

# Cyclohexane Oxidation: Synthesis of Iron (III)-Amino Acid and Amino Acid Schiff Base Complexes and Their Catalytic Activity Evaluation

S. Merajuddin Ahmed<sup>1\*</sup>, Ahmed T. Mubarak<sup>1</sup>, M. Mujahid Alam<sup>1</sup>  
and Halima A. Al-Ahmari<sup>1</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science, King Khalid University, P. O. Box 9004, Abha 61413, Saudi Arabia.

## Authors' contributions

*This work was carried out in collaboration between all authors. Author SMA performed the statistical analysis and wrote the protocol and first draft. Authors ATM, MMA and HAAA designed the study and managed the analyses of the study. All authors read and approved the final manuscript.*

Original Research Article

Received 25<sup>th</sup> January 2014  
Accepted 23<sup>rd</sup> March 2014  
Published 12<sup>th</sup> April 2014

## ABSTRACT

The amino acids, alanine (Ala) and phenyl alanine (Phe) and their Schiff bases (Ala-Sal), (Phe-Sal) were complexed with iron [III] metal. The complexes (Fe-Ala), (Fe-Phe) and Schiff bases complexes (Fe-Ala-Sal) and (Fe-Phe-Sal) were characterized by the UV, IR, NMR and SEM. The catalytic performance of prepared complexes were investigated by using various reaction conditions, such as temperature, pressure, amount of catalyst, time, oxidant to substrate ratio in order to find out the optimum conditions for the oxidation reaction of cyclohexane. The selective oxidation of cyclohexane to cyclohexanone and cyclohexanol (KA-oil) by various oxidants such as aqueous H<sub>2</sub>O<sub>2</sub>, Na<sub>2</sub>O<sub>2</sub>, KIO<sub>4</sub> and TBHP in presence of acetonitrile and without solvent system was investigated. Also, the amino acid Schiff base iron complexes were supported on zeolite "Y" and intercalated on montmorillonite clay to enhance their catalytic activity. The supported catalysts were also characterized by IR and Powder X-Ray diffraction XRD studies before their application to cyclohexane oxidation. The conversion of cyclohexane was up to 13% with the selectivity of cyclohexanone.

\*Corresponding author: Email: [sm\\_ahmed@hotmail.com](mailto:sm_ahmed@hotmail.com);

**Keywords:** Schiff base; iron complexes; L-alanine; L-phenylalanine; cyclohexane oxidation; zeolite; montmorillonite.

## 1. INTRODUCTION

Saturated hydrocarbons are plentiful in nature; they are the major constituents of crude oil and natural gases. They are essential feedstocks for chemical manufacture [1-3]. Cycloalkanes are the main chemical class of hydrocarbons [4] and have an important presence in traditional fuels [5].

Oxidation of cycloalkanes, particularly cyclohexane is one of the important bulk processes in the chemical industry. More than  $10^6$  tons per year of cyclohexanone and cyclohexanol, (KA oil) are produced worldwide by this process as a chemical intermediates in production of adipic acid and capolactum [6-9]. They are also used in the manufacture of polyamides and plastics [10]. Yet, this process seems to be one of the least efficient of all major industrial chemical processes. The desired products (*i.e.*, cyclohexanol and cyclohexanone) are intermediates in a sequence of complicated, multiple, free-radical chain reactions [11].

The finding of efficient catalysts for the selective insertion of one oxygen atom from oxygen donors, like dioxygen, hydrogen peroxide, alkyl hydroperoxide, sodium periodate into various organic molecules, under mild conditions, remains a difficult task in the fields of chemical and biological catalysis [12].

During the last two decades, considerable attention has been paid to the chemistry of metal complexes of Schiff bases containing nitrogen and other donors. This may be attributed to their stability, biochemical, analytical and potential applications in many fields such as oxidation catalysis [13]. Schiff bases have been used extensively as ligands in the field of coordination chemistry; some of the reasons are that the intramolecular hydrogen bonds between the (O) and the (N) atoms which play an important role in the formation of metal complexes and that Schiff base compounds [14-26]. In recent years great interest has been focused on Fe-Schiff base amino acid complexes for their application in cytotoxic and anti-tumor drugs.

In this paper, we have synthesized and characterized different amino acid Schiff bases and their complexes and applied as a biomimetic catalyst for the oxidation of cyclohexane using different oxidants ( $H_2O_2$ ,  $Na_2O_2$ ,  $KIO_4$  and TBHP) under acetonitrile as solvent, without solvent and in autoclave system. Further, these amino acid Schiff base complexes were coated on zeolites and clays and successfully applied for the oxidation reaction. During these studies we have used different amounts of catalysts and oxidants.

## 2. EXPERIMENTALS

### 2.1 Materials

The iron [III] chloride hydrate, salicylaldehyde, L-alanine, L-phenylalanine were purchased from Sigma Aldrich and used as received without further purification. Ethanol, chloroform, acetonitrile, cyclohexane, cyclohexanol, cyclohexanone were obtained from Fluka chemicals.  $H_2O_2$ ,  $Na_2O_2$ ,  $KIO_4$ , TBHP were purchased from Merck Co. Zeolite and montmorillonite clay were purchased by Sigma Aldrich. All chemicals and reagents used in the present study were of analytical grade.

