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Immobilized Complexes of the Salen Schiff's Base with Metal as Oxidation Catalysts[1]

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Abstract—The immobilized metal complexes with the Schiff's base of salen have shown high catalytic activity in oxidation of alkenes, cycloalkenes, and alcohols as compared with their unsupported analogs. Due to the heterogeneous nature of such catalysts, their separation and recycling is rather simple.

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Condensation of an aldehyde and an amine leading to the Schiff's base was first described in 1864 [1]. The Schiff's base ligands can coordinate various metals and stabilize them in different oxidation states; such complexes are used as catalysts in many important processes [2]. Metal complexes with the Schiff's bases have been extensively studied because of their attractive chemical and physical properties, and thus the wide range of scientific applications [3]. However, these homogenous catalysts are not easily separated and reused. Therefore, the attempts to develop their heterogeneous analogs have been made; in particular, immobilization of metal complexes on solid supports has been found fairly promising [4–9]. Furthermore, sometimes the support can enhance the activity and selectivity of the catalyst [10].

Several approaches can be utilized to immobilize the metal complex of the Schiff's base onto various supports to obtain heterogeneous catalysts. The most common immobilization strategies are as follows: physical absorption, ion exchange, coordination to polymer, chemical grafting, "ship-in-the-bottle" method, and sol-gel technology [11].

Oxidation reactions are among the most important processes in nature and industry, such as breathing, combustion, corrosion, and degradation. In the industrial processes, the catalyzed oxidation reactions are important to prepare oxygenated compounds, in particular, conversion of petroleum into useful chemicals and materials [12]. However, oxidation reactions are also among the most complicated processes. The stoichiometric amount of oxidizers based on heavy metal compounds have been widely used, forming huge volumes of toxic wastes, thus, such process are not "green." On the contrary, the immobilized metal-salen complexes catalysts are environmentally friendly and highly active towards oxidation of alkenes, cycloalkenes, and alcohols.

In this review, we discuss the methods of immobilization of metal complexes with the Schiff's bases onto solid supports, and such immobilized catalysts applications in the oxidation processes.

Preparation of Immobilized Catalysts Based on Metal Complexes with the Schiff's Bases

Physical absorption. Inorganic supports are widely employed to prepare heterogeneous form of the common homogenous catalysts, due to availability and low price of these materials. The physical absorption method usually implies impregnation of the metal complex into activated carbon, silica gel, Al_2O_3, etc. Prior to the complex immobilization, the support is activated via blowing a trace amount of oxygen through a quartz tube with the material at about 475 K for several hours, or via reflux in strong acidic or basic solution. Such activation (accompanie by formation of surface hydroxyl groups) is extremely important for the successful impregnation of the catalyst into the inorganic carrier. IR study is usually applied to monitor the activation process and to optimize its conditions.

The scheme of the anchoring procedure in the case of Co(salen) catalyst immobilization onto the air-oxidized activated carbon is shown in Fig. 1 [13].

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[1] The text was submitted by the authors in English.

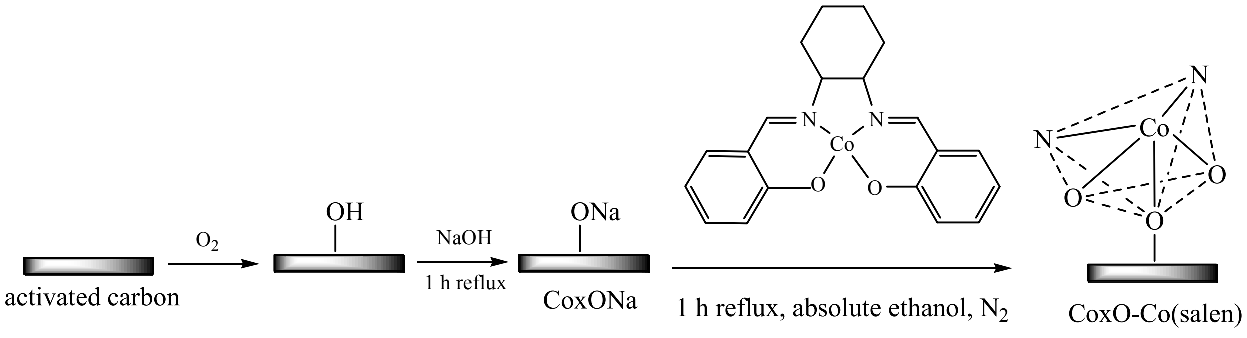


Fig. 1. Anchoring procedure of the Co(salen) catalyst onto the air-oxidized activated carbon via the physical absorption method.

Ion exchange. Ion exchange method is frequently used in the preparation of heterogeneous catalysts. The electrostatic interaction between metal salen complex and the support is a driving force of the immobilization. The process is simple, but suffers from some disadvantages such as the weak attraction between the support and active component, the leaching of active species, and the lower selectivity as compared with the catalysts immobilized by covalent bonds.

