of the Schiff-bases from 3-aminopropyltriethoxysilane and 2-acetylpyridine, 2-acetylpyrazine or 2,6-diacetylpyridine; (b) reduction of the Schiff-bases with $NaBH_4$ in methanol; (c) cogelification with tetraethyl orthosilicate (TEOS); (d) reaction of the obtained functionalized silica with $[PdCl_2(PhCN)_2]$ in CH_2Cl_2. The corresponding model ligands and palladium complexes were also prepared from the reaction of *n*-propylamine with the pyridine or pyrazine compound, followed by the reduction with $NaBH_4$ and the reaction with $[PdCl_2(PhCN)_2]$. The products were characterized by BET, FTIR, GC–MS, ^{1}H-NMR and elemental C–H–N analysis. The anchored Pd-complexes were tested as catalysts in [4]: (a) the Heck reaction of iodobenzene with ethyl acrylate or styrene (arylation of ethyl acrylate or styrene) in the presence of tributylamine as base and toluene or *p*-xylene as solvent (Scheme 3). (b) the carbonylation reaction of iodobenzene with CO, at atmospheric pressure, in methanol and in the presence of triethylamine or potassium acetate as base (Scheme 4). The catalysts were separated from the reaction mixtures and re-used many times. The best results were obtained in both reactions with the anchored Pd-complexes prepared from 2-acetylpyridine: 14 cycles in the Heck reaction (TON (turn over number) ≅ 4100 mmol product/mmol Pd) and 20 cycles in the carbonylation of iodobenzene (TON) ≅ 2300 mmol product/mmol Pd).



Scheme 3



Scheme 4.



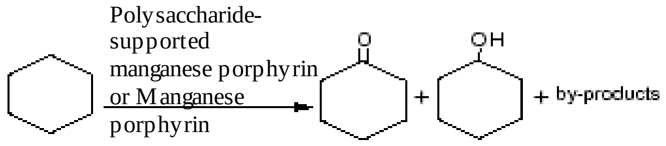
Phenol Catechol Hydroquinon

Scheme 5.

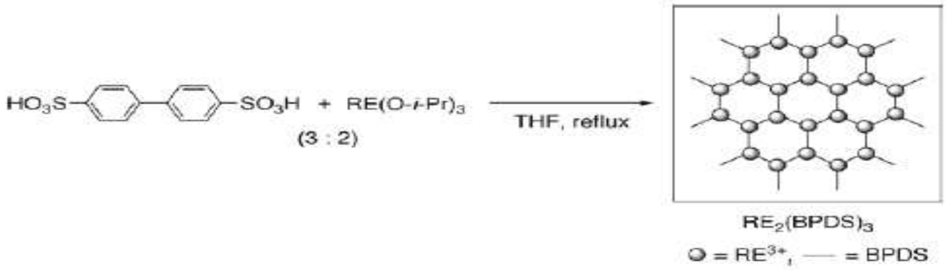
The objective was to prepare mononuclear, binuclear, and insoluble polynuclear oxovanadium(IV)–Schiff base complexes and to use them for sulfoxidation and epoxidation of organic substrates [5]. [VO(salen)] with tetradentate salen(salicylideneethylenediamine) being coordinated in the equatorial plane of oxovanadium(IV), [VO(salap)], and [$(VO)_2$(sal_2-dhdabp)] with tridentate salap(salicylideneorthoaminophenol) and sal_2-dhdabp(salicylidene-$3,3^{/}$-dihydroxy-$4,4^{/}$-diaminobiphenyl) being bound, respectively, in the equatorial plane, of which polynuclear complexes were constituted as monomer units, were prepared and spectroscopically characterized. A sulfide and olefins were oxidized by use of complexes [VO(salen)] and [VO(salap)] (mononuclear), complex [$(VO)_2$(sal_2-dhdabp)] (binuclear), and the polynuclear complexes (poly-VO(salen) and poly-$(VO)_2$(sal_2-dhdabp) synthesized with [VO(salen)] and [$(VO)_2$(sal_2-dhdabp)], respectively. The reaction rates for poly-VO(salen)and -$(VO)_2$(sal_2-dhdabp) were a little lower than those of the corresponding [VO(salen)] and [$(VO)_2$(sal_2-dhdabp)]. On oxidation of sulfides, poly-$(VO)_2$(sal_2-dhdabp) exhibited lowering of activity by about 15% in three cycles, while poly-VO(salen) showed significant lose of activity with each use. Poly-$(VO)_2$(sal_2-dhdabp) was eficient for the oxidation of the olefins only in the first cycle. It was suggested that the loss of activity depends not only on the coordination geometry of the oxovanadium complex, but also on the kind of the substrate.