## 2.2 Instruments

The FTIR spectra were recorded on a JASCO FTIR-460 plus spectrometer by standard methods as KBr pellets or neat. The Ultraviolet spectroscopic analysis of the compounds was performed on Shimadzu UV-2100 spectrophotometer. GC analysis of the products formed was seen on Shimadzu 2014 GC system equipped with fused and packed chromosorb column and FID detector. Scanning electron microscopy (SEM) analysis was made on gold coated samples by JEOL-JSM-6390 LV.  $^1\text{H}$  NMR spectra of ligands and complexes were measured on a Bruker 500-DRX Avance spectrometer at 500 MHz using TMS as internal standard. The elemental analysis of the complexes were recorded by using Perkin-Elmer CHN-2400 analyzer. Their results were compared with the calculated values and found acceptable. LUMINA fluorescence spectrometer of Thermo Scientific Co. USA was used for photoluminescence analysis of the complexes and ligands. The X-Ray Diffractions (XRD) of the complexes and their coating on zeolites and clay was measured on Shimadzu DX-600 X-Ray diffractometer using Cu for  $\text{K}\alpha$ -particle source.

## 2.3 Synthesis of Metal Complexes

### 2.3.1 General procedure for the preparation of iron [III] metal amino acid complex

In separate experiments, the iron [III] complex of L-Alanine and L-Phenylalanine were prepared in (2:1) (ligand: Metal) molar ratios. To a 50 mL ethanol solution of iron [III] chloride (2.7 g), 0.01 M  $\text{Na}_2\text{CO}_3$  solution was added to adjust  $\text{P}^{\text{H}}$  till 7.4. The ligands solution of L-alanine (1.8 g), and L-Phenylalanine (3.3 g) in ethanol was added to obtain 1:2 ratios. The resulting mixture was stirred under reflux at  $80^\circ\text{C}$  for 3 hrs. The reaction progress was observed by TLC. On observing the completion of the reaction, the contents were cooled at room temperature. The separation of solid product was made by filtration. The recrystallization of the crude product was made by a mixture of acetone and diethyl ether 1:2 ratio with heating and stirring. The resultant saturated mixtures thus obtained were cooled, and the solids products were separated out by filtration and dried under vacuum.

#### 2.3.1.1 Complex (Fe-Ala)

IR (KBr,  $\text{v cm}^{-1}$ ): 3087 ( $\text{v}_{\text{NH}_2}$ ), 1595 ( $\text{v}_{\text{C=O}}$ ), 1113 ( $\text{v}_{\text{Fe-O}}$ ), 543 ( $\text{v}_{\text{Fe-N}}$ ).

Elemental analysis: Anal. Calcd. for  $\text{C}_6\text{H}_{12}\text{Cl}_3\text{FeN}_2\text{O}_4$ : C 21.30, H 3.57, N 8.28, Cl 31.43; Found: C: 21.12, H 3.43, N 8.12, Cl 31.29.

#### 2.3.1.2 Complex (Fe-Phe)

IR (KBr,  $\text{v cm}^{-1}$ ): 3032 ( $\text{v}_{\text{NH}_2}$ ), 1598 ( $\text{v}_{\text{C=O}}$ ), 1086 ( $\text{v}_{\text{Fe-O}}$ ), 563 ( $\text{v}_{\text{Fe-N}}$ ).

Elemental analysis: Anal. Calcd. for  $\text{C}_{16}\text{H}_{16}\text{Cl}_3\text{FeN}_2\text{O}_4$ : C 41.55, H 3.49, N 6.06, Cl 23.01; Found: C 41.39, H 3.25, N 5.96, Cl 22.95.

## 2.4 Synthesis of Schiff Bases

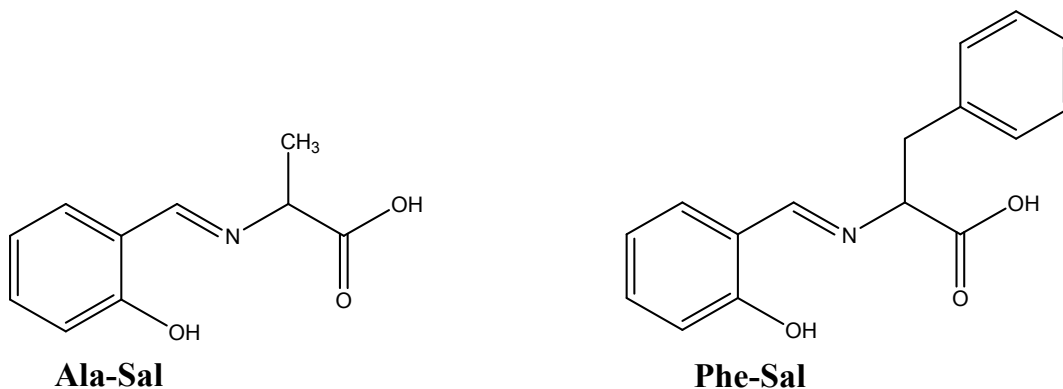
### 2.4.1 General procedure for the preparation of amino acid schiff bases

In separate experiments, the Schiff bases of amino acids, L-Alanine (4.5 g) and L-

Phenylalanine (8.5 g) were subjected to condensation with 6.2 mL of salicylaldehyde at 80 °C. When the Alanine and Phenylalanine solutions in ethanol were added dropwise into the round bottom containing salicylaldehyde solution, the color of solution changed to deep yellow. At this juncture catalytic amount of piperidine was added and the heating continued under reflux for 1 hr. Ten milliliter of CHCl<sub>3</sub> was slowly and dropwisely added. The reaction mixture was left for 4 hrs. The mixture was finally evaporated by rotatory evaporator. The product was precipitated as yellow solid and dried under vacuum.

Ala-Sal: IR (KBr,  $\nu$  cm<sup>-1</sup>): 3408 ( $\nu_{OH}$ ), 1604 ( $\nu_{C=N}$ ). <sup>1</sup>H NMR: (DMSO-*d*<sub>6</sub>,  $\delta$ , ppm) 2.5 (d, 3H, -CH<sub>3</sub>), 3.6 (q, 1H, -N-CH-), 6.3-6.8 (br, m, 5H, phenyl), 7.98 (s, 1H, Ph-CH=N-).

