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Clay-anchored non-heme iron–salen complex catalyzed cleavage of C═C bond in aqueous medium

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Abstract—Clay-anchored iron[*N*,*N*′-ethylenebis(salicylideneaminato)] complex, synthesized by direct exchange, oxidizes various olefins and chalcones in aqueous acetonitrile using hydrogen peroxide as terminal oxidant. Aldehyde and its derivatives are obtained as oxidation products by the cleavage of C═C double bond. In comparison with the catalysis by iron–salen complex in solution, the clay catalyzed pathway not only increases the rate of reaction significantly, but also provides selective oxidation toward the aldehyde. Some chalcones also give very good yield in water, compared to the solution and clay catalyzed pathways.

1. Introduction

In recent years, methods available for high-yielding, selective transformations of organic compounds have increased tremendously. Most of these reactions also lay emphasis on catalysis and ‘atom-economy’.[1] Iron–salen complexes are used as catalysts in allylic oxidation of olefins,[2] epoxidation of unfunctionalized olefins with iodosylbenzene,[3] and oxidation of adamantane in the presence of oxygen.[4] Furthermore, μ-oxo-bisiron–salen complexes are also used in the cyclopropanation of olefins.[5] Iron-catalyzed asymmetric oxidation of sulfides to sulfoxides has been achieved with high enantioselectivity using hydrogen peroxide as terminal oxidant.[6]

The progress in heterogeneous asymmetric synthesis, particularly in the asymmetric synthesis on chiral catalysts immobilized in porous materials by various approaches such as chemical grafting, encapsulation, organic–inorganic hybrid synthesis, intercalation in layered materials, ionic interaction for asymmetric reactions like epoxidation, hydrogenation, hydroformylation, carbon–carbon bond formation, ring opening of epoxides, and cyanohydrin synthesis was recently reviewed by Li.[7]

Immobilization of homogeneous catalysts has attracted significant interest because it could combine the advantages of both homogeneous and heterogeneous catalysis.[8] The various approaches include covalent binding to organic polymers,[9] layered double hydroxides,[8–10] ion exchange into the intracrystalline space of zeolite Y, Al-MCM-41,[11] and encapsulation in zeolite using ship in a bottle methodology.[12] Although immobilization shows increase in the catalytic activity of homogeneous catalysts,[13] it is often accompanied by a decrease in enantioselectivity. Although a few reports are available on immobilization of both achiral and chiral manganese–salen complexes onto the interlayers of montmorillonite clays[14] for enantioselective epoxidation of nonfunctionalized olefins using NaOCl as oxidant, attempts have not been made to oxidize olefins to the corresponding aldehydes. To achieve this objective, clay-supported iron–salen complexes are prepared and used in the present study.

Oxidative cleavage of olefins is one of the often used reactions in organic chemistry. The various reagents used for the cleavage of C═C bond are cobalt(II)–Schiff base complexes,[15] $KMnO_4$ under acidic conditions,[16] thiyl radical,[17] OsO_4–oxone,[18] OsO_4–$NaIO_4$,[19] Ru(II),[20] and Au(I).[21] Although good results are obtained, the high cost of many of these catalysts is a drawback. An alternative and underexplored option is the use of iron catalysts, which possess many advantages over traditional catalysts due to their nontoxic and inexpensive nature.

2. Results and discussion

In the present work, the catalytic activity of the clay-supported iron–salen complexes is studied in the oxidative cleavage of olefins and chalcones (Scheme 1) using hydrogen

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Keywords: Iron–salen complex; K10-montmorillonite; Aldehyde; Aqueous medium; Cleavage of C═C bond.

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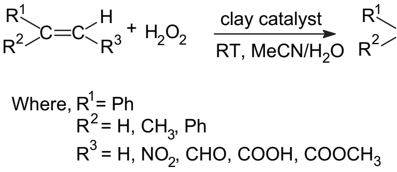
peroxide as oxidant. To study the influence of ligand, ferric chloride, iron–salen complex, and oxidant in the oxidation of C═C bond, control experiments are carried out with styrene using hydrogen peroxide in the presence of oxygen (air). The results show that the oxidation is very slow when only the ligand/$FeCl_3$/complex is present.