Kim et al. immobilized chiral salen ligands onto mesoporous MCM-41 by ion exchange method, as shown in Fig. 2 [11]. The chiral Mn(salen) complexes immobilized onto mesoporous MCM-41 were stable under the epoxidation conditions and exhibited higher enantioselectivity compared with the homogeneous complexes.

Coordination to polymer. The functionalized porous cross-linked polymers are used to prepare the polymer-supported Schiff's base complexes via attaching of the amine nitrogen to the polymer chain. The polymer-supported metal complexes with the Schiff's bases show higher catalytic activity as compared with their unsupported analogs. However, they suffer from the metal leaching from the polymer matrix in the course of long-term application in continuous and fixed bed reactors. The leaching of metal ions from the supported catalysts can be reduced

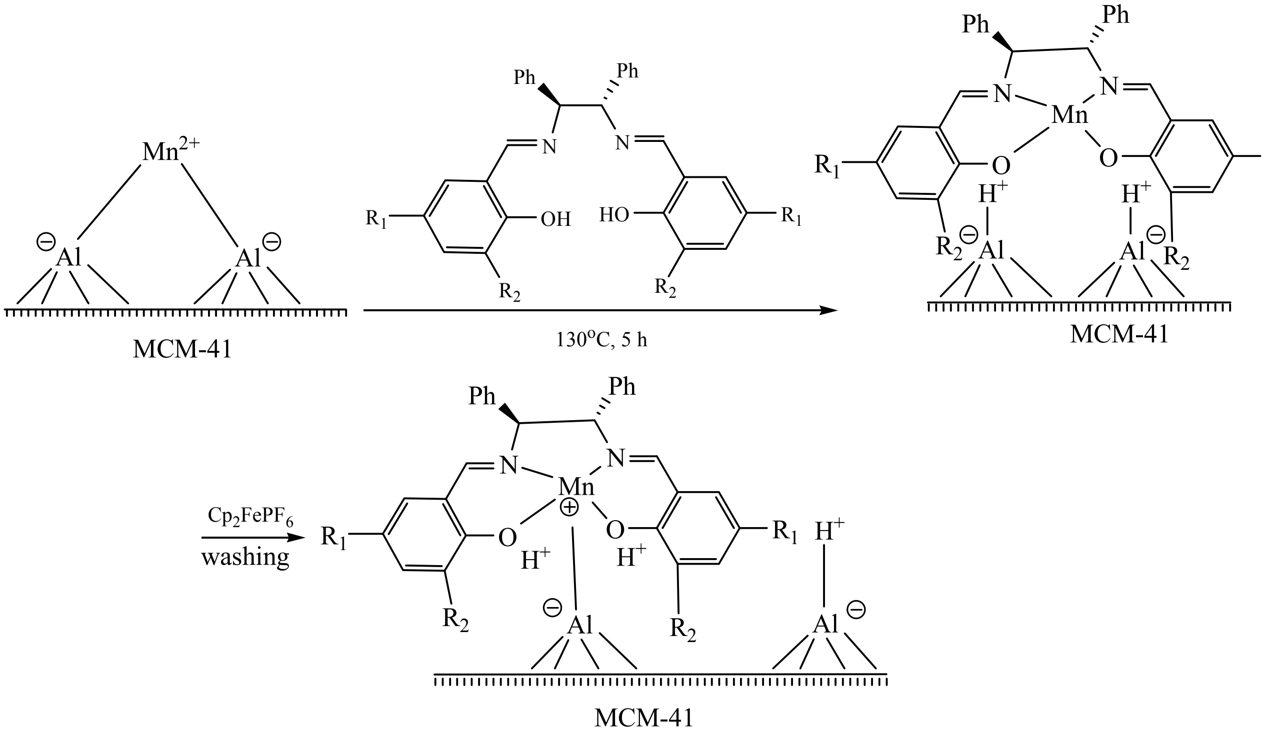


Fig. 2. Immobilization of Mn(salen) onto MCM-41 via the ion exchange method.