Phe-Sal: IR (KBr,  $\nu$  cm<sup>-1</sup>): 3031 ( $\nu_{OH}$ ), 1618 ( $\nu_{C=N}$ ), 1587 ( $\nu_{as COO}$ ), 1414 ( $\nu_{sCOO}$ ), 1210 ( $\nu_{Ph-O}$ ). <sup>1</sup>H NMR: (DMSO-*d*<sub>6</sub>,  $\delta$ , ppm) 3.8 (d, 2H, -CH<sub>2</sub>-Ph), 4.7 (t, 1H, -N-CH-), 7.1-7.3 (br, m, 9H, Phenyl), 7.99 (S, 1H, Ph-CH=N-).



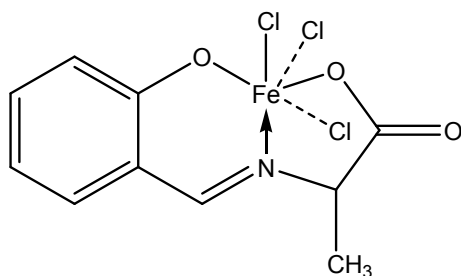
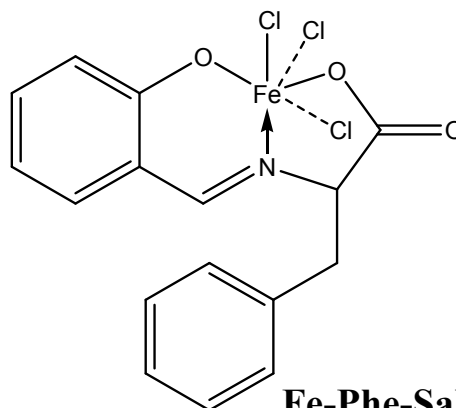
#### 2.4.1.1 General procedure for synthesis of iron [III] Schiff base complex (Fe-Ala-Sal and Fe-Phe-Sal)

In separate experiments, the iron [III] was complexed with Schiff bases of L-Alanine and L-Phenylalanine. To a 40 mL ethanol solution of iron [III] chloride (1.62 g). The Schiff base ligands of Ala-Sal (2.12 g) and Phe-Sal (2.87 g) was dissolved in 50 mL ethanol was added dropwise. The resulting mixture was stirred under reflux at 80°C for 3 hrs. The reactants to products formation ratio was seen by TLC. When the product formation was seen maximum on TLC the contents of the reaction flask was brought to room temperature the crude product was filtered to separate then subjected to recrystallization using acetone and diethyl ether 1:2 with heating and stirring. The resultant saturated complexed solution was cooled and the beautiful colored solids were separated by filtration, and dried under vacuum. The products were in beige yellow and dark violet color respectively.

Fe-Ala-Sal: IR (KBr,  $\nu$  cm<sup>-1</sup>): 3434 ( $\nu_{OH}$ ), 1604 ( $\nu_{C=N}$ ), 1153 ( $\nu_{Fe-O}$ ), 544 ( $\nu_{Fe-N}$ ).

Fe-Phe-Sal: IR (KBr): 3413 ( $\nu_{OH}$ ), 1621 ( $\nu_{C=N}$ ), 1036 ( $\nu_{Fe-O}$ ), 523 ( $\nu_{Fe-N}$ ).

Geometry optimization of the Fe-Schiff base amino acid complexes showed that all the complexes had octahedral co-ordination [27].

**Fe-Ala-Sal****Fe-Phe-Sal**

## 2.5 Encapsulation of Amino Acid Schiff Base Iron [III] Complexes in Various Matrixes

Insertion of organic or organometallic species into inorganic solids offers an attractive route to nanohybrids in which complementary properties of the two components are expressed in a single material.

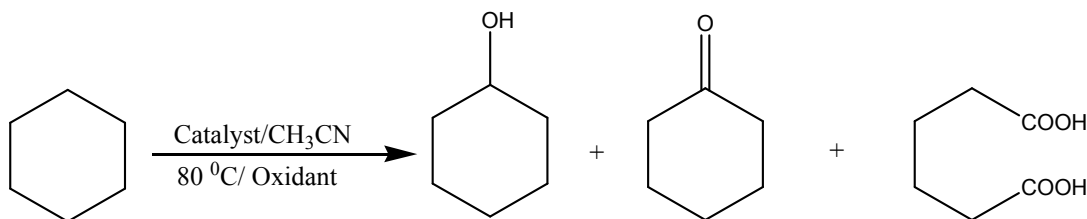
Iron [III] amino acid Schiff base complexes were supported on Montmorillonite Clay, Molecular Sieves powder with Zeolite Y. Prior to coating, the materials were dried under vacuum at 200°C.

In a typical procedure, encapsulation of metal complex was performed with the Flexible Ligand Method (FLM). First, the materials to be coated *i.e.*, Montmorillonite Clay (2 g), Molecular Sieves powder with Zeolite Y (2 g) were taken in the specially designed catalyst coating reactor and heated at 200 °C under nitrogen atmosphere for 1 hr. Then it was allowed to cool and THF was added under stirring at 80°C and THF was removed so that coating materials *i.e.*, zeolite and clay should perfectly be clean and devoid of other dissolved foreign materials. Now, fresh THF was added to the coating materials and the amino acid Schiff base metal complexes was applied in dissolved THF for coating under nitrogen with the help of cannula. The contents were heated with stirring for another 3 hrs. Later, the flask was brought suddenly to 0°C and the contents were kept at this temperature for another 1 hr. Finally, the contents were filtered and washed successfully with n-pentane. Thus, the coated material was dried and taken for the application of oxidation reaction. The coated catalyst was analyzed by IR data. The IR of the coated material was in good agreement with the parent complex. No major change was observed in the coated catalyst.