The polymer anchored transition metal complexes of *N*,*N*`-bis(*o*-hydroxy acetophenone)ethylene diamine (HPED) Schiff base were prepared by reacting *N*,*N* $^{/}$-bis(4-amino-*o*-hydroxy acetophenone)ethylene diamine (AHPED) Schiff base with cross-linked chloromethylated polystyrene beads and then loading of iron(III), cobalt(II) and nickel(II) ions in methanol [6]. The rout of preparation of the all the compounds used under investigation can be summarized in steps as in Fig. 1. The free and polymer supported metal complexes were analyzed for molecular weight (Mw) and composition by elemental analysis. The UV, IR and magnetic measurements of free and polymer supported metal complexes have confirmed the octahedral geometry for iron(III) and square planar geometry for cobalt(II) and nickel(II) ions complexes. The thermogravimetric analysis (TGA) of Schiff base has shown 55% weight loss at 500 ^{0}C but iron(III), cobalt(II) and nickel(II) ions complexes have shown 30%, 40% and 48% weight loss at same temperature. The iron(III), cobalt(II) and nickel(II) ions complexes have shown temperature of maximum decomposition rate (T_{max}) as 325, 319 and 281 ^{0}C, respectively. The unsupported HPED Schiff base complexes of metal ions were found to be less stable although the trend in their thermal stability was almost same. The catalytic activity of free and polymer anchored HPED Schiff base complexes was evaluated by studying the oxidation of phenol at 70 ^{o}C (Scheme 5) [6]. The percent conversion of phenol and turn over number (TON) was found to be optimum at 1:1:1 molar ratio of phenol, H_2O_2 and metal ions in both free and polymer supported metal complexes. The activation energy for oxidation of phenol by polymer supported HPED Schiff base complex of iron(III) was found to be low (25 kJ mol^{-1}) in comparison to HPED Schiff base complexes of cobalt(II) (57 kJ mol^{-1}) and nickel(II) ions (31 kJ mol^{-1}).

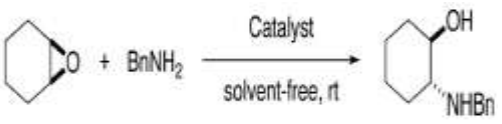
Manganese tetraphenylporphyrin (Mn TPP) has been successfully supported on chitosan (CTS), chitin (CTN) and cellulose (CLS) by means of physical adsorption, and they are characterized by UV–Vis spectroscopy. The supported four synthesized catalysts exhibit enhanced activity and effective recycle (except for Mn TPP/CLS) for oxidation of cyclohexane in the presence of air as oxidant [7]. The cyclohexane oxidation catalyzed by four catalysts with air, respectively, was observed in Scheme 6. The main oxidation products were cyclohexanone and cyclohexanol, with the by-products, cyclohexyl hydrogen peroxide, hexanedioic acid and esters, as confirmed by GC–MS analysis. The obtained results pointed out that the three supported catalysts had better catalytic activity than Mn TPP, and the catalytic activity order was as follows: Mn TPP/CLS > Mn TPP/CTS > Mn TPP/CTN. It is probable that the supports had assistance for Mn TPP as catalyst for cyclohexane oxidation. But, it is not clear why the chosen supports have changed the catalytic properties of Mn TPP. It was suggested [7] that the supports, first, may prevent Mn TPP molecular aggregation and other destructive reactions of Mn TPP under oxidizing conditions; they, second, may provide Mn TPP with friendly microenvironment, which promote a combination of Mn TPP and molecular oxygen, further forming an activated radical species ($PMn^{III}O$) on supports. Moreover, Both Mn TPP/CTS and Mn TPP/CTN show higher selectivity for cyclohexanone and cyclohexanol, whereas Mn TPP/CLS shows lower selectivity. The kind of support influences the catalytic activities and the selectivity for the supported catalysts. Appearance of the catalytic differences is attributed to the presence of the microenvironment differences for the supports.



Scheme 6.



Scheme 7.



Scheme 8.

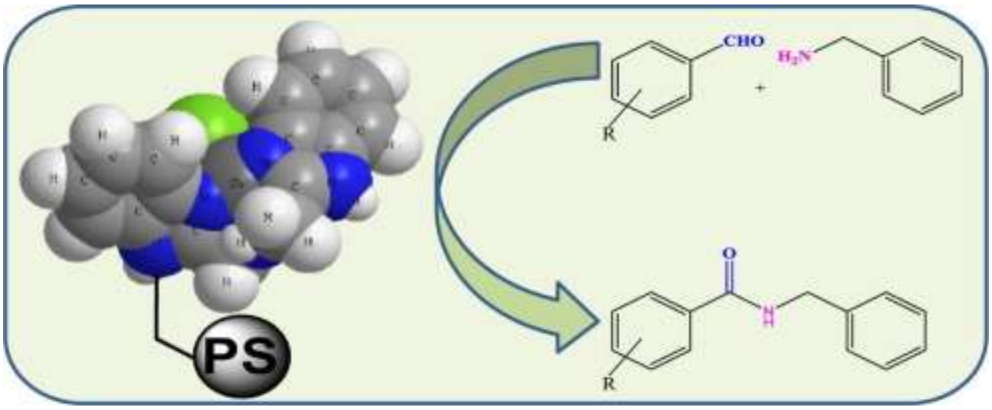
Table 1. Catalytic ring-opening reaction of cyclohexene oxide with benzylamine ($BnNH_2$).

Entry	Catalyst	(mol%)	Time (h)	Yield (%)[a]
1[b]	$Sc(OPf)_3$	2.5	24	30
2[b]	$Sc_2(BPDS)_3$	5.0	40	40
3	$Sc(OPf)_3$	2.5	2	99
4	$Sc_2(BPDS)_3$	5.0	12	99
5	$Yb_2(BPDS)_3$	5.0	12	99
6	$Y_2(BPDS)_3$	5.0	12	89
7	$La_2(BPDS)_3$	5.0	12	38

