

Al₂O₃ supported-Fe^{III} Schiff base complexes : Syntheses, characterizations and their applications in various oxidation reactions

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Abstract : Three mononuclear asymmetric Fe^{III}-Schiff base complexes, namely FeL¹Cl, FeL²Cl and FeL³Cl were prepared. These complexes were loaded over neutral active alumina to prepare alumina supported three heterogeneous catalysts, namely Ct-I, Ct-II and Ct-III. The catalysts were characterized by UV-Vis and FT-IR spectroscopy, thermogravimetric analysis and FE-SEM study. Finally, these catalysts have been studied for the oxidation of different types of organic substrate in the presence of hydrogen peroxide and appear to be easily recyclable.

Keywords : Schiff base complex, alumina, heterogeneous catalysts, H₂O₂, oxidation.

Introduction

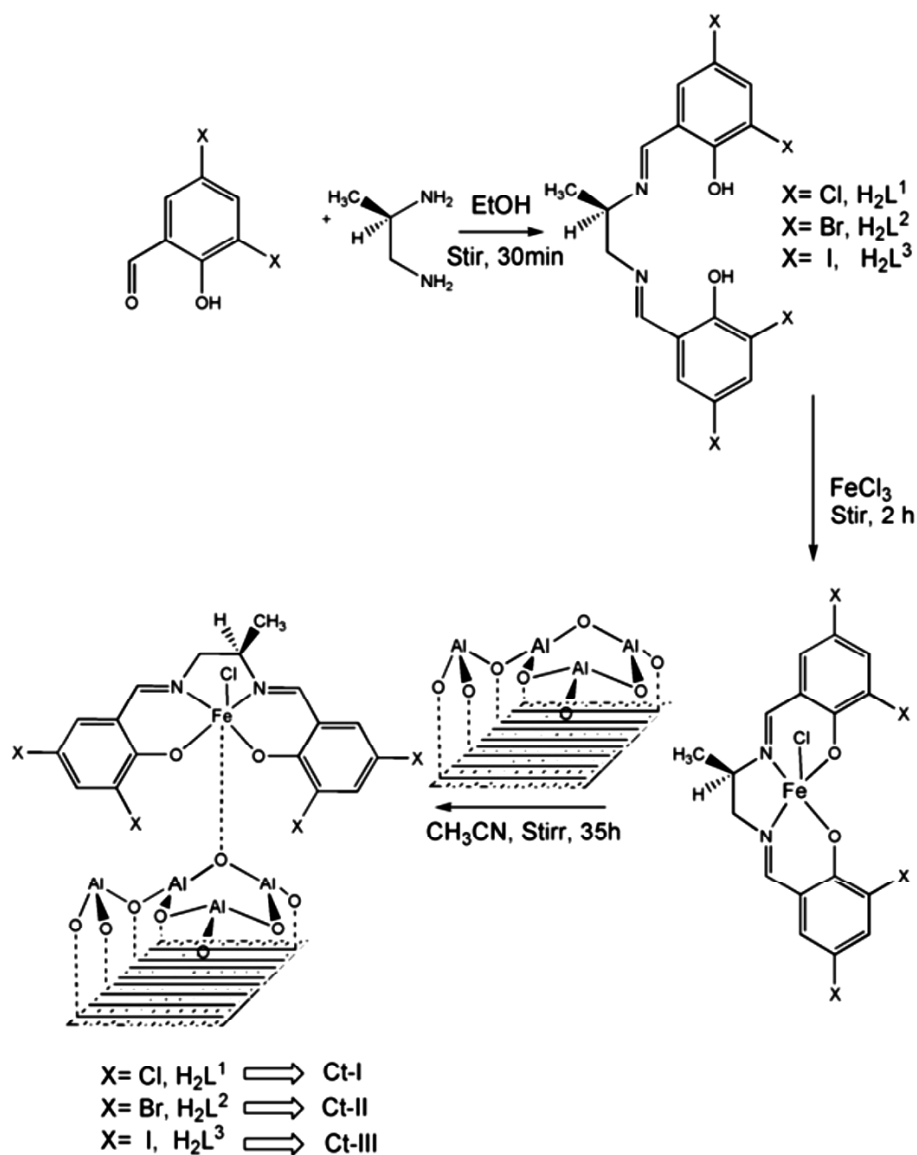
The oxidation of organic substrates is a very important organic reaction for both in the laboratory and in the industry¹. The traditional oxidizing reagents often used in stoichiometric amounts are often hazardous or toxic². Thus, the development of an environmentally friendly oxidation technology is always welcomed. In the last few years mostly there has been a strong emphasis on so-called 'Green Chemistry' to protect the environment from pollutants³. Hence, in terms of economical and environmental uneasiness, catalytic oxidation processes with cheap and environmental oxidants are extremely valuable. Hydrogen peroxide is one of the favorite oxidant, because water is the only byproduct of such oxidative reactions. The efficiency of homogeneous catalysts is much more comparing to heterogeneous catalysts. But the separation methods for heterogeneous catalysts are really difficult task. Hence we can avoid this problem with heterogeneous system⁴⁻⁶. Heterogenization of homogeneous catalysts is the most attractive research area currently⁷⁻¹⁹. Among them alumina-supported catalysis has been receiving interest in oxidation reactions presently^{12,20-25}. We are deeply engaged to find out an efficient catalyst for oxygenation of organic substrates^{12,13,15,26}. Here, we have immobilized