## 2.6 Cyclohexane Oxidation Reactions

All the catalytic reactions were performed either in 50 mL glass flask or in autoclave, where the glass flask was sealed with teflon faced silicon septa. Reactions were performed under magnetic stirring, at 80 °C, for 2 hr and 4 hr. Cyclohexane oxidation was carried out using various oxidants H<sub>2</sub>O<sub>2</sub>, Na<sub>2</sub>O<sub>2</sub>, KIO<sub>4</sub> and TBHP as oxygen donor in presence of acetonitrile as solvent and without solvent system. The reaction mixtures, after dressing were directly analyzed by packed chromosorb column gas chromatography, and the retention times of the products were confirmed by comparison with that of authentic product samples. Each reaction was accomplished at least three times, and the reported data represent the average

of the results of these reactions. The errors in yields and selectivity were calculated based on the reproducibility of the reactions. Control reactions were conducted in the absence of the catalyst, under the same conditions no product formation was observed (Scheme 1) [28-29].



**Scheme 1**

### 3. RESULTS AND DISCUSSION

#### 3.1 Characterization of Complexes

##### 3.1.1 FTIR spectra

The products, obtained at different steps, were characterized by FTIR. The assignments of the prominent absorption peaks are shown in Fig. 1. The vibrational for alanine modes due to carboxylate and amino groups was found to exist at 1680–1540  $\text{cm}^{-1}$  ( $\text{COO}^-$ ), 3150–3000  $\text{cm}^{-1}$  ( $-\text{NH}_2$ ). Further to this 1410  $\text{cm}^{-1}$  (weak) for symmetric stretching of  $\text{COO}^-$  and 660  $\text{cm}^{-1}$  for  $\text{COO}^-$  (deformation). Moreover, 1660–1610  $\text{cm}^{-1}$  and 1550–1480  $\text{cm}^{-1}$  were also assigned for ( $-\text{NH}_2$ ) vibrations for bending. Changes were observed in the IR bands of ( $-\text{NH}_2$ ) and ( $\text{COO}^-$ ). New bands were exhibited in the range of 400–660  $\text{cm}^{-1}$ , which are tentatively assigned for the M–N coordination and M–O coordinated bands were also seen in the range of 940–1210  $\text{cm}^{-1}$ , along with metal carbonyl (M–C=O) and metal amine (M– $\text{NH}_2$ ) bands were shifted. It provides a veiled information of metal complex formation with a bidentate mode.

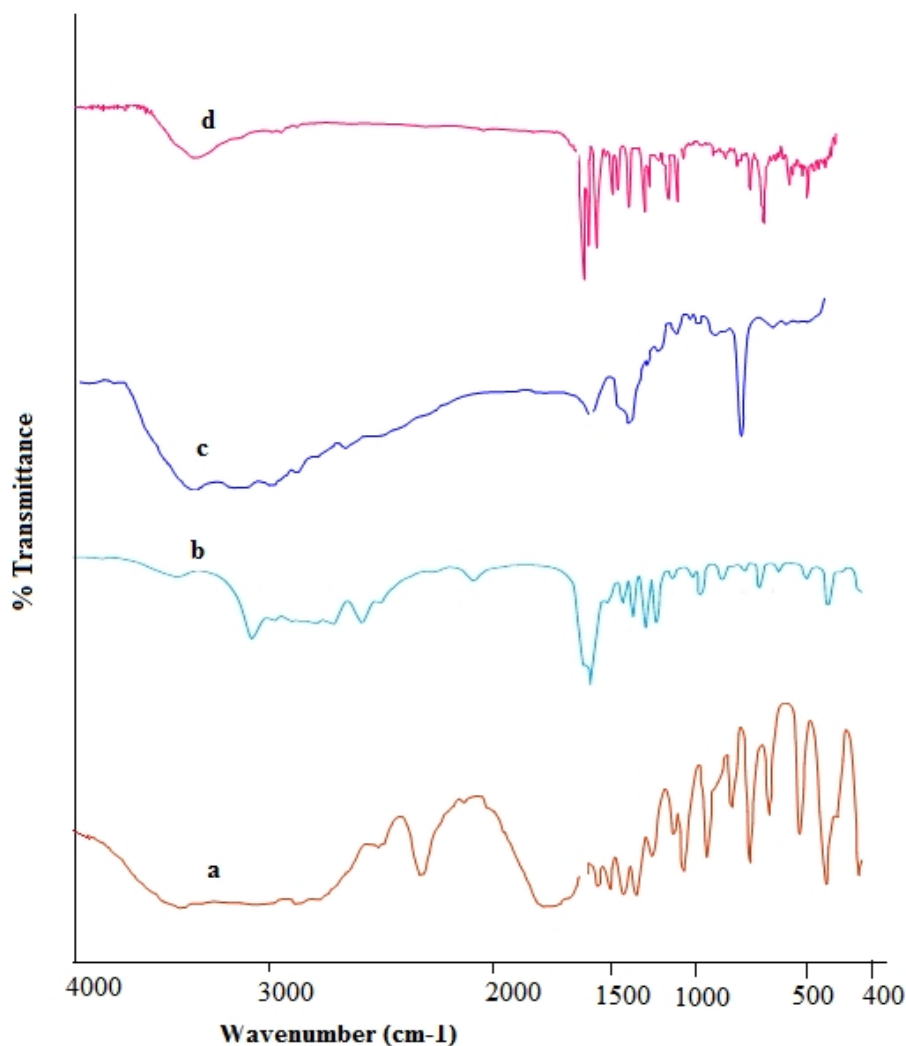
The IR spectra of the prepared Schiff base gives stretching vibration absorption bands for  $\text{COO}^-$  at 1621  $\text{cm}^{-1}$  and 1410  $\text{cm}^{-1}$ , while C=N<sup>-</sup> at 1632  $\text{cm}^{-1}$  and in case of ph–O at 1250  $\text{cm}^{-1}$ . The synthesized iron amino acid salen complexes IR spectra were compared with the parent ligand, shifts in the  $\text{COO}^-$  and C=N<sup>-</sup> bands are observed along with the Fe–O and Fe–N bands, which are newly shown in the IR spectra.