[a] Isolated yield, [b] Toluene was used as the solvent

Novel polymeric rare earth complexes, $RE_2(BPDS)_3$ (RE = rare earth metal, BPDS = biphenyl-4,4`-disulfonate), in which the metal ions are homogeneously dispersed, were synthesized by the self-organization of the metal ion and the corresponding aryldisulfonate and successfully used as a reusable Lewis acid catalyst for the ring-opening reaction of epoxides with amines to give the desired α-amino alcohols in excellent yields under solvent-free heterogeneous conditions [8]. The polymeric rare earth complexes were prepared in one step by refluxing RE $(O\text{-}i\text{-}Pr)_3$ (RE = Sc, Yb, Y, La, O-*i*-Pr = triisopropoxides polymer) and biphenyl-4,4`-disulfonic acid in THF as shown in Scheme 7 and the results are shown in Table 1. The complexes were dried at 200 ^{0}C under vacuum before use. The catalytic activity of $RE_2(BPDS)_3$ as well as $Sc(OPf)_3$ ($Pf = SO_2C_8F_{17}$) was tested for the ring-opening reaction of cyclohexane oxide with benzylamine (Scheme 8). When the reactions were carried out by using 2.5 mol% of $Sc(OPf)_3$ or 5 mol% of $Sc_2(BPDS)_3$ in toluene at room temperature under heterogeneous conditions, the desired amino alcohol was obtained in only low yield, respectively (Table 1, entries 1 and 2). On the other hand, under solvent-free conditions the reaction proceeded smoothly to give the product in excellent yields (entries 3 and 4). The catalytic activity of $Yb_2(BPDS)_3$ complex was found to be as effective as $Sc_2(BPDS)_3$ (entry 4), but the activity was generally decreased as the ionic radius of the metal complex increased; thus, the yield of the product catalyzed by $La_2(BPDS)_3$ complex was very low (entry 7). As the reaction catalyzed by $Sc_2(BPDS)_3$ complex proceeded under heterogeneous conditions, we checked the reusability of the catalyst. Although the recovered $Sc(OPf)_3$, which was dried at 100 ^{o}C for 10 h before use, seriously lost the original activity, the recovered $Sc_2(BPDS)_3$ did not lose the activity; it could be successfully reused for five times (5th run; 97% yield).

A polymer supported Cu(II) complex has been synthesized and characterized by CHN analyses, IR and UV–Vis spectral studies, ESR and thermogravimetric analyses, ICP-OES, surface area measurements. This complex was screened for their catalytic study towards the direct amidation reaction. The effects of solvents, reaction time, temperature and catalyst amount for the direct formation of amides from aldehydes and benzylamine with the aid of heterogeneous copper complex were reported, Scheme 9 [9]. The polymer supported Cu(II) catalyst could be reused more than five times without appreciable loss of its initial activity. The plausible reaction mechanism has been proposed. The catalytic activity of the unsupported complex was also compared with the polymer supported Cu(II) complex.



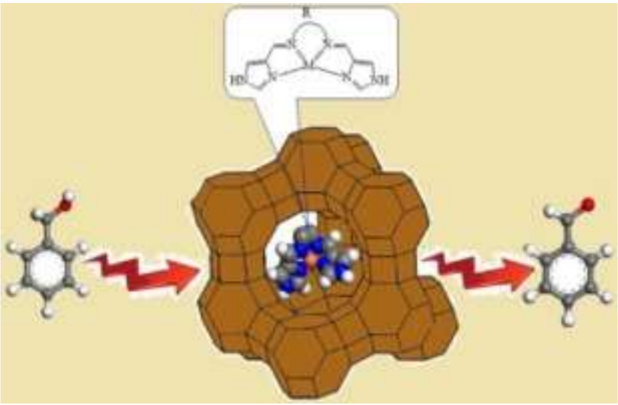
Scheme 9.

A heterogeneous catalyst was prepared by attaching Fe(III) into organically modified chloromethylated polytstyrene and characterized by AAS, IR, PXRD, TG-DTA, UV–Vis, and SEM studies. In presence of H_2O_2 and KBr as bromine source, the catalyst showed remarkably high conversion with para-selectivity towards the oxidative bromination reaction in acetic acid medium. The catalyst was also very active and highly efficient for the production of spiropiperidine derivatives through multi-component reaction in isopropyl alcohol at room temperature [10].

2.4. Zeolite encapsulated transition metal complex catalysts

In spite of lot of knowledge has been acquired regarding to heterogeneous catalysis, there is need to find efficient and ecofriendly catalyst system which would operate under mild conditions. Various attempts for the development of new catalyst system led to the emergence of a new class of catalyst called " zeolite encapsulated metal complexes " (ZEMC). There were basically three approaches to the preparation of these ship-in-a-bottle chelate complexes, namely the flexible ligand method, the template synthesis method and the zeolite synthesis method. In the first approach, a flexible ligand must be able to diffuse freely through the zeolite pores but upon complexation with a previously exchanged metal ion, the complex becomes too large and rigid to escape the cage [11,12]. The template synthesis method is exemplified by the preparation of intrazeolite metallophthalocynines [13-15] where the diffused four dicyanobenzene (DCB) into the zeolite pores can cyclize around a resident metal ion to form a complex which is too large to exit. The third approach referred to as the zeolite synthesis method which is the newest method for encapsulating metal complexes in zeolites where the metal complex is added, possibly in a template role, during the crystallization of the zeolite host [16,17]. Generally, the intrazeolite complexes have been characterized by different techniques including FTIR, UV-Vis., Raman, ESR, NMR, Mossbauer and XPS spectroscopy as well as X-ray diffraction and microscopy. Additionally, surface area measurements, adsorption studies and thermal analysis have provided an evidence for the intrazeolite location of the metal complexes. A number of encapsulated metal complexes have been reported [18,19] and these catalysts under ideal conditions can mimic certain enzymes [20-23]. In fact large number of encapsulated metal complexes have been studied and prepared using different classes of ligand e.g. phthalocyanines [24], Schiff bases [19, 20] poly(pyridines) [25,26], oxime [27], alkanes [28] and some amines [29]. Such hybrid materials have numerous potential applications including catalysis, gas separation, artificial photosynthesis and photocatalysis.