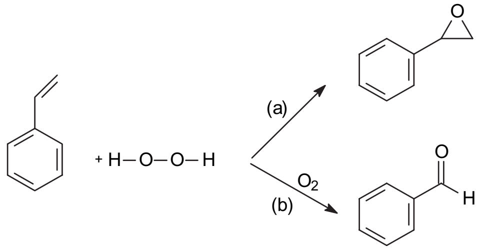


Scheme 1.

Cleavage of C═C double bond was studied with olefins such as styrene, α-methylstyrene, β-nitrostyrene, 1,1-diphenylethylene, cinnamic acid derivatives, and chalcones. In Table 1 the results of the oxidation of these olefins by 30% hydrogen peroxide as oxidant in the presence of iron–salen complex and clay-supported iron–salen complex are presented and a significant increase in yield of aldehydes is noticed in the clay-supported iron–salen complex oxidations. Oxidation by iron–salen complex is monitored by three ways. In method A, only iron–salen complex, without any clay support, is used. Methods B and C employ clay-supported iron–salen complex in acetonitrile and in acetonitrile–water mixture (0.5:2.5 mL), respectively. Method C is adopted to explore the potential utility of this novel oxidant in an ecofriendly solvent (water). The observed results provide very interesting features. For example, when the reaction is performed in acetonitrile at room temperature with 30% hydrogen peroxide in the presence of molecular oxygen and iron–salen complex, the conversion of styrene to benzaldehyde is only 14% (incomplete even after 48 h and which also furnishes benzoic acid). Under these conditions, no epoxide and diol are observed. The same reaction also fails to furnish aldehyde with nonpolar solvents such as diethyl ether and hexane.

When clay iron–salen complex (heterogenized onto the layers of clay) is used as catalyst, with the objective of improving the stability of the metal complex under the reaction conditions by preventing the catalytic active species from aggregating and also to fine-tune the selectivity of the reaction on the interlayers of clay solid via steric constraints, the reaction proceeds more rapidly, affording benzaldehyde and substituted benzaldehydes in moderate to good yield. Other advantages are the absence of over oxidized product (benzoic acid) and a typical GC and GC–MS analysis shows the absence of epoxide and phenylacetaldehyde also. Reactions of various olefins with heterogeneous catalysts by method B are examined and the results are shown in Table 1. Two different pathways are likely in the oxidation of styrene.[22] First pathway (a) leads to epoxidation of styrene to form styrene oxide and is not dependent on oxygen, whereas the second (b) leads to the formation of benzaldehyde and is dependent on oxygen (Scheme 2). When the oxidation is performed in air under the reaction conditions, benzaldehyde is obtained as the sole product.

In an analogous manner, other olefins such as 1,1-diphenylethylene and α-methylstyrene are also oxidized by method B and the yields are 98 and 76%, respectively. When the oxidation is extended to β-nitrostyrene, the yield of benzaldehyde decreases marginally when method B is employed in contrast to method A. All other olefins (namely *trans*-cinnamaldehyde, *trans*-cinnamic acid, and *trans*-methyl cinnamate) give a much better yield by method B. These results amply demonstrate that this method for C═C double bond cleavage is also effective with unsaturated compounds bearing electron-withdrawing substituents. Furthermore, the competing allylic oxidation of the methyl group in α-methylstyrene (by a radical route) is not observed under the present conditions. In addition, this efficient and mild oxidizing system does not disturb the functionalities such as aldehyde and esters.



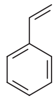
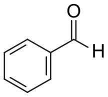
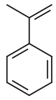
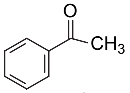
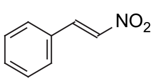
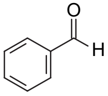
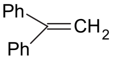
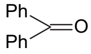
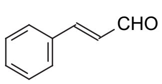
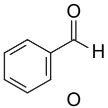
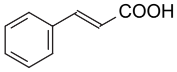
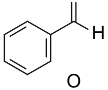
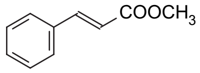
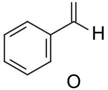
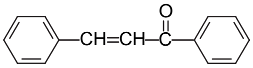
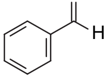
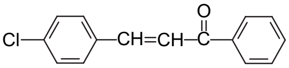
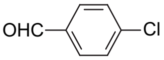
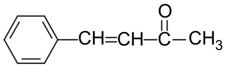
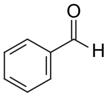
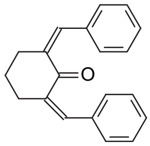
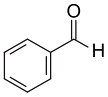
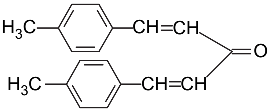
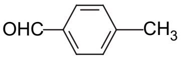
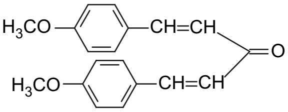
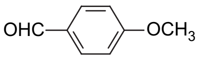
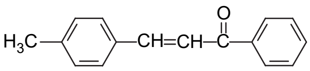
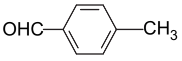
Scheme 2.