The IR spectral analysis for the Fe–phenylalanine metal complex, Phenylalanine Schiff base and Fe–Phe–Sal have shown in Fig. 2. The widening of bands between 3360–3040 and 1660–1540  $\text{cm}^{-1}$ , the comparative evidence from the free amino acid and their metal complex spectra clearly reveals that the complexation is successful. Further, satisfaction to our findings was found in the recent related work appeared.

##### 3.1.2 Sem results

The SEM images of the complexes suggested the morphology of the complexes. Further, the macroscopic inter spaces clearly reveals that the complexes molecules are well dispersed and not present in a coagulated form or bunch.

The SEM images of (Fe-Ala), (Fe-Phe.ala) and (Fe-Ala-Sal) have shown in Figs. 3, 4 and 5. As can be seen, the morphology of the Fe-Ala complex showed the rods with inter spaces and clean surfaces. The morphology of Fe-Phe.ala complex showed the spherical structure as beads with spongy surfaces with soft macroscopic separations. Whereas, Fe-Ala-Sal morphology showed crinkly and layered structure. Its EDX image has shown in Fig. 5a.

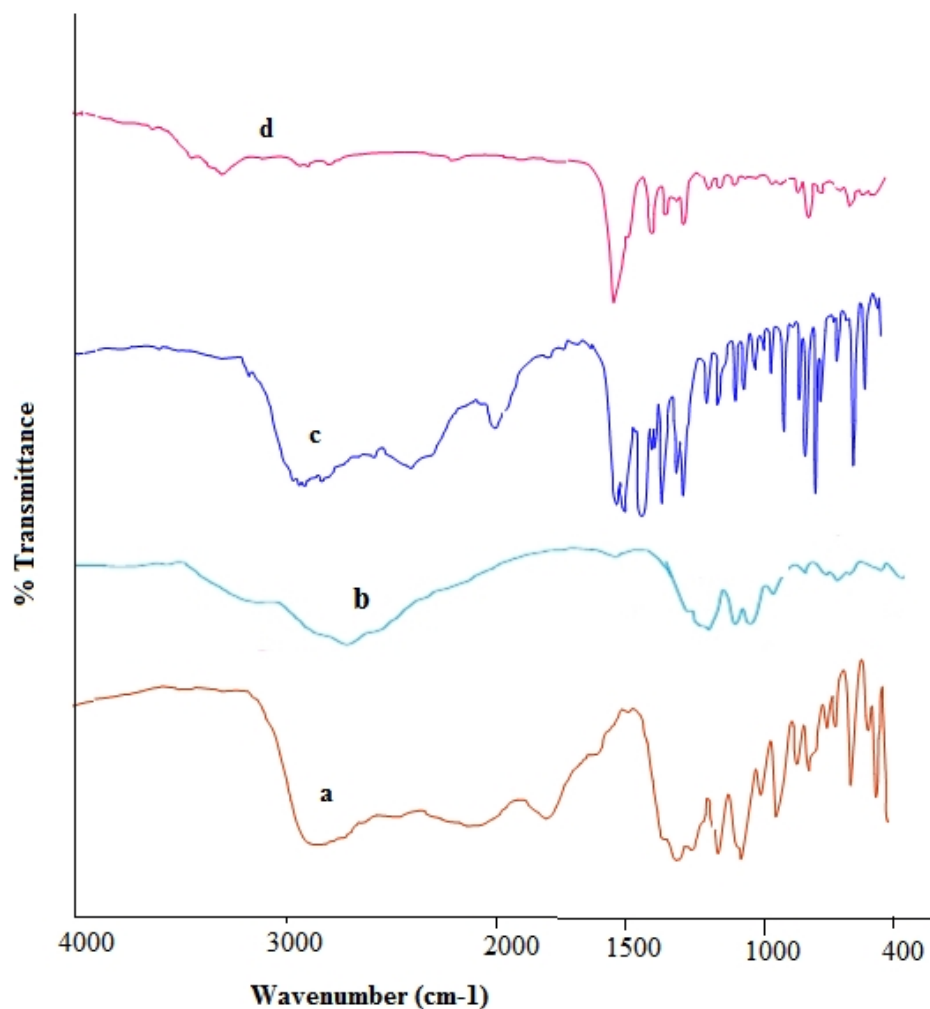


**Figure 1.** FT-IR spectra of (a) pure Alanine, (b) Fe-Alanine complex, (c) Alanin Schiff base ligand, (d) Fe-Ala-Sal complex

### **3.1.3 Nmr results**

The NMR spectra of the Schiff bases were recorded. Ala-Sal showed peaks at  $\delta$  2.5 (d, 3H, -CH<sub>3</sub>),  $\delta$  3.6 (q, 1H, -N-CH-), and 7.98 (s, 1H, Ph-CH=N-) gives along with the phenolic protons at  $\delta$  6.8-7.2 (m, 4H) and 8.9 (1H, OH). Whereas the phenolic protons of Phe-Sal appeared at  $\delta$  6.3-6.8 (br, m, 4H) and the intensity of Phe-Sal protons are more in the range of  $\delta$  6.4-6.8 and also at  $\delta$  7.1-7.3 as (br, m, 5H, phenyl). The other protons at 3.8 (d, 2H, -

CH<sub>2</sub>-Ph) and 4.7 (t, 1H, -N-CH-). Thus, the NMR results have proved the purity of the synthesized Schiff bases and their suggested structures.