our previously prepared²⁶ three Fe^{III}-Schiff base complexes onto anhydrous neutral active alumina (Al₂O₃) (Scheme 1). The heterogeneous catalysts were characterized by solid UV-Vis spectroscopy, FT-IR spectroscopy, thermogravimetric analysis and SEM analysis. Catalytic activity for the oxidation of organic substrates were evaluated by varying different parameters such as reaction temperature, time, molar ratio of oxygen donor and amount of the catalysts. The recycled catalysts have also been thoroughly characterized and their activities were evaluated under optimized conditions.

Results and discussion

Synthesis procedure and characterization :

Here, we have prepared and characterized three asymmetric Fe^{III}-Schiff base complexes (**1-3**) in a similar procedures as we reported earlier²⁶. These complexes on further treatment with neutral active alumina generate three new asymmetric heterogeneous catalysts, namely **Ct-I**, **Ct-II** and **Ct-III** respectively. These three catalysts are further characterized by different physicochemical methods. FT-IR spectra of complexes (**1-3**) are presented in Fig. 1. Here, we have observed FT-IR bands in the range of ~ 1609-1638 cm⁻¹ (C=N vibrations) and ~ 1498-1526



Scheme 1. Synthetic route of two catalysts (Ct-I, Ct-II and Ct-III).

cm^{-1} (skeletal vibrations) for these three complexes²⁶. FT-IR spectra (Fig. 2) of Ct-I, Ct-II and Ct-III also show two characteristic peak around 1640 cm^{-1} and 1450 cm^{-1} which clearly indicate that incorporation of complexes are taken place over alumina surface. Similar type of broad peaks in the region of $500\text{--}1000 \text{ cm}^{-1}$ are present in FTIR spectra of three catalysts as reported recently¹³. UV-Vis spectra of 10^{-3} M acetonitrile solution of all the complexes (1-3) are presented in Fig. 3. Electronic spectra of these complexes show one shoulder band around 500 nm due to d-d band²⁶. Solid state UV-Vis spectra of Ct-I, Ct-II and Ct-III are presented in Fig. 4. They have bands at

almost similar wavelength as mentioned for complexes which clearly reveal well absorption of complex onto alumina. We also investigated thermogravimetric analyses of Ct-I, Ct-II and Ct-III to identify the percentage of loading of the complexes (Fig. 5). We observed earlier that at the temperature ranges from $30\text{--}800 \text{ }^\circ\text{C}$ neutral active alumina loses only 97.58% ¹³. At that temperature range, Ct-I, Ct-II and Ct-III lose 88.77% , 90.38% and 89.31% respectively. All the data imply that 8.81% , 7.14% and 8.27% of complexes 1, 2 and 3 are loaded in Ct-I, Ct-II and Ct-III respectively. The data of weight loss and loading are tabulated in Table 1. We also studied the morpho-