Organometallic catalysts in aqueous systems offer exciting prospects, both from academic and industrial points of view. The use of transition metal catalysts in water or in a two-phase system offers the same advantages as in an organic medium. However, they simplify the separation of the catalyst from the products, eventually for its recycling and this is significant in large scale chemical processes. The use of water as solvent can also exhibit different selectivities to those shown in organic medium. Wacker oxidation of olefins to ketones catalyzed by palladium complexes is a well known process, which has been applied to numerous olefins.[23] However, selective oxidation of C_8–C_{16} α-olefins remains a challenge. Mortreux et al. have developed a new catalytic system for the quantitative and selective oxidation of higher α-olefins in aqueous medium.[24–26]

These exciting results of organic reactions in water have prompted us to study the oxidation of olefins, using hydrogen peroxide as oxidant in acetonitrile–water mixture with a heterogeneous catalyst (method C). As anticipated, selective oxidation of olefin is achieved to yield aldehyde or ketone as the sole products as indicated by GC and GC–MS. The ratio of acetonitrile–water is fixed in such a way that the substrate dissolves completely. It is also observed that the oxidation is slowed down when 100% water is used as solvent. α-Methylstyrene, 1,1-diphenylethylene, and cinnamic acid are also oxidized by method C in a moderate yield. On the other hand, excellent yields of 94 and 92% are observed in the oxidation of dibenzylidenecyclohexanone and 4,4′-dimethoxydibenzylideneacetone, respectively. For these two substrates the rate of the reaction is accelerated when compared to methods A and B. The lower reactivity of methyl cinnamate, benzylideneacetone, and 4-methylchalcone is probably due to their poor solubility in water.

These interesting results have prompted an extension of the study to chalcones and its derivatives for oxidative cleavage

Table 1. Oxidation of C=C double bond in olefins and chalcones by hydrogen peroxide, catalyzed by iron–salen complex under various reaction conditions

Entry	Substrate	Method[a]	Product	Yield (%)[b]	TON[c]
1		A		14	09
2		B		30	20
3		C		10	07
4		A		27	18
5		B		76	51
6		C		43	26
7		A		34	23
8		B		32	22
9		C		23	15
10		A		68	27
11		B		98, 86[d]	38
12		C		41	16
13		A		32	22
14		B		53	36
15		C		16	11
16		A		50	34
17		B		65, 58[d]	44
18		C		53	36
19		A		23	15
20		B		65	44
21		C		09	06
22		A		34	23
23		B		70	47
24		C		45	30
25		A		27	14
26		B		82	42
27		C		60	31
28		A		44	30
29		B		22	15
30		C		06	04
31		A		—	—
32		B		87	59
33		C		100, 91,[e] 96[d]	67
34		A		32	19
35		B		92	55
36		C		68	40
37		A		38	20
38		B		85	45
39		C		100, 94,[e] 97[d]	53
40		A		47	28
41		B		45	27
42		C		05	03

[a] Method A: olefin (50 mg), iron–salen complex (10 mg), 30% H_2O_2 (0.6 mL), MeCN (3 mL); method B: olefin (50 mg), clay-anchored iron–salen complex (30 mg), 30% H_2O_2 (0.6 mL), MeCN (3 mL); method C: olefin (50 mg), clay-anchored iron–salen complex (30 mg), 30% H_2O_2 (0.6 mL), MeCN (0.5 mL)–H_2O (2.5 mL). All reactions are carried out in the presence of oxygen.

[b] Determined by GC; error limit ±3%.

[c] Turnover number (TON): millimole of product/millimole of catalyst.

[d] Catalyst reused.