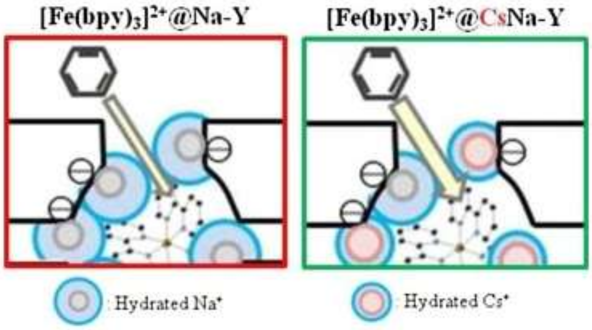
Zeolite Y encapsulated Cu (II) and Zn (II)-imidazole-salen were synthesized within the cavities of Y zeolite. The Cu-salen^{II}Y exhibited a prominent catalytic efficiency for the selective oxidation of benzyl alcohol (Scheme 10). Specifically, the activity and selectivity of the encapsulated catalyst were comparable to those of the free Cu-salen^{II} complex in solution. Furthermore, the high activity and selectivity were preserved during the repeated cycles. The similarity in the initial activity implies that the Cu-salen^{II} complex just resides in the cavity of the zeolite Y, and its intrinsic properties responsible for the catalytic activity keep intact after encapsulation.



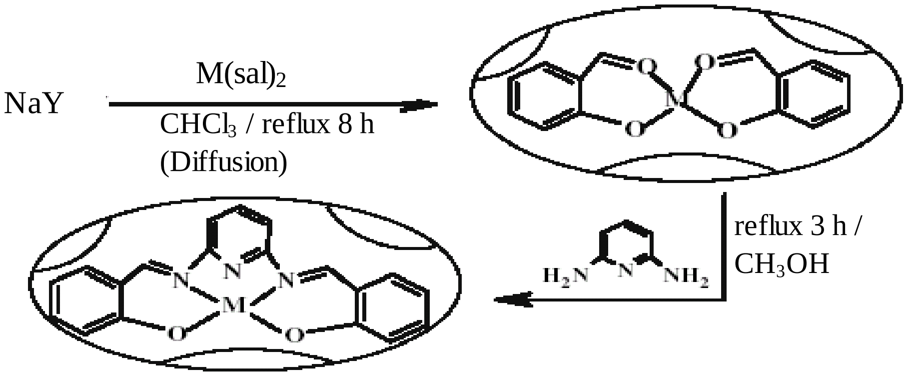
Scheme 10.

Cu(opbmzl)$_2$ [ohpbmzl = 2-(2′-hydroxyphenyl)benzimidazole] was encapsulated within the super-cage of zeolite-Na-Y through a facile ligand approach and characterized by various analytical techniques such as elemental analysis, X-ray diffraction, inductively coupled plasma-atomic emission, FT-IR, UV–vis-DRS and EPR spectroscopy, thermogravimetric analysis (TGA), BET surface area measurements, pore volume by Horvath-Kawazoe (HK) method and cyclic voltammetry (CV) [31]. The catalytic activity of Cu-Y, non-encapsulated and encapsulated complex was evaluated for phenol and styrene oxidation. As very low selectivity and formation of tarry products (for phenol oxidation) prevailed with t-butyl hydroperoxide (TBHP), H_2O_2 was reported to be the reasonable oxidant for the probe reactions. The influence of reaction parameters such as catalyst dosage, substrate concentration, substrate: H_2O_2 mole-ratio, temperature, time and solvent effects were investigated in detail. The encapsulated complex exhibited better catalytic activity and selectivity than the non-encapsulated complex for the probe reactions, associated with exceptional structural stability during the recycling process. From the results, it was derived that the reactions proceeded without the involvement of free radicals and the probable mechanistic pathways based on the intermediate complexes associated with Cu-O species were proposed tentatively.

On the other hand, Fe-bipyridine complexes were encapsulated into cation-exchanged Y-type zeolites (M-Na-Y: M = K^+, Cs^+, Mg^{2+}, Ca^{2+}, NH_4^+, TMA^+, and TBA^+) and their catalytic activities for oxidation of benzene with hydrogen peroxide (H_2O_2) to phenol were investigated in three types of solvents (CH_3CN, H_2O, and CH_3CN + H_2O(1:1)) [32]. Regardless of the kind of solvent, the counter cation in $[Fe(bpy)_3]^{2+}$@M-Na-Y did not affect the selectivity to phenol. No significant difference in catalytic activity of $[Fe(bpy)_3]^{2+}$@M-Na-Y appeared in CH_3CN + H_2O (1:1), while a difference on catalytic activity appeared in each CH_3CN and H_2O solvent. It was suggested that the catalytic activity is related with the accessibility of benzene to $[Fe(bpy)_3]^{2+}$ site in $[Fe(bpy)_3]^{2+}$@M-Na-Y, controlled by the hydrated ionic radius of the counter cation introduced (Scheme 11). The effect of ligand coordinated with Fe ion was investigated by comparing the catalytic activities for oxidation of cyclic hydrocarbons (benzene, cyclohexane, and cyclohexene) over $[Fe(bpy)_3]^{2+}$@Na-Y, $[Fe(phen)_3]^{2+}$@Na-Y, and $[Fe(terpy)_2]^{2+}$@Na-Y (phen = 1,10-phenanthroline and terpy = 2,2′;6′,2″-terpyridine). It was suggested that the expansion of π-electron over the ligands such as phen and terpy improves the uptake ability of substrates having π-electron such as benzene.