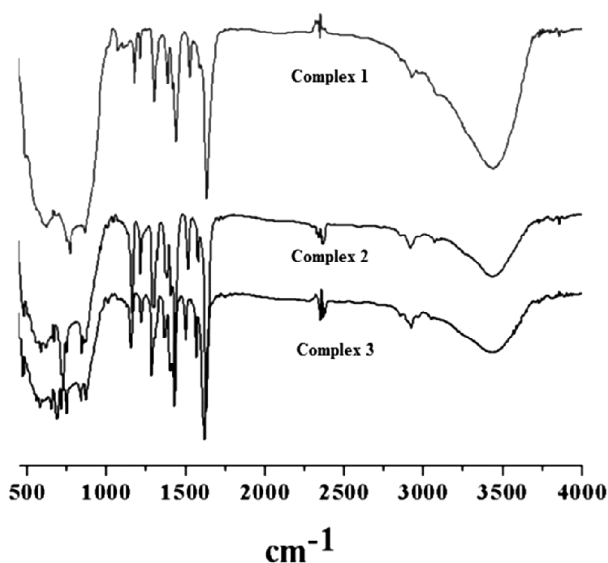


Fig. 1. FTIR spectra of complexes (1-3).

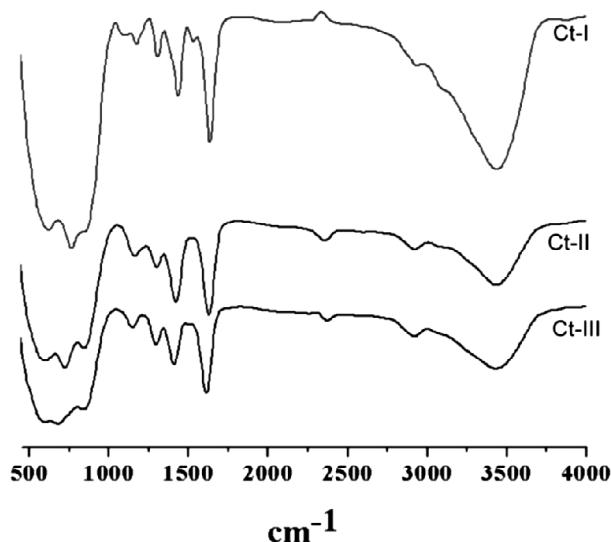


Fig. 2. FTIR spectra of Ct-I, Ct-II and Ct-III.

logy of all heterogeneous catalysts (Ct-I, Ct-II and Ct-III). Scanning electron micrographs of Ct-I, Ct-II and Ct-III (Fig. 6) suggested clearly that adsorption of complexes (1-3) on the alumina surface.

Evaluation of optimum reaction conditions for catalysts (Ct-I, Ct-II and Ct-III) :

Firstly, we found out the optimum reaction conditions to achieve the maximum yield for oxidation of different substrate. We varied different parameters, e. g. : (i) amount of 30% H₂O₂, (ii) amount of catalysts and (iii) time pe-

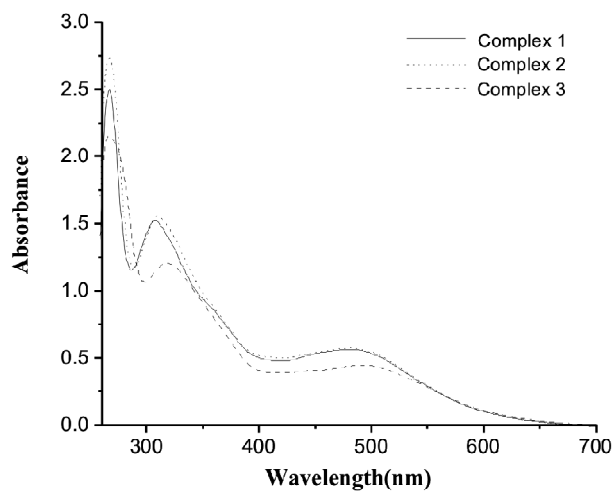


Fig. 3. UV-Vis spectra of complexes (1-3).