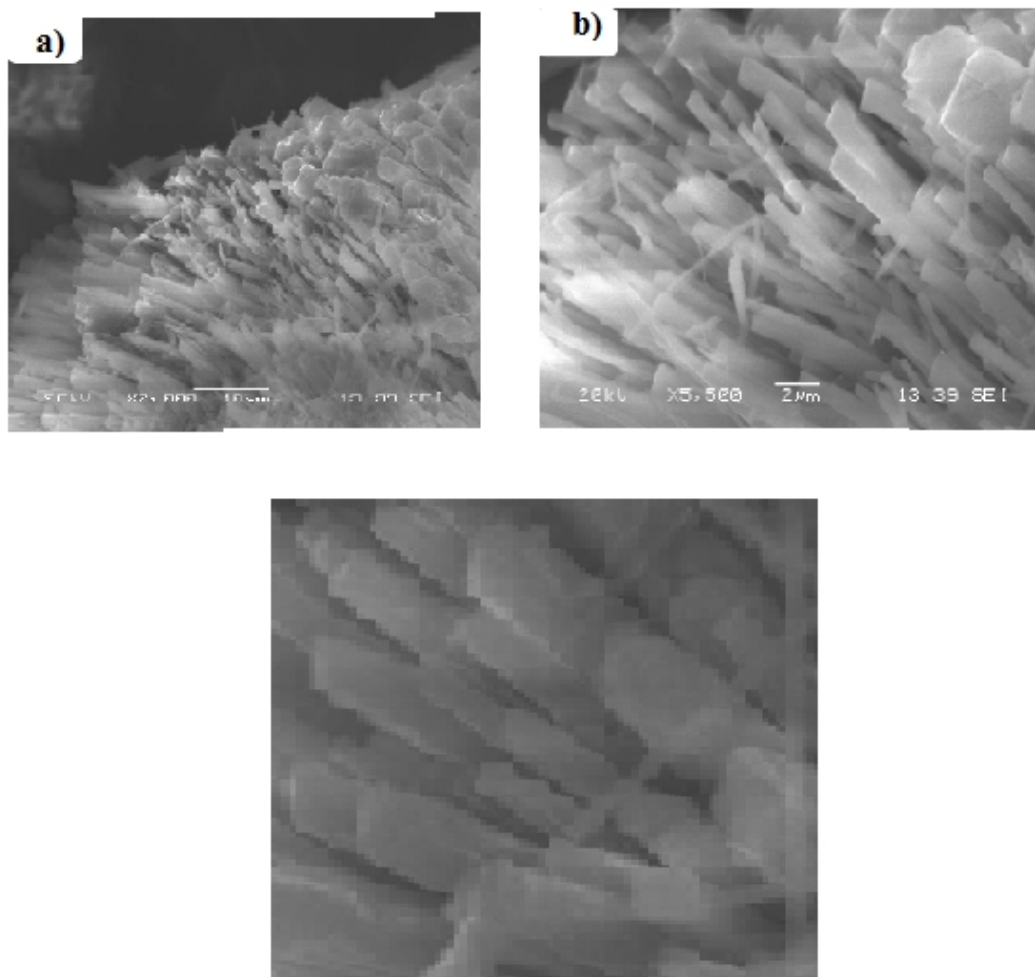
**Figure 2.** FT-IR spectra of (a) pure Phenylalanine, (b) Fe-Phenylalanine complex, (c) Phenylalanine Schiff base ligand, (d) Fe-Phe.ala-Sal Complex

After authenticating the ligands, FeCl<sub>3</sub> was complexed with these ligands giving resulted complex in good yield.

Most informative spectroscopic data to support the covalent anchoring of the complexes on the matrixes were obtained from the comparison of the set of IR corresponding to the complex and catalyst and by XRD.

The photoluminescence emission spectra showed an interesting evidence for the complex formation. The emission  $\lambda_{\max}$  556-566 and 660-730 nm provide evidence that the metal atoms are transferring energy to the ligand (alanine) and to the benzene ring (Phe) and hence promoting the photoluminescence to the organic ligand.