[e] Isolated yield.

in solution as well as on clay-supported iron–salen complex. As expected, chalcones also undergo oxidative cleavage to corresponding aldehydes by method A (Table 1). Oxidations of chalcones are also extended to method B using 30% hydrogen peroxide as oxidant in presence of molecular oxygen. The yield has increased in a heterogeneous medium when compared to solution reaction except in the case of benzylideneacetone. It is likely that the interaction of hydrogen peroxide with the heterogeneous catalyst in the presence of oxygen has prompted the formation of active oxygenating

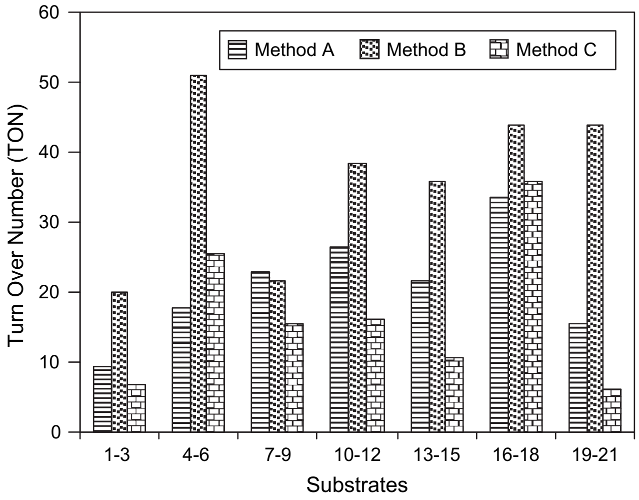


Figure 1. Oxidation of C=C double bond in olefins with molecular oxygen in various reaction conditions as a function of turnover number (TON).

species. Also the clay interlayer localizes the substrate and the active oxo complex in close proximity, which is not the case in solution reaction. Increased steric hindrance to oxidation in the case of chalcone may also have contributed to the lower reactivity. In some cases, it is very interesting to note that oxidation of chalcone by clay-supported iron–salen complex is even faster in aqueous acetonitrile (entries 33 and 39, method C) than with only acetonitrile (method B). Moreover, various functional groups such as alkyl, alkoxy, and halide groups on phenyl rings are well tolerated under this oxidizing system. With methyl group at *para* position of chalcone, potential byproducts from the radical oxidation of the methyl group are not observed (entries 34–36 and 40–42, Table 1).

The catalyst turnover number (TON, the ratio between number of millimoles of product formed and number of millimoles of catalyst used), increases for methods B and C in contrast to method A (Figs. 1 and 2). The most important advantages of heterogeneous catalysis over the homogeneous counterpart are the increase in complex stability in reaction media and the possibility of reusing the catalyst by simple filtration, without neither loss of selectivity nor activity. In some cases, the catalyst is reused in the oxidation of olefins and chalcones (by methods B and C) and the results are given in Table 1. It is also observed that this oxidation is inhibited to a greater extent by the addition of sodium azide, which suggests a radical pathway. It is relevant to note that in the presence of hydrogen peroxide, azide ion interacts with ferric native state of catalase to generate azidyl radical, which in turn reacts with the heme group of catalase thus inactivating the enzyme.[27]

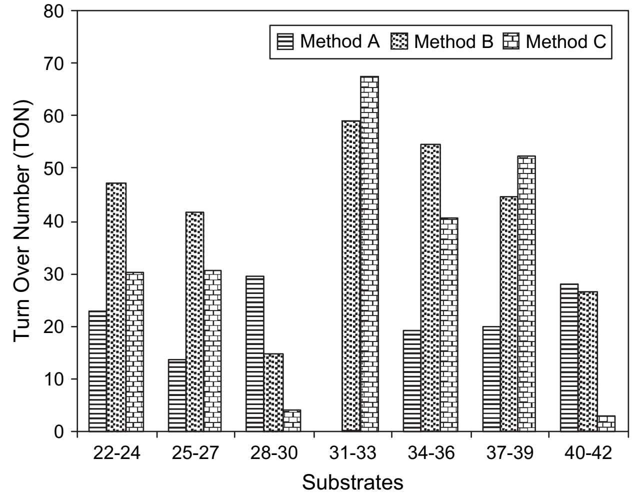
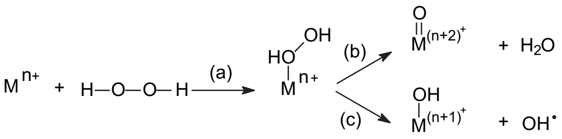