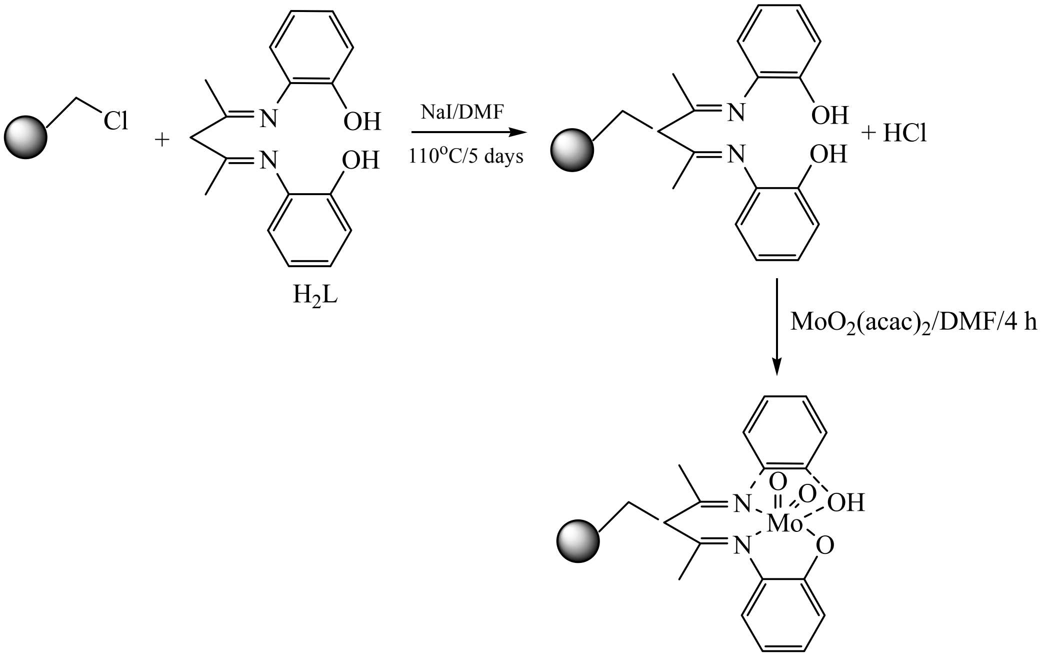


Fig. 3. Preparation of the polymer-supported Mo-containing Schiff's base catalyst via the coordination method.

either by increasing the amount of ligands immobilized at the polymer chains, by using the chelating ligands, or by avoiding the coordinating solvents.

Jacobsen et al. demonstrated the efficiency of Co(salen) complexes supported by the functionalized polystyrene in various reactions, including hydrolysis, resolution of race epoxides, and enantioselective parallel synthesis [14, 15]. Grivani et al. applied the polymer-supported bis(2-hydroxylanyl) acetylacetone Schiff's base ligand for epoxidation of various alkenes in the presence of *t*-BuOOH in CCl_4. Those supported materials showed high reactivity and selectivity in the oxidation reactions [16]. The procedure to preparation the above-mentioned molybdenum catalyst is illustrated in Fig. 3. The chiral polymer-supported Cu(salen) complex catalyst could be immobilized using the similar approach [17a].

Chemical grafting. Chemical grafting is the method to covalently immobilize the metal complexes onto the inorganic carrier via attaching to the reactive groups. The examples of such carriers are MCM-41 and mesoporous Al_2O_3 modified by 3-APTES. The grafting of inorganic carrier with the groups capable of formation of strong covalent bonds with the metal complex is an essential step. As an example, Co(salen) immobilization using the silanol chemistry is shown in Fig. 4 [17b].

Li et al. immobilized the Cu(II) and Co(II) salen complexes onto graphene oxide and examined their catalytic activity in the styrene epoxidation [18]. It was found that heterogeneous catalysts were active and could be recovered without significant loss in activity and selectivity. Jones et al. reported the preparation of novel hybrid organic/inorganic catalysts by supporting organic and organometallic Co–salen complexes onto the magnetic Fe_3O_4 nanoparticles, as shown in Fig. 5 [19]. Kim et al. studied the chiral salen complexes immobilized at the siliceous MCM-41 by using (3-aminopropyl)triethoxysilane and 2,6-diformyl-4-*tert*-butylphenol. The immobilized chiral Mn(III)–salen complexes were stable under conditions of epoxidation of styrene and α–methylstyrene and exhibited relatively high enantioselectivity [20]. The scheme of MCM-41 grafting with the chiral salen complexes is shown in Fig. 6.

Ship-in-the-bottle method. The ship-in-the-bottle strategy is a simple and practical approach for immobilizing the metal salen complex catalysts inside the carrier cavity. In general, caged faujasite zeolite NaY is used as carrier, due to its relatively small outer channel opening (about 0.74 nm), while the molecular sieve cavity is larger (~1.3 nm). The metal complex dimensions are about 0.8–0.9 nm, thus the complex can be hardly immobilized into the zeolite cage directly; however, the ship-in-the-bottle technology