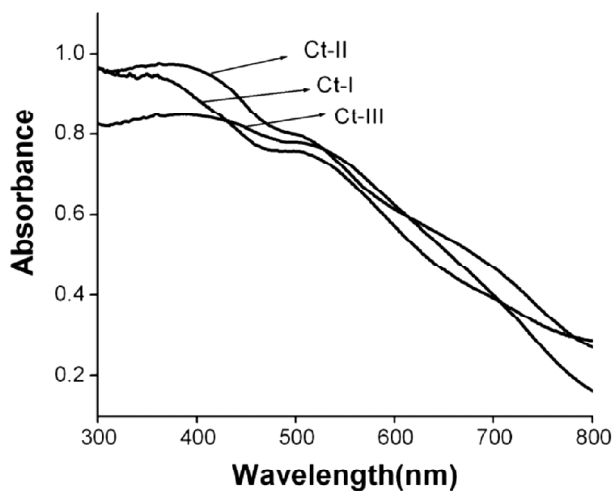


Fig. 4. Solid UV-Vis spectra of Ct-I, Ct-II and Ct-III.

riod. Here we took benzyl alcohol, benzaldehyde, ethyl benzene and benzyl amine as the test substrate to optimize the reaction condition for oxidation of alcohol, aldehyde, alkane and amine respectively. We used same conditions for other test substrates and obtained good results. Here it is noteworthy that we did not find any leaching of catalysts during the catalytic reaction.

We studied four different substrates to H₂O₂ molar ratios (1 : 5, 1 : 10, 1 : 15 and 1 : 20), keeping other parameters fixed : namely amount of catalysts (150 mg), temperature (30 °C) and reaction time (4 h). We found the most favorable substrate to H₂O₂ ratios is 1 : 10 for all the oxidation reactions. The amount of catalysts has an important effect on the oxidation of styrene. Six different

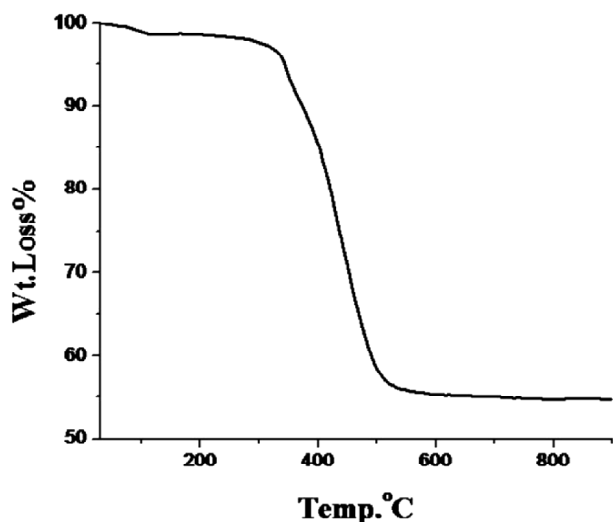


Fig. 5. Thermogravimetric analysis plot of Ct-I (representative of all heterogeneous catalysts).

Table 1. Loading of the complex 1, 2 and 3 over alumina
% Weight loss at 30–800 °C

Al ₂ O ₃	Ct-I	Ct-II	Ct-III
97.58	88.77	90.38	89.31
Loading of complex over Al ₂ O ₃	8.87%	7.67%	8.67%

amounts of catalyst (Ct-I or Ct-II or Ct-III) viz. 100, 150, 200 and 250 were used keeping fixed all other reaction parameters, namely temperature (30 °C), substrate amount (1 mmol) and reaction time (4 h). The maximum percentage yield was observed with 150 mg Ct-I, 150 mg Ct-II and 100 mg Ct-III respectively. This amount was taken as optimal. The percentage of conversion was monitored at different reaction times keeping fixed all other reaction parameters, namely temperature (30 °C), substrate amount (1 mmol), H₂O₂ (10 mmol), amount of Ct-I (150 mg) or Ct-II (150 mg) or Ct-III (100 mg). The conversion (%) increases with the reaction time. The maximum percentage conversion was observed for 4 h of reaction time.