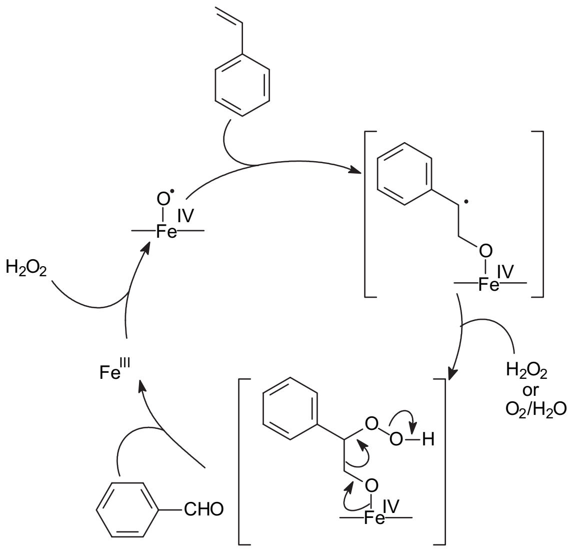
Figure 2. Oxidation of C=C double bond in chalcones with molecular oxygen in various reaction conditions as a function of turnover number (TON).

Complete mechanistic interpretation of these results requires consideration of two main pathways in which the O–O bond of hydrogen peroxide can be cleaved upon reaction with the catalyst (Scheme 3). Hydrogen peroxide typically reacts with a metal complex to form an initial metal–allylperoxo intermediate (a). The O–O bond of the coordinated peroxide can then cleave heterolytically to form high-valent metal oxo complex and water (b) or homolytically to form OH radicals and a metal hydroxide complex (c).



Scheme 3. Possible pathways of O–O bond cleavage in hydrogen peroxide.

In the proposed mechanism (Scheme 4), the active oxidizing species (formed upon reaction of hydrogen peroxide with the catalyst) is described as high-valent Fe(V)=O.[28] It can add onto the double bond leading to a carbon radical intermediate (proposed by Tuynman et al.).[29] This carbon radical intermediate is trapped by molecular oxygen followed by the abstraction of hydrogen or by the reaction between the carbon radical and activated hydrogen peroxide, which finally rearranges to give benzaldehyde as the sole product.



Scheme 4. Possible mechanism for the oxidative cleavage of C=C double bond in presence of molecular oxygen.

3. Conclusion

In summary, we have developed a novel method to oxidize olefins and chalcones to ketones/aldehydes in aqueous medium using hydrogen peroxide as oxidant within the microenvironment of clay interlayer wherein the local concentration of active oxygenating species and substrate are more localized. In almost all the cases where selective catalytic oxidations of olefin are carried out, second- or third-row transition metal complexes are involved. This is the first report wherein the first-row transition metal is utilized for oxidation of olefin to carbonyl compounds in aqueous medium. In addition, the present study highlights the activation of oxygen and its subsequent transfer to the substrate. A range of functional groups, which includes electron-withdrawing groups can be tolerated and this oxidation proceeds under mild conditions in water. Turnover number has increased from method A to B for most of the substrates and method B to C for 4,4′-dimethoxydibenzylideneacetone and dibenzylidenecyclohexanone. As the polarity of the reaction medium is increased by water–acetonitrile mixture, more substrates may be intercalated into the layers of clay to increase their local concentration in a heterogenous medium with faster reaction rate. The catalyst can also be reused without any loss in the selectivity and activity.

4. Experimental

4.1. General methods

All reagents were obtained commercially and used without further purification unless otherwise noted. The starting materials (chalcones and its derivatives) were synthesized by following previous procedures.[30] Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on Bruker 300 MHz and carbon nuclear magnetic resonance (^{13}C NMR) were recorded on 75 MHz Bruker instrument using TMS as an internal standard. UV–visible spectra for complexes were recorded using Jasco V-550 instrument. IR spectra for neat and immobilized complexes were recorded as KBr pellet in a Shimadzu FT-IR (8400 S) instrument. TGA analyses were carried out using Netzsch STA 409 PC model instrument. The percentage conversion, purity, and relative yields of the final products were confirmed and their characterization were carried out using gas chromatograph (Shimadzu GC-17A model, ZB-5 (10%) capillary column with FID detector and high purity nitrogen as carrier gas). The products were identified by comparing with authentic samples and the retention time of the starting material was taken as internal reference. In most cases the mass balance is $>80\%$. GC–MS analyses were also carried out in a Finnigan GC–MS with RTX5-MS capillary column and high purity helium as the carrier gas.