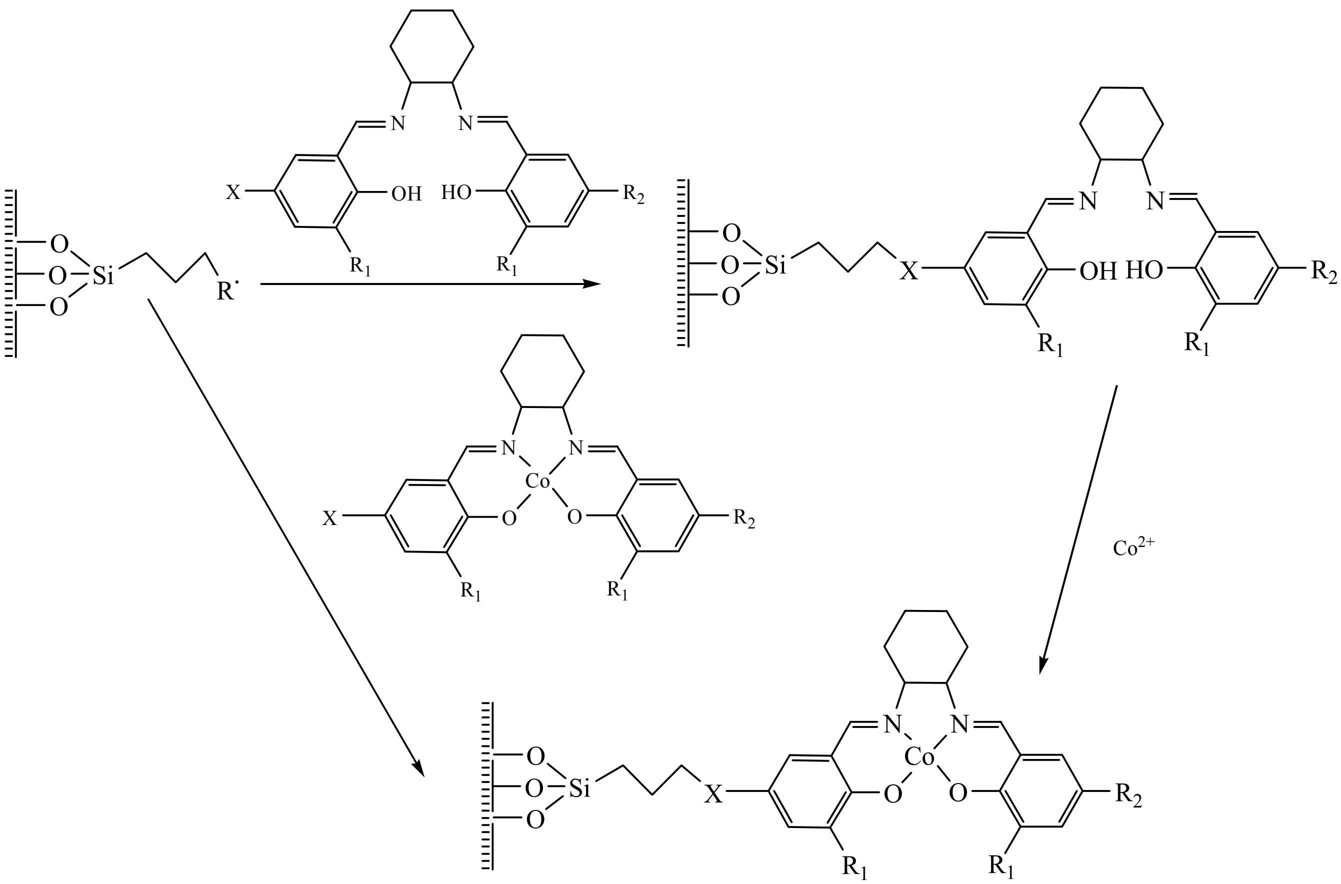


Fig. 4. Schematic workflow of the chemical grafting immobilization.