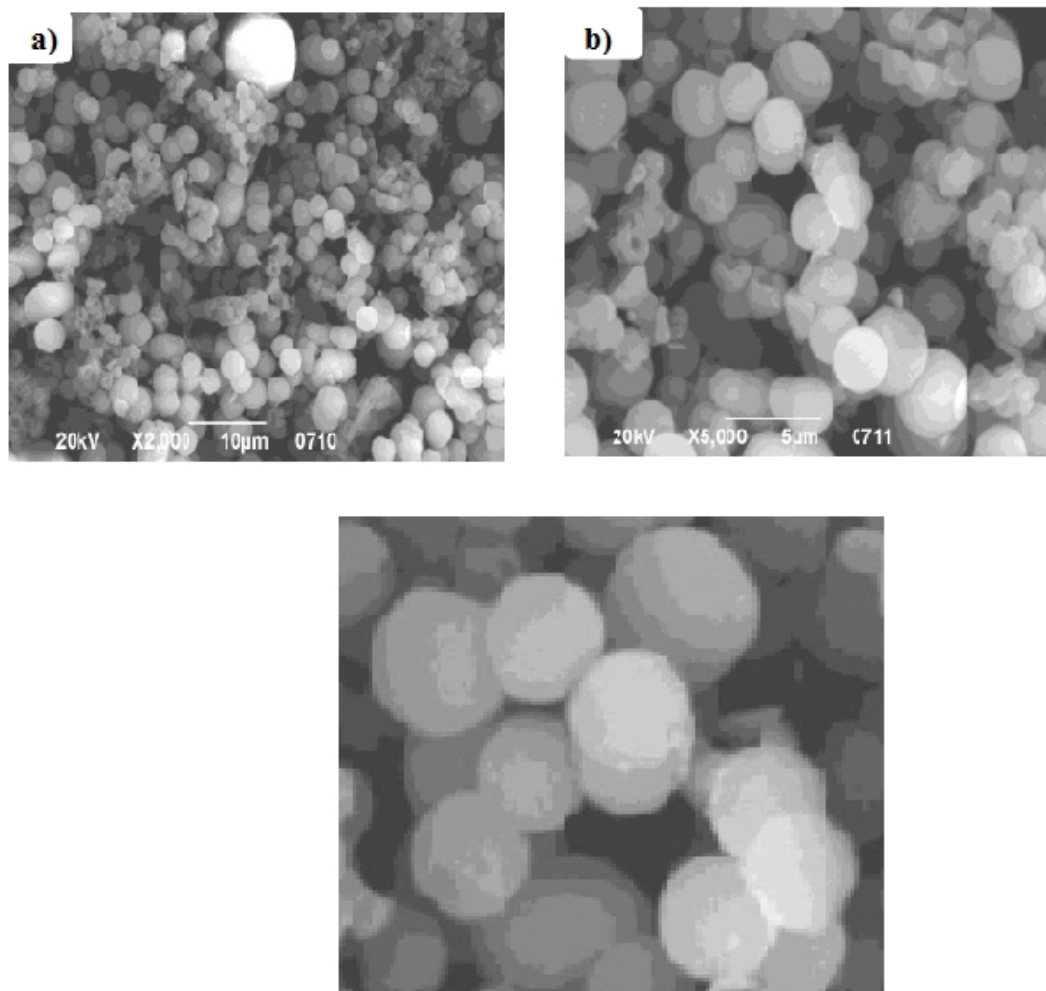


**Fig. 3. SEM micrograph of Fe-alanine complex; a) General view of the complex; b) showing the structure possessing rods with inter spaces and clean surfaces**

The well characterized synthesized complexes were applied for cyclohexane oxidation reactions using different methods and oxidants. Such as acetonitrile as solvent and cyclohexane itself as solvent using different ratios of oxidants with different time intervals at 80°C in glass flask. The similar reactions were also conducted in autoclave.

### **3.2 Oxidation of Cyclohexane using Metal Complexes with Different Oxidants in solvent System**

In a general procedure, the cyclohexane oxidation was conducted using acetonitrile as solvent and H<sub>2</sub>O<sub>2</sub>, Na<sub>2</sub>O<sub>2</sub>, KIO<sub>4</sub> and TBHP as oxidants. In a simple method the oxidants were taken in acetonitrile (30 mL) and the oxidants ratio was 2:10, 5:10 (1:5, 1:2) with respect to cyclohexane (10 mL).



**Fig. 4. SEM micrograph of Fe-phenylalanine complex; a) general view; b) showing the structure possessing spherical structure as beads with spongy surfaces with soft macroscopic separations**

The oxidation procedure, where the complexes and oxidants were taken in septa sealed two necked flask with reflux condenser. Then 30 mL acetonitrile was chosen as inert solvent. To the well connected system the cyclohexane was added drop wise to the contents of the flask containing complex and oxidant using syringe and needle. The reaction contents were kept at fixed temperature (i.e at 80°C) with stirring for 2 hrs and 4 hrs. At each time intervals, the samples were collected, dressed and analyzed by GC. The results are presented in Table 1.

**Table 1. Results of Cyclohexane Oxidation with Metal Complexes and Different Oxidants in Acetonitrile at 80°C**

Compound	Oxidant with product <i>i. e.</i> , cyclohexanone formation							
	H <sub>2</sub> O <sub>2</sub>		Na <sub>2</sub> O <sub>2</sub>		KIO <sub>4</sub>		TBHP	
	2 hr	4 hr	2 hr	4 hr	2 hr	4 hr	2 hr	4 hr
Ala	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Phe	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Fe-Ala	2-3%	5-8%	Traces	2-3%	2-3%	2-3%	8-10%	8-10%
Fe-Phe	10-12%	10-12%	Nil	5-7%	Nil	Nil	8-10%	8-10%
Fe-Ala-Sal	6-7%	6-7%	Nil	2-3%	Nil	Nil	7-8%	7-8%
Fe-Phe-Sal	8-10%	8-10%	Nil	2-3%	Nil	Nil	8-10%	8-10%

### 3.3 Oxidation of Cyclohexane using Metal Complexes with Different Oxidants under Solvent free System

In a modified solvent free method the oxidants H<sub>2</sub>O<sub>2</sub>, Na<sub>2</sub>O<sub>2</sub>, KIO<sub>4</sub> and TBHP were taken along with complexes in cyclohexane, which is now acting as a solvent come reactant. The contents were held at 80°C for 2 hrs and 4 hrs with continuous stirring. At each time intervals the samples were taken out and analyzed by GC for the product formation analysis. The results are summarized in Table 2.