4.1.1. Procedure for C═C bond cleavage in homogeneous medium (method A). To a solution of olefin (50 mg) in 3 mL acetonitrile iron–salen complex (10 mg), 30% hydrogen peroxide (0.6 mL) was added. The reaction mixture was stirred for 24 h at room temperature. The progress of the reaction was monitored by the color change from dark pink to pale pink as the reaction time increased. Then the reaction mixture was quenched with water, extracted with diethyl ether, and the organic layer dried over anhydrous sodium sulfate.

4.1.2. Heterogeneous oxidation of olefin (method B or C). To a solution of olefin (50 mg) in 3 mL of acetonitrile, the heterogeneous catalyst was added followed by the addition of 30% hydrogen peroxide as terminal oxidant. Then the reaction mixture was stirred for 24 h at room temperature. The reactants were extracted from the heterogeneous catalyst, upon stirring with diethyl ether for 8 h and filtered. The filtrate was washed with water and the organic layer was dried over anhydrous sodium sulfate.

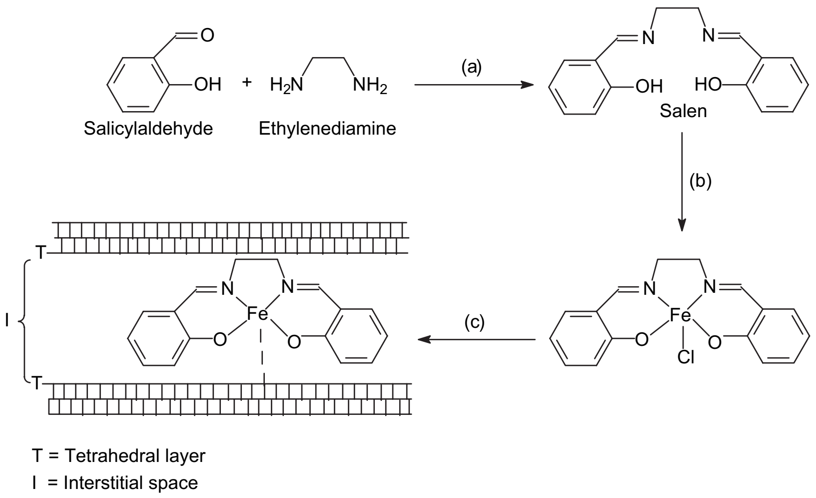
4.1.3. Synthesis of iron(III)–salen complex. The Schiff base salen ligand was prepared according to the established procedure.[31] To an ethanolic (15 mL) solution of salicylaldehyde (2.40 g) was added an ethanolic (15 mL) solution of ethylenediamine (0.67 g) and the resulting mixture was allowed to reflux for 1 h. The progress of the reaction was monitored by TLC. This mixture was allowed to cool at about 10 °C. The yellow crystalline product was filtered and dried and the formation of the ligand was confirmed by FTIR analysis.

An ethanolic (15 mL) solution of anhydrous iron(III) chloride (0.8 g) was added to a solution of salen ligand (1.34 g) in absolute ethanol (25 mL). The resulting dark brown suspension was refluxed for 1 h and allowed to cool to room temperature. Then it was filtered, washed with ethanol, and dried at 50–60 °C for 1 h.

4.1.4. Preparation of heterogeneous Fe(salen) catalyst. To a solution of iron(III)–salen complex in acetonitrile (250 mg), 500 mg of K10-montmorillonite was added and the resulting suspension was stirred for 30 h at room temperature. This heterogeneous catalyst was filtered, washed with acetonitrile, and dried at 60 °C prior to use. The filtrate was concentrated and it was found that around 95–98% of the complexes were anchored onto the interlayer of the clay as shown in Scheme 5.