Control experiment :

All synthesized complexes were active towards the oxidation of organic substrates as we observed in our previous work²⁶. The control experiment with Al₂O₃ was carried out under optimized conditions with above said substrates and H₂O₂. Here we did not observe any oxidized product. Thus, Al₂O₃ is inactive towards the oxidation of styrene indicating that the catalytic activity occurs

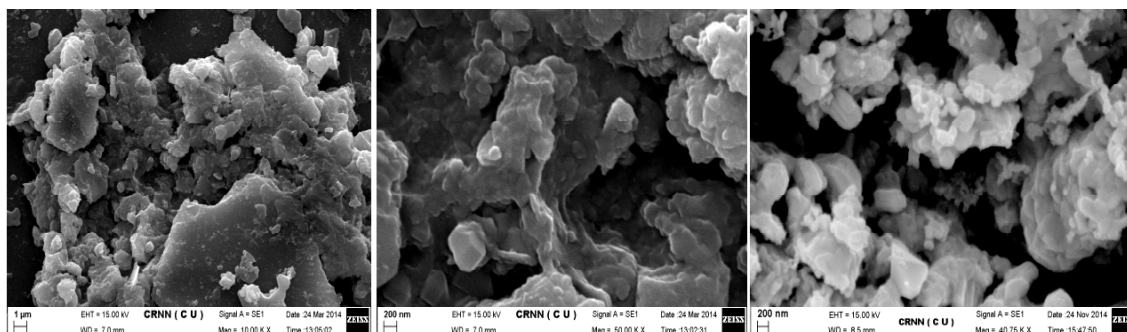


Fig. 6. FE-SEM images of Ct-I, Ct-II and Ct-III.

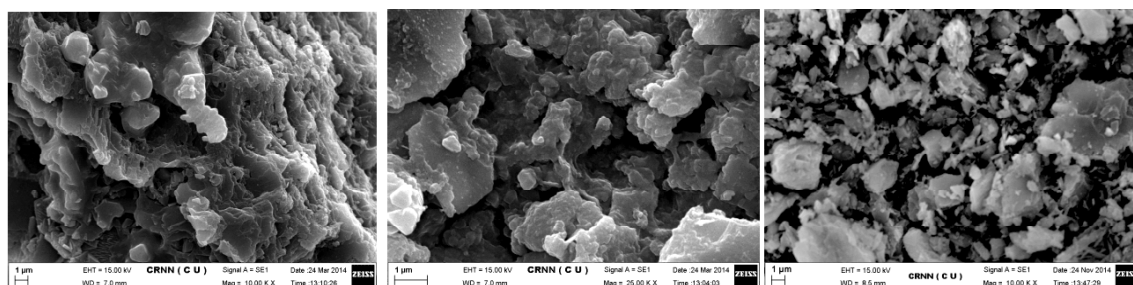


Fig. 7. FE-SEM images of reused Ct-I, Ct-II and Ct-III.

in presence of the complex only. These results clearly indicate that the complexes are the real active species. Thus, we succeeded in supporting the complex onto Al₂O₃ without any significant loss in activity, hence overcoming the traditional problems of homogeneous catalysis.

Alcohol oxidation with Ct-I, Ct-II and Ct-III :

The conversion (%), maximum isolated yields (%) and turn over number for Ct-I, Ct-II and Ct-III catalyzed oxidation of three different alcohols, using 30% H₂O₂ as terminal oxidants in CH₃CN are shown in Fig. 8. We observed 73.5%, 75.8% and 74.6% isolated yield for benzyl alcohol, 1-phenyl ethanol and 2-octanol respectively when we used Ct-I as catalyst, whereas when we used Ct-II as catalyst, we observed 78.2%, 75.3% and 76.4% isolated yield for benzyl alcohol, 1-phenyl ethanol and 2-octanol respectively. We found 74.8%, 77.4% and 76.8% isolated yield for benzyl alcohol, 1-phenyl ethanol and 2-octanol respectively when we used Ct-III as catalyst.