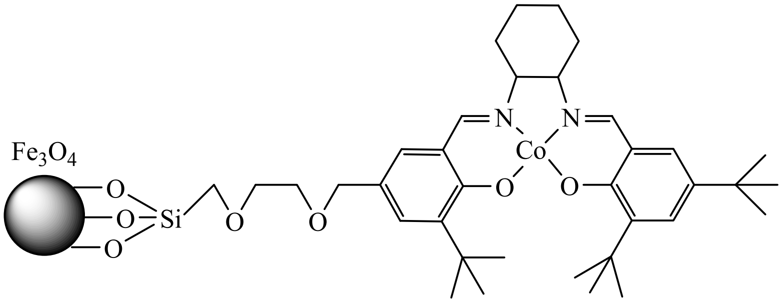
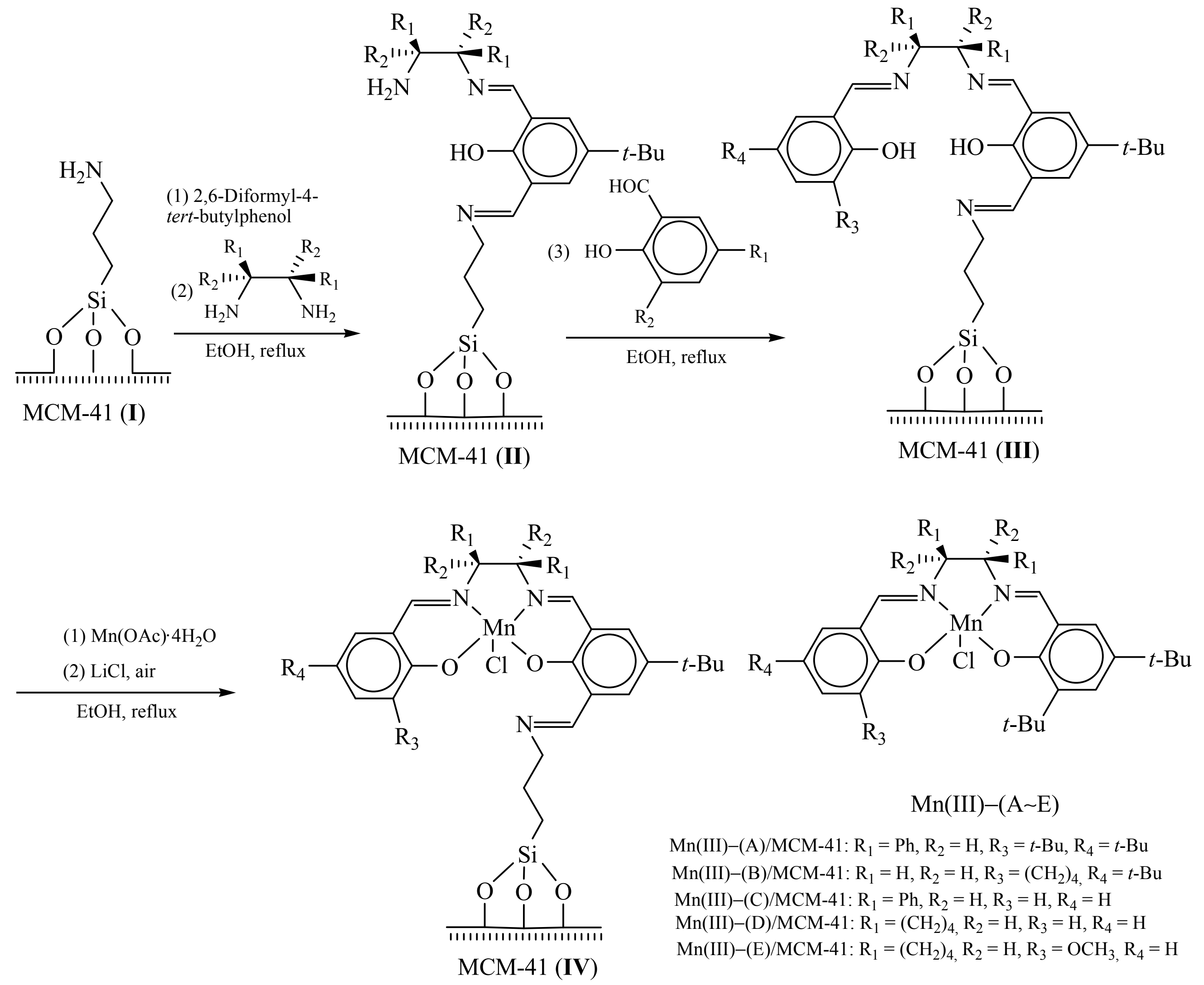


Fig. 5. Co(salen) complex immobilized on the magnetic Fe_3O_4.

allows immobilization of the salen ligand (which is about 0.65–0.7 nm in size) and subsequent assembly with the metal ions inside the super-cage of molecular sieve (Fig. 7) [21]. Once assembled successfully, metal salen complexes cannot pass the channel opening and are thus almost irreversibly immobilized. Also, the zeolite matrix enhances the catalyst selectivity due to special structure of the carrier channels.

Fan et al. successfully encapsulated iron and copper salen complexes in zeolite Y, as confirmed by IR, diffuse UV-vis reflectance, TGA, DTA, and N_2 adsorption/desorption studies [22]. The prepared material showed much higher activity than the neat Cu(salen) and Fe(salen) complexes in the oxidation of cyclohexane with H_2O_2.

Sol-gel technology. Sol-gel route comprises the dissolution of the organic and inorganic compounds, followed by sol and gel formation stages (solidification), and finalized by thermal annealing. Commonly, amorphous polymer hybrid carrier is obtained via the



Mn(III)–(A)/MCM-41: R_1 = Ph, R_2 = H, R_3 = t-Bu, R_4 = t-Bu
Mn(III)–(B)/MCM-41: R_1 = H, R_2 = H, R_3 = $(CH_2)_4$, R_4 = t-Bu
Mn(III)–(C)/MCM-41: R_1 = Ph, R_2 = H, R_3 = H, R_4 = H
Mn(III)–(D)/MCM-41: R_1 = $(CH_2)_4$, R_2 = H, R_3 = H, R_4 = H
Mn(III)–(E)/MCM-41: R_1 = $(CH_2)_4$, R_2 = H, R_3 = OCH_3, R_4 = H

Mn(III)–(A)/MCM-41: R_1 = Ph, R_2 = H, R_3 = t-Bu, R_4 = t-Bu
Mn(III)–(B)/MCM-41: R_1 = $(CH_2)_4$, R_2 = H, R_3 = t-Bu, R_4 = t-Bu
Mn(III)–(C)/MCM-41: R_1 = Ph, R_2 = H, R_3 = H, R_4 = H
Mn(III)–(D)/MCM-41: R_1 = $(CH_2)_4$, R_2 = H, R_3 = H, R_4 = H
Mn(III)–(E)/MCM-41: R_1 = $(CH_2)_4$, R_2 = H, R_3 = OCH_3, R_4 = H