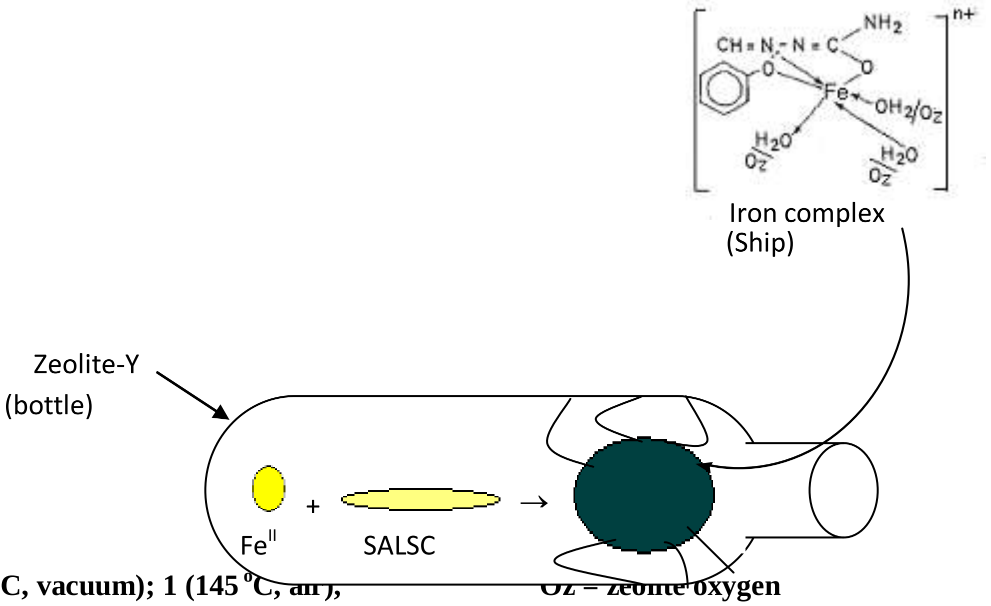
Scheme 11.



M = Mn(II), Co(II), Cu(II) and Ni(II)

Scheme 12.

Transition metal (M = Mn(II), Co(II), Ni(II) and Cu(II)) complexes with pentadendate Schiff-base ligand; N,N$^{/}$-bis(salicylidene)-2,6-pyridinediaminato, H_2[sal-2,6-py]; was entrapped in the nanocavity of zeolite-Y (Scheme 12) by a two-steps process in the liquid phase: (i) adsorption of bis(salicylaldiminato)metal(II), diffusion; [M(sal)$_2$]-NaY; in the supercages of the zeolite, and (ii) Schiff condensation of the metal(II) precursor complex with the corresponding 2,6-pyridinediamine; [M(sal-2,6-py)]-NaY. The new materials were characterised by several techniques: chemical analysis, spectroscopic methods DRS (diffuse reflectance spectra), BET, FTIR and UV/Vis), conductometric and magnetic measurements. Analysis of the data indicates that the M(II) complexes are encapsulated in the nanodimensional pores of zeolite-Y and exhibit different from those of the free complexes, which can arise from distortions caused by steric effects due to the presence of sodium cations, or from interactions with the zeolite matrix. The Host–Guest nanocomposite Materials (HGNM); [M(sal-2,6-py)]-NaY; catalyzes the oxidation of cyclohexene with tert-butylhydroperoxide (TBHP) [33]. Oxidation of cyclohexene with HGNM gave 2-cyclohexene-1-one, 2-cyclohexene-1-ol and 1-(tert-butylperoxy)-2-cyclohexene. [Mn(sal-2,6-py)]-NaY showed significantly higher catalytic activity than other catalysts. On the other hand, the abovementioned synthesis method and studies were repeated on another similar Schiff base; *N,N$^{/}$*-bis(salicylidene)phenylene- 1,3-diamine, H_2[sal-1,3-phen] [34]. The host–guest nanocomposite materials showed also a significantly higher catalytic activity.



n = 0 (145 °C, vacuum); 1 (145 °C, air); Oz = zeolite oxygen
Scheme 13.