4.1.5. Characterization. The UV–visible spectra of salen ligand recorded in acetonitrile medium show two characteristic absorptions at 253 and 326 nm, which are attributed to ligand $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ charge transfer bands, respectively. Iron–salen complex exhibits a broad band around 473 nm and the absence of 253 and 326 nm bands confirm the absence of ligand in the complex (Fig. 3a). The diffuse reflectance spectra of clay-anchored iron–salen complex too exhibit a band at 473 nm, which confirms the presence of iron–salen complex onto the layers of clay (Fig. 3b).

IR spectra were recorded for salen ligand, iron–salen complex, and heterogeneous catalyst using preactivated KBr as standard. As seen from Figure 4, the spectrum of the salen–Fe(III) clay complex coincided with that of the chloride salt of the same complex, thus establishing the purity and identity of salen–Fe(III) clay. In addition, the most characteristic band associated with the salen ligand appearing at 1500 cm^{-1} was absent for clay sample, indicating that all the ligands had reacted with metal to form complex.



Scheme 5. Reagents and conditions: (a) salicylaldehyde (2 equiv), ethylenediamine (1 equiv), ethanol, reflux 1 h, 90–93%; (b) anhydrous ferric chloride (1 mol), salen ligand (1 mol), ethanol, 85–90%; (c) K10-montmorillonite, iron–salen complex, acetonitrile, 30 h.

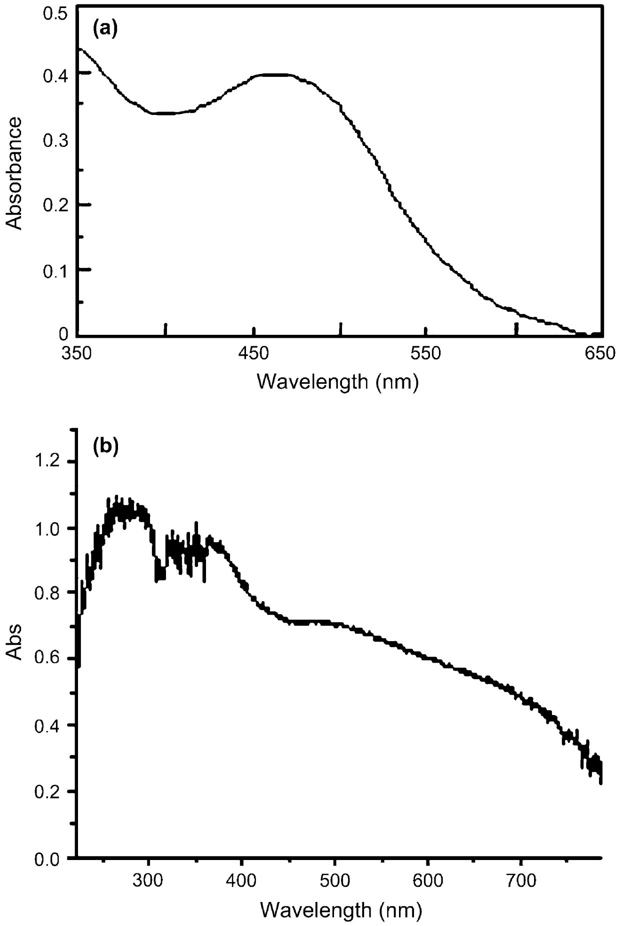


Figure 3. (a) UV–visible spectrum of iron–salen complex in acetonitrile and (b) diffused reflectance spectra of clay-supported iron–salen complex.

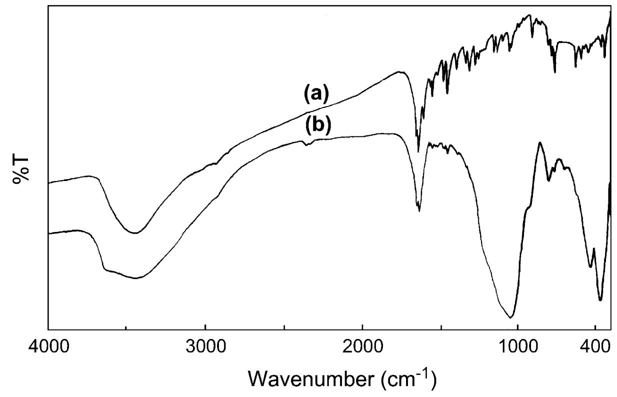


Figure 4. FTIR spectra of (a) iron–salen complex and (b) iron–salen complex immobilized on clay matrix.