Fig. 6. Immobilization of Mn(III)–salen complexes immobilization onto MCM-41 via the chemical grafting method.

combination of the silanized organic compound with *n*-alkyl silicate. The silane coupling agent can be represented as Y-R-SiX_3 with X, a hydrolyzable group (acetoxy or alkoxy), Y, a reactive group bounding the organic compound (halogen, amino, thiol, or epoxy group), and R, a short-chain saturated hydrocarbon bridge. The principle of the sol-gel method is as follows: firstly, the metal complex precursor reacts with Y groups of the coupling agent, followed by hydrolysis and condensation of *n*-alkyl orthosilicate $Si(OR)_4$ and X groups in the coupling agent to form SiO_2 network. Thus, the organic-inorganic hybrid composite is fabricated.

Murphy et al. applied the sol-gel process to immobilize the Co and Cu salen complexes into silica aerogels and xerogels (Fig. 8, [23]). The sol-gel route allows the entrapment of inorganic catalysts into the porous matrix with formation of designed microstructures at low temperature, resulting in hybrid materials with intriguing properties [24].

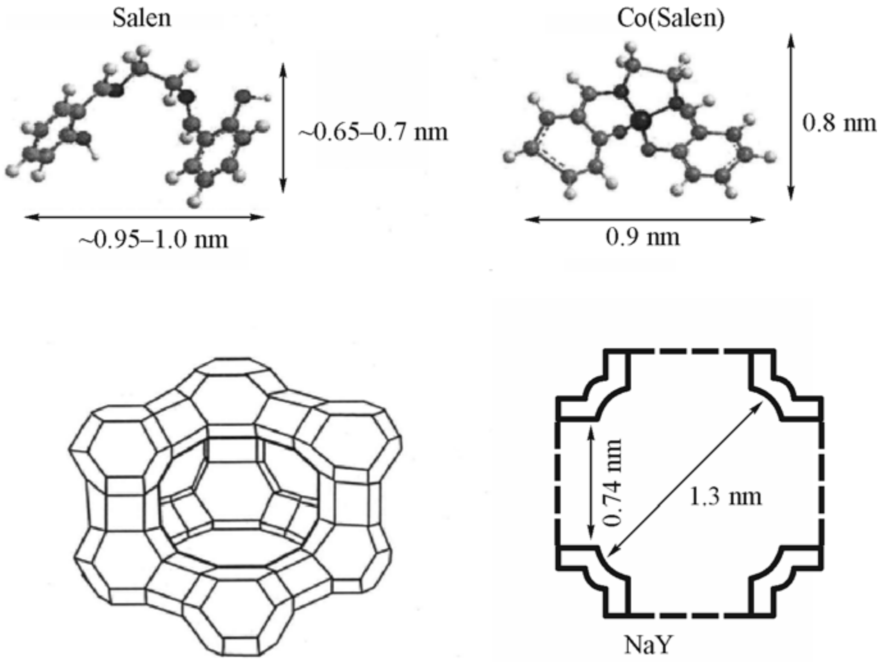


Fig. 7. The structure of salen, Co(salen), and NaY.

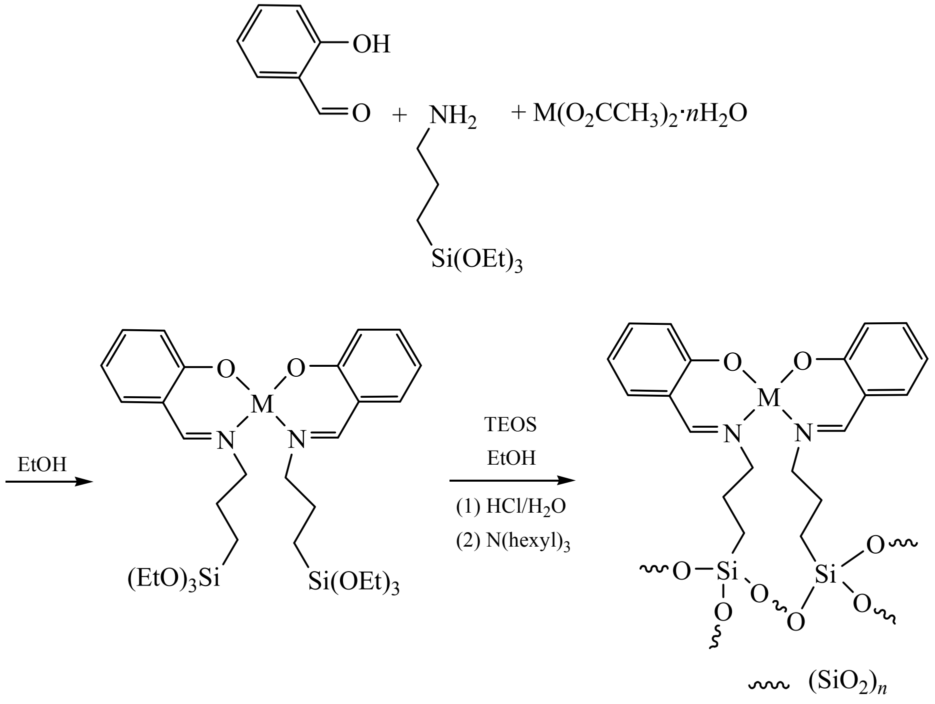


Fig. 8. Preparation and immobilization of silyl ether modified salen catalysts via the sol-gel process.