Physicochemical properties of metallosalen complexes entrapped within NaX zeolite and their catalytic activities in the oxidation of cyclooctane with dioxygen in the absence of a reducing agent were studied, and compared with free metallocomplexes [35]. Broadening of the zeolite structure-sensitive vibrations observed after the encapsulation gives the evidence of the zeolite framework changes due to the presence of the ‘‘ship-in-the-bottle’’ species. EPR spectroscopy evidences the inclusion of metallosalen complexes since it distinguishes between encapsulated metallocomplexes and those adsorbed on the zeolite external surface. UV–vis spectra confirm the immobilization and stabilization of the metallocomplexes inside the zeolite structure. The three series of catalysts in the oxidation of cyclooctane with dioxygen: neat and encapsulated metallosalen complexes as well as the zeolite X exchanged with the same metals [M= Mn, Fe, Co, Ni and Cu] have been studied. All catalysts were found to be active catalysts in the oxidation reaction. The main products of cyclooctane oxidation are cyclooctanol and cyclooctanone (Scheme 13, almost identical to Scheme 6). The oxidation of cyclooctane produced cyclooctanone as the main product and also cyclooctanol in small yields. The most active catalysts are free metallosalen complexes. It was found that the activity of these complexes increases in the order Ni(salen), Fe(salen), Mn(salen), Cu(salen) and Co(salen) with triple difference in the catalytic activity between the most and the least active catalyst. Upon encapsulation their activity drops about two times. Only Ni(salen) after heterogenization does not change its catalytic activity. The reduction of catalytic activity of the encapsulated catalysts is probably governed by two factors: constraints in the formation of the intermediate complex and change of the redox potential of the metal in the salen complex. No reaction was observed in the blank experiment when the NaX zeolite was used as a catalyst. The zeolites exchanged with different transition metals show catalytic activity, which was however distinctly smaller than that observed for salen complexes. Among them the CoNaX catalyst appeared to be the least active, whereas the highest activity exhibited NiNaX and CuNaX. The less active samples of Mn, Co and Fe exchanged zeolites demonstrate the highest selectivity to cyclooctanone. Among the homogeneous metallosalen catalysts, the following order of catalytic activities can be obtained: Co(salen) > Cu(salen) > Mn(salen) > Fe(salen) > Ni(salen). The selectivities of manganese and nickel catalysts to ketone appeared to be almost two times higher than that of iron, cobalt or copper catalysts. Fig. 2 summarizes the catalytic results for the three investigated series of catalysts. It is clear that the efficiency of the catalytic system as well as the distribution of the reaction products strongly depends on the nature of the central metal. The most active catalysts are the neat metallosalen complexes.

Catalytic oxidation of C–H bonds in saturated hydrocarbons is one of the key steps in functionalizing hydrocarbons and rapidly building functionality into a range of molecules. This is because alcohols and ketones, like cyclohexanone, are important intermediate materials for the manufacture of many important products, such as fiber, drugs and perfume. A variety of transition metal (M = Cu, Co, Fe and Mn) tetrahydro-Schiff base complexes (denoted as M–[H$_4$]Schiff with Schiff = salen, salpn and salicyhexen, Fig. 3) have been encapsulated in zeolite Y with flexible ligand method for the first time [36]. The prepared samples were characterized with X-ray diffraction, diffuse reflectance UV–vis spectroscopy, Infrared spectroscopy, N$_2$ adsorption/desorption at -196 ^{0}C, elemental analysis, as well as thermo-gravimetry and differential-thermal analysis techniques. The formation of tetrahydro-Schiff base ligand was confirmed with ^{1}H NMR and IR spectroscopy before complexing. Accorrding to The catalytic results for the oxidation process over various catalysts, Cu–Y was inactive for the oxidation of cyclohexane, while M–Schiff and M–[H_4]Schiff complexes and their encapsulated analogues in zeolite Y exhibited activity. This substantiates that the active sites are transition metal Schiff base and tetrahydro-Schiff base complexes, not metal ions.

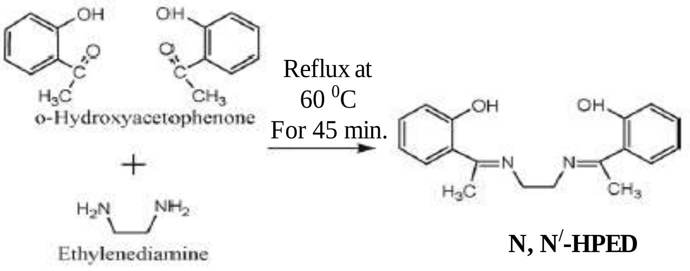
Iron(III), chromium(III) and bismuth(III) complexes of amidate ligand 1,2-bis(2-hydroxybenzamido) ethane (H_2hybe), (Fig. 4), encapsulated in the super cages of zeolite-Y have been isolated and characterized by various physico-chemical measurements. 3D model structure generated for $[Fe(hybe)\cdot 2H_2O]^+$ suggests that zeolite-Y can accommodate these complexes in its super cages without any strain. These encapsulated complexes catalyze hydroxylation of phenol using H_2O_2 as oxidant to give catechol as a major and hydroquinone as a minor product (almost identical to Scheme 5) [37]. The catalytic hydroxylation of phenol using three different catalysts viz. $[Fe(hybe)\cdot 2H_2O]Cl$–Y, $[Cr(hybe)\cdot 2H_2O]Cl$–Y and $[Bi(hybe)\cdot 2H_2O]Cl$–Y and H_2O_2 as oxidant in acetonitrile was studied as a function of time. The two products catechol and hyrdoquinone, as shown by Scheme 5, were observed with a mass balance of >95%. During catalytic oxidation, the encapsulated complexes react with H_2O_2 to give peroxo intermediate complexes, which ultimately transfer oxygen to the substrate. Asuitable reaction condition has been optimized for $[Fe(hybe)\cdot 2H_2O]Cl$–Y by considering the effect of various parameters such as concentration of substrate, amount of oxidant and catalysts, reaction time, temperature, and volume of solvent for the maximum hydroxylation of phenol. The results obtained over these new encapsulated catalysts showed that selectivity of the catechol formation is ca. 85%, though transformation of phenol varied in the order $[Fe(hybe)\cdot 2H_2O]Cl$–Y (43.5%) > $[Cr(hybe)\cdot 2H_2O]Cl$–Y (32.8%) > $[Bi(hybe)\cdot 2H_2O]Cl$–Y (30.6%). Their catalytic activities are only due to encapsulated complexes as no leaching of metal ions or metal complexes were detected in solution when blank reaction was carried out using 5.67 g H_2O_2, 0.025 g catalyst in 2ml of MeCN at 80 ^oC for several hours. Under the best-suited reaction conditions, the selectivity of catechol formation is 85–90% with these catalysts. Such high selectivity has only been noticed with oxovanadium(IV) complexes of H_2salen family [38].