Thermogravimetric analysis (TGA) in air profile showed the decomposition of iron–salen complex and iron–salen clay complex with residues amounting iron oxide. As seen from Figure 5a, the decomposition was complete for iron–salen complex at 610 °C. However on immobilization, the final decomposition temperature was shifted to 720 °C (Fig. 5b). The increase in temperature observed for immobilized sample is due to stabilization of the complex inside the interlayer of clays.

Direct evidence for the +3 oxidation state of iron–salen complex was obtained by cyclic voltammetry technique.

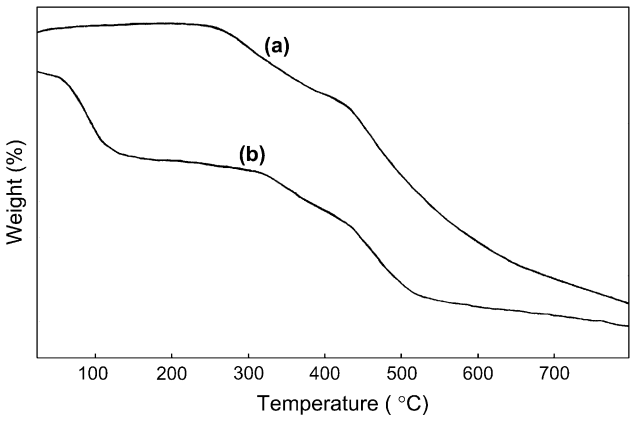


Figure 5. Thermogravimetric analysis (TGA) of (a) iron–salen complex and (b) iron–salen complex immobilized in the clay matrix.

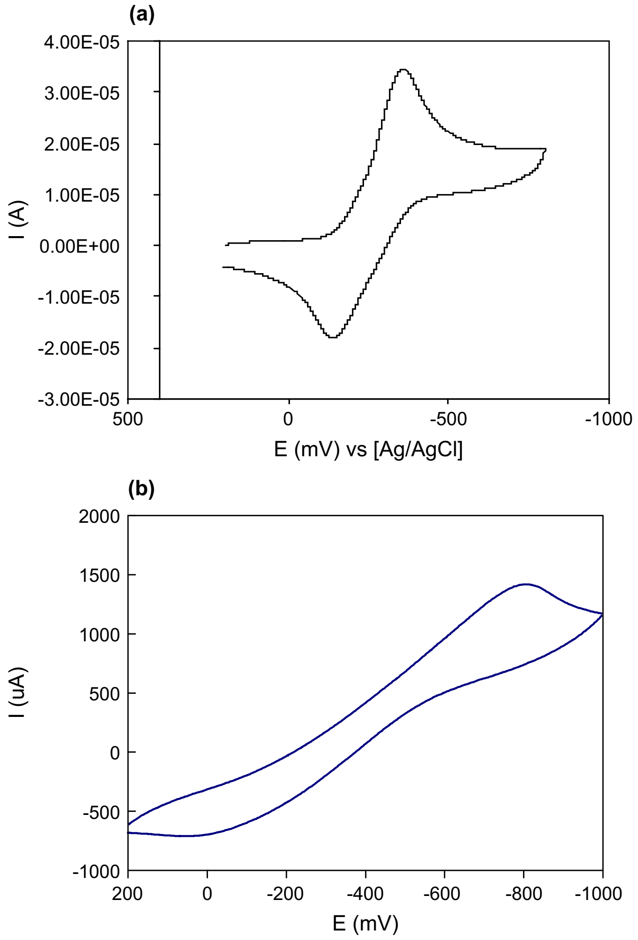


Figure 6. (a) Cyclic voltammogram of iron–salen complex in acetonitrile containing $LiClO_4$ and (b) cyclic voltammogram of iron–salen complex immobilized onto the clay interlayer and graphite composite (1:1, w/w) in acetonitrile as solvent.

The electrochemical behavior of the iron–salen complex in acetonitrile showed reduction potential of −0.360 V vs Ag/AgCl (Fig. 6a). Also, cyclic voltammogram was recorded for iron–salen complex immobilized onto the interlayer of clay by mixing equal amount (w/w) of iron–salen immobilized complex and graphite with a small amount of paraffin liquid as binder, which shows a quasi reversible behavior with single reduction potential at −0.75 V (Fig. 6b). The existence of single redox process for the salen complex immobilized in clay implies that the complex exist as monomeric species in the clay microenvironment.

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