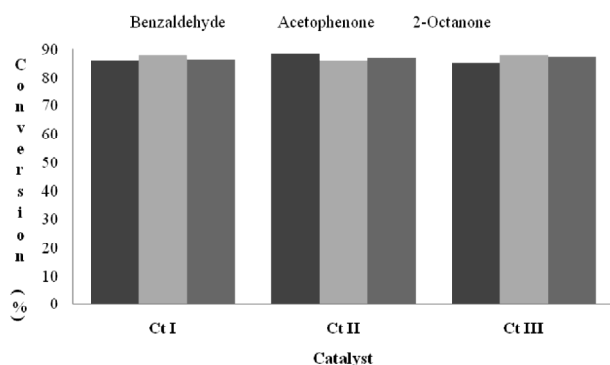


Fig. 8. Conversion of different alcohols catalyzed by Ct-I, Ct-II and Ct-III in CH₃CN with 30% H₂O₂.

Aldehyde oxidation with Ct-I, Ct-II and Ct-III :

The conversion (%), maximum isolated yields (%) and turn over number for Ct-I, Ct-II and Ct-III catalyzed oxidation of three different aldehydes, using 30% H₂O₂ as terminal oxidants in CH₃CN. We observed 77.8%, 78.9% and 78.2% isolated yield for benzyl aldehyde, 4-methyl-benzaldehyde and 4-methoxy-benzaldehyde respectively when we used Ct-I as catalyst, whereas when we used Ct-II as catalyst, we observed 76.7%, 77.2% and 78.1% isolated yield for benzyl aldehyde, 4-methyl-benzaldehyde and 4-methoxy-benzaldehyde respectively. We found 76.3%, 77.6% and 76.9% isolated yield for benzyl

aldehyde, 4-methyl-benzaldehyde and 4-methoxy-benzaldehyde respectively when we used Ct-III as catalyst.

Alkane oxidation with Ct-I, Ct-II and Ct-III :

The conversion (%), maximum isolated yields (%) and turn over number for Ct-I, Ct-II and Ct-III catalyzed oxidation of three different alkanes, using 30% H₂O₂ as terminal oxidants in CH₃CN. We observed 75.4%, 76.2% and 75.3% isolated yield for ethyl benzene, tetraline and diphenylmethane respectively when we used Ct-I as catalyst, whereas when we used Ct-II as catalyst, we observed 77.3%, 77.8% and 76.5% isolated yield for ethyl benzene, tetraline and diphenylmethane respectively. We found 77.1%, 78.2% and 76.6% isolated yield for ethyl benzene, tetraline and diphenylmethane respectively when we used Ct-III as catalyst.

Amine oxidation with Ct-I, Ct-II and Ct-III :

The conversion (%), maximum isolated yields (%) and turn over number for Ct-I, Ct-II and Ct-III catalyzed oxidation of three different amines, using 30% H₂O₂ as terminal oxidants in CH₃CN. We observed 78.8%, 77.3% and 77.1% isolated yield for benzyl amine, 4-methyl-benzylamine and 4-methoxy-benzylamine respectively when we used Ct-I as catalyst, whereas when we used Ct-II as catalyst, we observed 78.1%, 78.7% and 77.3% isolated yield for benzyl amine, 4-methyl-benzylamine and 4-methoxy-benzylamine respectively. We found 78.6%, 78.1% and 77.8% isolated yield for benzyl amine, 4-methyl-benzylamine and 4-methoxy-benzylamine respectively when we used Ct-III as catalyst.

Characterization of regenerated catalysts :

Regenerated catalysts (Ct-I, Ct-II and Ct-III) were further characterized by SEM analysis which confirm that all the catalysts were structurally unchanged after completion of oxidation even after their five time uses (Fig. 7).

Reusability of the catalysts :

We have investigated the recycling efficiency of the catalysts (Ct-I, Ct-II and Ct-III) i.e. whether the catalysts can be reused further for several cycles. Benzyl alcohol, benzaldehyde, ethyl benzene and benzyl amine respectively have been chosen as a representative case for recycling experiments. After each reaction cycle the catalysts were recovered by filtration, washed thoroughly with

Table 2. Reusability of **Ct-I**, **Ct-II** and **Ct-III** with 30% H₂O₂ in CH₃CN