Complexes of Mn(II), Mn(III) and Cu(II) with hydrazone ligand (SBSH) derived from benzenesulphonyl hydrazide and salicylaldehyde have been encapsulated in zeolite Y-supercages by a diffusion method [39,40]. Investigation of the stereochemistry of these incorporated chelates pointed out that, Mn(II) complex is tetrahedral with involvement of zeolite oxygen in coordination, Mn(III) complex is octahedral without contribution of lattice oxygen meanwhile Cu(II) complex has a distorted tetrahedral geometry. The composition and structure of the encapsulated copper complex differ to a large extent from that of free one prepared by a traditional method. The distortion in the structure of the prepared immobilized copper complex and its deviation from the known solution chemistry was expected because of spatial constraints imposed by the dimensions of the zeolite cage. Moreover, it has been reported that the intrazeolitic Mn(II) and Mn(III)-SBSH complexes are thermally stable up to 1000 ^oC without decomposition while the encapsulated Cu(II)-SBSH is stable up to ≅ 533 ^oC. Catalytic activity towards CO adsorption for these synthesized materials has been investigated using in situ FT-IR spectroscopy. The results revealed that, Mn^{II}(SBSH)/Y, Mn^{III}(SBSH)/Y and Cu^{II}(SBSH)/Y can be used as reactive catalysts in water gas shift reaction (WGSR). Copper(II)-containing complex of the Schiff base derived from salicyaldehyde and p-aminobenzoic acid has been encapsulated in the intracrystalline voids of NaY zeolite by the above method [41]. The resulting complex has been characterized by various physico-chemical techniques. Adsorption of CO on the resulting Cu^{II}(SPAB)/Y complex formed $Cu^I(CO)_2$ species under equilibrium CO pressure. Besides, CO-attached Cu(I) species were developed that showed stability toward thermal evacuation as compared with those on Cu^{II}–Y under the experimental conditions applied. Consequently, formate, carbonate and carboxylic species were detected on Cu^{II}(SPAB)/Y while they did not form on Cu^{II}–Y.

The deep purple colored [Cu(3-EtO-salen)] [3-EtO-salenH_2 = N,N$^/$-bis-(3-ethoxysalicylaldehyde)-ethylenediimine] turns yellow when encapsulated in NaY zeolite. The hybrid materials Cu(3-EtO-salen)–NaY as well as the pristine complex [Cu(3-EtO-salen)] have been characterized using several techniques like IR spectroscopy, electronic spectroscopy, X-ray powder diffraction, EPR spectroscopy to understand the mechanism of the color change [42]. The hybrid material showed excellent catalytic activity in hydroxylation reactions towards phenol and 1-naphthol. The results of the reactions indicate that in all the reactions, the hybrid catalyst showed excellent catalytic activity. It is noteworthy that the Cu-exchanged mother zeolite (Cu–NaY) exhibited no noticeable catalytic activity. On the other hand, the pristine complex [Cu(3-EtOsalen)] appears to be almost inactive towards the reactions have been studied. This was interpreted due to degradation of the metal complex in the presence of H_2O_2.

Complexes of Mn(II) and Mn(III) with semicarbazone ligand (SALSC) derived from salicylaldehyde and semicarbazide have been occluded in zeolite-Y super-cages by a diffusion method. The synthesized host/guest materials have been isolated and characterized by various physico-chemical techniques [43]. The results showed that, SALSC can coordinate to Mn(II) in a O,N-bidentate manner through the (C=N) and deprotonated phenolic (OH) groups forming 1M:2L occluded tetrahedral complex; and towards Mn(III) ions in a O,N,O-tridentate manner through the (C=N), deproto-nated enolic (C=O) and phenolic (OH) groups forming 1M:1L occluded penta-cordinated complex. A stable five membered chelate ring was formed in both cases. The zeolite oxygen (Oz) was not involved in coordination in each cases due to the unchanged in the positions and The results showed that, SALSC can coordinate to Mn(II) in a O,N-bidentate manner through the (C=N) and deprotonated phenolic (OH) groups forming 1M:2L occluded tetrahedral complex; and towards Mn(III) ions in a O,N,O-tridentate manner through the (C=N), deproto-nated enolic (C=O) and phenolic (OH) groups forming 1M:1L occluded penta-cordinated complex. A stable five membered chelate ring was formed in both cases. The zeolite oxygen (Oz) was not involved in coordination. in each cases due to the unchanged in the positions and features of the zeolite sensitive bands. The immobilized SALSC complexes are not decompose inside Y zeolite up to 260 ^{o}C assuming the zeolite shielding which increases the thermal stability of the encapsulated complexes. Studying the hydroxylation of benzene using H_2O_2 as oxidant and zeolite containing Mn(II), Mn(III)-semi-carbzone complexes as catalysts states evidently that the accommodation of Mn(II), Mn(III)-complexes in zeolite-Y decreases the selectivity towards the formation of phenol compared with Mn^{II}-Y zeolite. This can be supposed on the basis of the constrains in the formation of the intermediate complex and/or change of the redox potential of the metal in the SALSC complex. The order of catalytic activity is Mn^{II}-Y > [Mn^{III}(SALSC)/Y > [Mn^{II}(SALSC)/Y which is the reverse of the order of increasing redox potential of the M(n + 1)/Mn^{n+} couple of the central metal atom. The changes in molecular and electronic structure are responsible for the enhanced activity of encapsulated SALSC complexes. In agreement with above complexes Fe(II) and Fe(III)-SALSC have been isolated and characterized [44]. The results showed that, the SALSC coordinates to Fe(II) and Fe(III) ions in a binegative tridentate (O, N, O-) manner through the (C=N) and deprotonated enolic (C=O) and phenolic (OH) groups forming 1M:1L occluded complexes (Scheme 10). The zeolite oxygen (Oz) was involved in coordination in each case due to the mutation in the positions and features of some zeolite sensitive bands. The immobilized SALSC complexes did not decompose inside Y zeolite up to 800 ^{o}C. Studying the hydroxylation of benzene using H_2O_2 as oxidant and the isolated clathrates as catalysts states evidently that the encapsulation of Fe(II), Fe(III)-complexes in zeolite-Y decreases the selectivity towards the formation of phenol compared with Fe^{II}-Y zeolite. This is supposed on the basis of constrains in the formation of the intermediate complex and/or change of the redox potential of the metal in the SALSC complex. The phenol hydroxylation activity was noticed to be enhanced by increasing the dosage of catalyst, which is related to the number of active sites.