To conclude, the methods of immobilization of metal complexes with the Schiff's bases can be classified into two groups: physical and chemical methods, summarized in the table. Generally, physical methods of immobilization through absorption, impregnation, and precipitation are good due to the low price and simplicity, but suffer from relatively weak interaction between the metal complex and the support, leading to the catalyst leaching. On the contrary, chemical immobilization via the ion

Comparison of different methods for immobilization of the Schiff's bases complexes

Type	Method	Interaction type	Interaction strength	Catalyst leaching	Support	Notes
Physical methods	Physical absorption	Adsorption	Weak	High	Inorganic	simple low-cost process
	"Ship-in-the-bottle"	Encapsulation	Weak	Medium	Molecular sieve	Simple process, the shape-selective catalytic effect
	Sol-gel	Encapsulation and adsorption	Weak	Medium	Inorganic or organic	Simple process
Chemical methods	Ion exchange	Electrostatic	Medium	Medium	Inorganic or organic	Simple process
	Coordination to polymer	coordination bond	Strong	High at prolonged processes	Organic	high catalytic activity
	Chemical grafting	Covalent bond	Strong	Low	Inorganic	Long complicate process

exchange, coordination to polymer, and chemical grafting, lead to stronger catalyst binding but are relatively complicated.

Oxidation Reactions Catalyzed by the Immobilized Metal Complexes

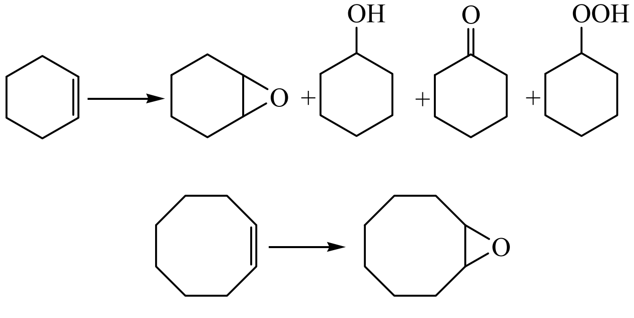
Alkenes oxidation. Epoxides, particularly ethylene and propene oxides, are key materials for the synthesis of a variety of products such as glycols, glycol ethers and alkanolamines and for preparation of polyesters and polyurethanes. Ethylene oxide is produced commercially (Union Carbide and Shell) by vapor-phase oxidation of ethylene with air or oxygen in the presence of alkali metal promoted silvery catalyst; this method has replaced ethylene oxidation via chlorohydrin process [25]. Concerning the environmentally friendly oxidants, air and hydrogen peroxide, the immobilized Schiff's base complexes are promising catalysts for alkenes oxidation.

Recently, oxidation of linear and cyclic alkenes, in particular, of propylene and cyclohexene, catalyzed by metal complexes has been intensively investigated [26–32]. In particular, Agashe groups investigated the liquid phase oxidation of olefins by *t*-BuOOH or O_2/isobutyraldehyde in the presence of copper and cobalt salen complexes immobilized at MCM-41 [27, 28]. The oxo-metal and acyl peroxy radicals, predominantly formed with isobutyraldehyde, gave higher yield of epoxide, as compared to the oxidation by *t*-BuOOH. The Cu-based catalysts gave 100% conversion of styrene at high turnover number of 3144 in the reaction of 5 mmol styrene, 15 mmol isobutyraldehyde, 10 g acetonitrile, and molecular oxygen at 313 K. Roy et al. investigated the catalytic action of chiral dimeric Mn–salen complex immobilized on silica in epoxidation of chromenes, indene, styrene, and *cis*-β–methyl styrene by NaOCl in the presence of axial base pyridine N-oxide at 273 K [31]. The immobilized catalyst system showed high turnover frequency of about $\sim 1.74\times10^{-3}$ s^{-1} and enantioselectivity (enantiomeric excess of up to 98%) in the case of small and bulky alkenes. Kuzniarska-Biernacka et al. immobilized the chiral Mn salen complex onto a natural clay and onto the porous clay heterostructure functionalized with 3-aminopropyltriethoxysilane, and studied their catalytic activity in the epoxidation of styrene and methylstyrene [32]. The immobilized catalysts showed high catalytic activity (turnover number of 1066) and high epoxide yield.