Catalyst	Catalyst amount (mg)	H ₂ O ₂ (mmol) Reused number →	Substrate (1 mmol)	Time (h)	Yield (%) ^a				
					1	2	3	4	5
Ct-I	150	1	Benzyl alcohol	4	74	73	73	74	74
	150	1	Benzaldehyde	4	78	77	78	78	77
	150	1	Ethyl benzene	4	75	75	74	75	74
	150	1	Benzyl amine	4	79	78	78	79	79
Ct-II	150	1	Benzyl alcohol	4	78	78	77	77	77
	150	1	Benzaldehyde	4	77	77	77	76	76
	150	1	Ethyl benzene	4	77	76	76	77	77
	150	1	Benzyl amine	4	78	78	77	78	77
Ct-III	100	1	Benzyl alcohol	4	75	74	75	75	74
	100	1	Benzaldehyde	4	76	75	75	76	75
	100	1	Ethyl benzene	4	77	77	76	77	76
	100	1	Benzyl amine	4	79	78	79	78	78

acetonitrile. Finally they were dried at 30 °C for 2 h. For all cases, we have followed the same experimental procedure as that with the original catalysts. We did not observe any significant different yields in the catalytic reactions through first to fifth use as shown in Table 2.

Conclusion

We, here show a simple technique to heterogenized structurally characterized efficient homogeneous catalysts based on Schiff base complexes via immobilizing on neutral active alumina. The catalytic activity of these heterogeneous catalysts for oxygenation of various organic substrates have been thoroughly investigated and reported here. However, as our heterogeneous catalysts are very robust, no leaching is observed during catalytic reaction and can be reused several times just after simple filtration. The overall activity of these three heterogeneous catalysts is far better than their respective homogeneous counterpart

Experimental

Methods and materials :

Infrared spectra (4000–500 cm⁻¹) were recorded at 27 °C using a Perkin-Elmer RXI FT-IR spectrophotometer with KBr pellets. Thermal analyses (TG-DTA) were carried out on a Mettler Toledo (TGA/SDTA851) thermal analyzer in flowing dinitrogen (flow rate : 30 cm³ min⁻¹). Field Emission Scanning Electron Microscope (FE-SEM) measurement was carried out with JEOL JSM-6700F field-

emission microscope. All chemicals were obtained from commercial sources and used as received. Solvents were dried according to standard procedure and distilled prior to use. Neutral active Al₂O₃ (Activity I-II, according to Brockmann, Loba Chemie, Mumbai) was used as received.

Syntheses of the complexes :

Complexes **1-3** were synthesized by similar procedures as we described earlier²⁶.

Synthesis of catalysts (Ct-I/II/III) :

The catalyst, **Ct-I** ([FeL¹Cl]-Al₂O₃), was synthesized by impregnating 1 g of Al₂O₃ with a solution of FeL¹Cl (0.5 g in 50 ml of acetonitrile) with stirring for 30 h and dried at 100 °C for 10 h. The obtained material was designated as FeL¹Cl-Al₂O₃. IR (KBr) : ν(C=N) 1631 cm⁻¹; ν(skeletal vibration) 1526 cm⁻¹. UV λ_{max} (solid)/nm ~ 512sh, ~ 675sh. **Ct-II** and **Ct-III** were prepared in adopting the similar procedure as for **Ct-I** by using FeL²Cl and FeL³Cl respectively instead of FeL¹Cl. **Ct-II** : IR (KBr) : ν(C=N) 1631 cm⁻¹; ν(skeletal vibration) 1526 cm⁻¹. UV λ_{max} (solid)/nm ~ 512sh, ~ 675sh. **Ct-III** : IR (KBr) : ν(C=N) 1631 cm⁻¹; ν(skeletal vibration) 1526 cm⁻¹. UV λ_{max} (solid)/nm ~ 512sh, ~ 675sh.

Oxidation of various organic substrate catalyzed by Ct-I/II/III :

To a solution of experimental organic substrate (1 mmol) in acetonitrile (50 mL), catalyst [**Ct-I** (150 mg) or **Ct-II** (150 mg) or **Ct-III** (100 mg)] was suspended and then 30% H₂O₂ (1 mmol) was added and the resultant mixture

were stirred at room temperature for 4 h in air. Here we added 30% H₂O₂ portionwise to the solution. The reaction progress was monitored by TLC. After completion of the reaction, the catalyst was filtered off and the solvent was removed by rotary evaporator. The crude product was thus obtained was purified by flash chromatography. Identification of the product was performed by ¹H NMR spectroscopy.

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