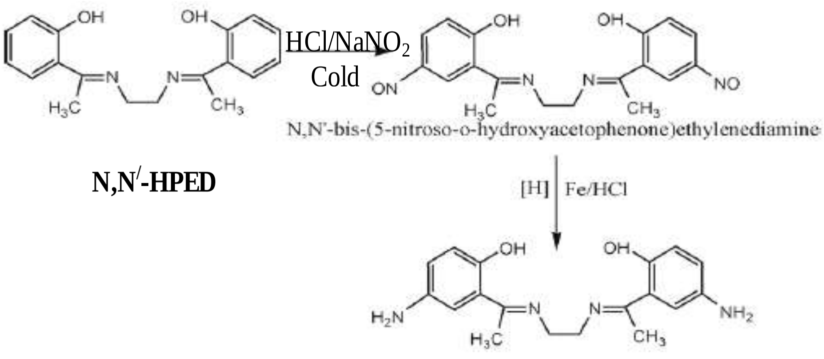
Step1. Synthesis of *N,N/*-bis(*o*-hydroxy acetophenone)ethylene diamine Schiff base (HPED).



Step 2. Synthesis of *N,N/*-bis(4-amino-*o*-hydroxy acetophenone)ethylene diamine Schiff base (AHPED).

HPED **M-HPED**

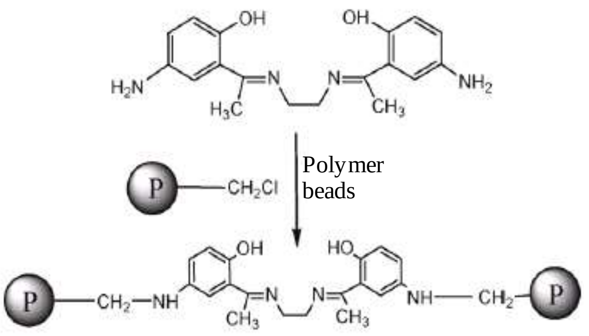
Step 3. Synthesis of polymer anchored Schiff base (P-HPED).



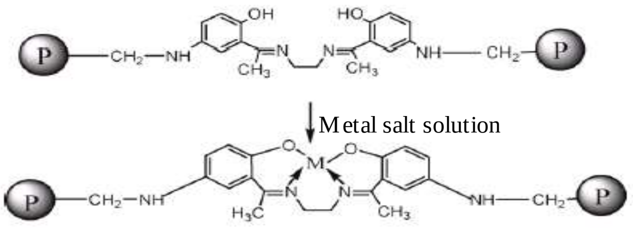
N,N/-HPED

N,N/-AHPED

Step 4. Loading of metal ions on unsupported Schiff base (HPED-M).



Step 5. Loading of metal ions on polymer supported Schiff base (P-HPEDM).



M= Fe^{III}, Co^{II} and Ni^{II}

Fig. 1. The rout of preparation of Schiff base complexes supported on polymer.

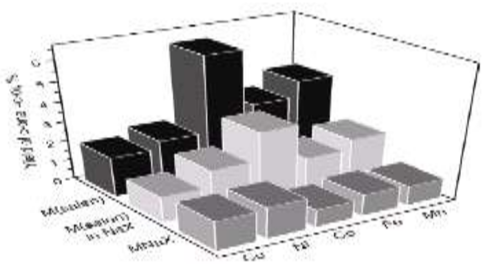
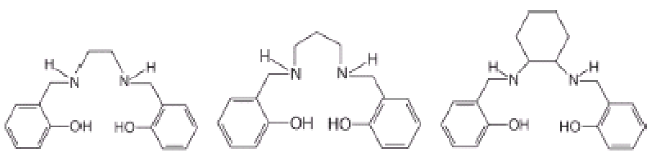


Fig. 2. Yield of products of cyclooctane oxidation in the presence of catalysts with different metal atoms.



$H_2[H_4]$salen **$H_2[H_4]$salpn** **$H_2[H_4]$salicyhexen**

Fig. 3. Chemical structures of M–$[H_4]$Schiff with Schiff = salen, salpn and salicyhexen.

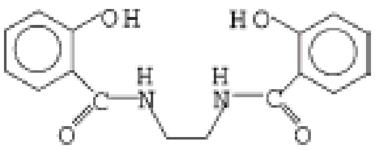


Fig. 4. Chemical structure of H_2hybe

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