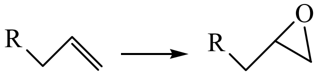
Alkanes oxidation. The oxidative modification of alkanes gives valuable products such as alcohols, aldehydes, carboxylic acids, and their derivative. The first step in alkanes oxidation is to create a reactive radical through homolytic cleavage of C–H bond; however, this process is not smooth due to high energy of the C–H bond [10]. The selective transformation of low molecular weight alkanes is complicated due to their low reactivity, but it can be enhanced by proper choice of the catalyst, reaction mixture composition, and other conditions. The complexes of Ti(IV), Mo(VI), Mn(III), Cr(VI), and Fe(III) immobilized on the solid porous support have been used as catalysts of alkanes oxidation by hydrogen peroxide, PhIO, *t*-BuOOH, NaOCl, etc., but systematic studies on activity of the supported metal salen complexes catalysts in the oxidation of alkanes are scarce [33].

The oxidation of cycloalkanes and benzenoids has been more investigated than that of linear alkanes. Fan et al. studied the oxidation of cyclohexane with iron and copper salen complexes simultaneously encapsulated in zeolite Y [22]. The mentioned catalyst was more active (turnover number of 74) than the homogenous Cu(salen) and Fe(salen) (turnover number of 57), and the optimum molar ratio of Cu^{2+} to Fe^{3+} in the prepared material was of 1.93 : 1. Mirkhani et al. reported on the oxidation of (*Z*)-cyclooctene, styrene, and cyclohexane catalyzed by Mn salen complexes entrapped in alumina in the powder form by a non-hydrolytic sol-gel route. The results demonstrated the importance of the non-hydrolyzed alumina matrix in enhancing the activity of the Jacobsen catalyst and avoiding its destruction and/or dimerization [34]. The catalytic activity of Fe(salen)–polyoxometalate with hydrogen peroxide as oxidant was also reported [34]. Mac Leod et al. reported oxidation of linear (*n*-pentane, *n*-hexane, *n*-heptane, and *n*-octane) and cyclic (1,2-dimethylcyclohexane) alkanes into the corresponding secondary alcohols and ketones, as well as oxidation of toluene into benzaldehyde with *t*-BuOOH under mild conditions, catalyzed by Mn(III)–salen complex immobilized at poly(dimethylsiloxane)-based membrane [24]. The oxidations were markedly promoted by the addition of various acids, and proceeded with participation of *t*-BuO· and alkylperoxyl radicals. The toluene oxidation featured high selectivity towards the formation of benzaldehyde and remarkably high catalyst turnover number (up to 1700).

Alcohols oxidation. The oxidation of alcohols is one of the most important transformations in organic chemistry. The early protocols used the stoichiometric amount of chromium(VI) oxidants. The development of new environmentally friendly methods for the catalytic oxidation of alcohols to aldehydes and ketones is a topical issue of modern chemical synthesis. Various systems have been reported for catalytic oxidation of alcohols, involving transition metal catalysts. In particular, metal salen complexes have been efficient in oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones [10].



Scheme 1. Oxidation of cyclic alkenes.

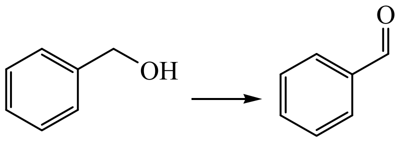


$R = H, CH_3, (CH_2)_n–CH_3$.

Scheme 2. Epoxidation of linear alkenes.

The catalytic activity of free and solid-supported metal complexes was evaluated in the oxidation of phenol with hydrogen peroxide [10, 35, 36]. The selective oxidation of phenol to catechol and hydroquinone was attributed to the enzyme-like behavior of metal complexes on polymer support.

The selective oxidation of benzyl alcohol to benzaldehyde with hydrogen peroxide was catalyzed by the Schiff's base complex under mild conditions [37, 38]. With Cr(salen) as homogenous catalyst, the benzyl alcohol conversion was of 11.3%, and selectivity was low (65.5%) due to the simultaneous formation of benzoic acid (22.7%) and benzyl benzoate (11.8%). However, when the reaction was performed in the presence of the immobilized complex, the selectivity of benzaldehyde formation was significantly improved. At the best, benzyl alcohol conversion reached 52.5% at 100% selectivity [Cr(salen) at MCM-41].



Scheme 3. Oxidation of benzyl alcohols to benzaldehyde.

CONCLUSIONS

The immobilized catalysts based on metal complexes with the salen Schiff's base have revealed high activity in a variety of oxidation processes. The immobilization methods described in this review have opened new avenues for major growth in the area of organic chemistry. The oxidation of alcohols, alkanes, benzylic substrates, and alkenes has been intensively explored. The reports have demonstrated the potential of the immobilized metal salen complexes as catalysts due to better recyclability and higher activity. Efforts in this area should lead to development of efficient environmentally friendly technologies in the future.

ACKNOWLEDGMENTS

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