**Table 2. Oxidation of Cyclohexane using Metal Complexes with Different Oxidants under solvent free system at 80°C**

Compound	Oxidant with product <i>i. e.</i> , cyclohexanone formation							
	H <sub>2</sub> O <sub>2</sub>		Na <sub>2</sub> O <sub>2</sub>		KIO <sub>4</sub>		TBHP	
	2 hr	4 hr	2 hr	4 hr	2 hr	4 hr	2 hr	4 hr
Fe-Ala	3-5%	3-5%	Traces	Traces	3-5%	3-5%	5-7%	5-7%
Fe-Phe	2-3%	2-3%	Traces	Traces	3-5%	3-5%	5-7%	5-7%
Fe-Ala-Sal	5-6%	5-6%	Nil	Nil	3-5%	3-5%	7-8%	7-8%
Fe-Phe-Sal	6-7%	6-7%	Nil	Nil	3-5%	3-5%	9-10%	9-10%

### 3.4 Cyclohexane Oxidation in Autoclave using Metal Complexes, Different Oxidants in Cyclohexane under Solvent Free System

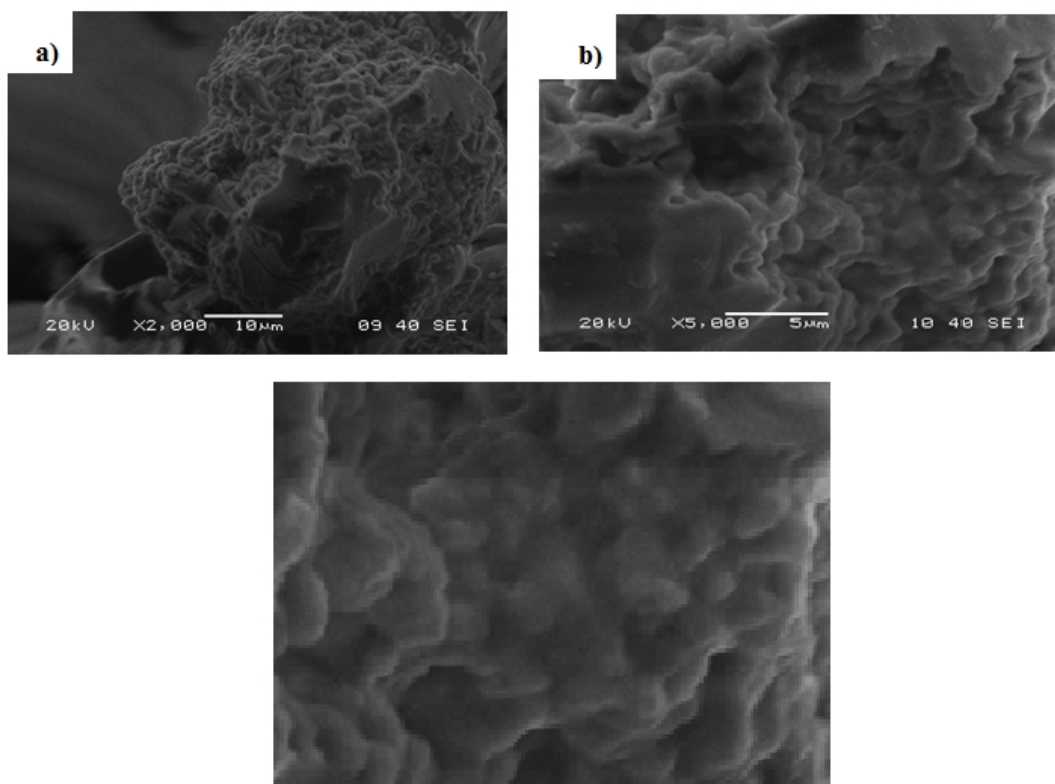
In a simple selective way, the complexes were taken for oxidation processes in cyclohexane, which is now acting as solvent and reactant using various oxidants *i.e.*, H<sub>2</sub>O<sub>2</sub>, Na<sub>2</sub>O<sub>2</sub>, KIO<sub>4</sub> and TBHP in autoclave.

In different experiments the contents cyclohexane (20 mL) complex (100 mg and 200 mg) and oxidants (1 mole and 2 moles) were taken and kept stirred at 80°C and 100°C for different period of time *i.e.*, 2 hrs and 4 hrs. The autogenous pressure developed during the course of stirring in the autoclave was 1 bar and 2 bar. The samples were taken out at regular time intervals and the product formation (cyclohexanone) was seen by GC and IR analysis. The results are presented in Table 3.

**Table 3. Oxidation of Cyclohexane using Metal Complexes with Different Oxidants in autoclave under solvent free system**

Compound	Oxidant with product <i>i.e.</i> , cyclohexanone formation							
	H <sub>2</sub> O <sub>2</sub>		Na <sub>2</sub> O <sub>2</sub>		KIO <sub>4</sub>		TBHP	
	2 hr	4 hr	2 hr	4 hr	2 hr	4 hr	2 hr	4 hr
Fe-Ala	3-5%	3-5%	Traces	Traces	2-4%	2-4%	3-5%	3-5%
Fe-Phe	10-12%	10-12%	Nil	Traces	Traces	Traces	10-12%	10-12%
Fe-Ala-Sal	7-9%	7-9%	Nil	2-3%	Traces	2-3%	8-10%	8-10%
Fe-Phe-Sal	8-10%	9-10%	2-3%	2-3%	Nil	2-4%	10-13%	10-13%

When similar reactions were carried out under same reaction conditions using ligands (Alanine and Phenylalanine) no product formation was observed, this shows that amino acids itself can't initiate the oxidation reaction.



**Fig. 5. SEM micrograph of Fe-alanine Schiff base complex; a) general view; b) showing the structure possessing crinkly and layered structure**

### 3.5 Oxidation of Cyclohexane using Oxidant (H<sub>2</sub>O<sub>2</sub> & TBHP) and Schiff Base Catalyst

The Schiff base catalysts *i.e.*, (Fe-Ala-Sal) and (Fe-Phe.ala-Sal) coated on Zeolite (encapsulation) and on Montmorillonite clay (intercalation) were subjected for cyclohexane

oxidation using H<sub>2</sub>O<sub>2</sub> and TBHP in autoclave at 100 °C with molar ratio of (1:2, oxidant : substrate). The autogenous pressure was 1.5 to 2 bar. The reaction was kept at this temperature well stirred for 2 hrs. After passing the time the contents were taken out and analyzed by GC. The results are shown in Table 4.

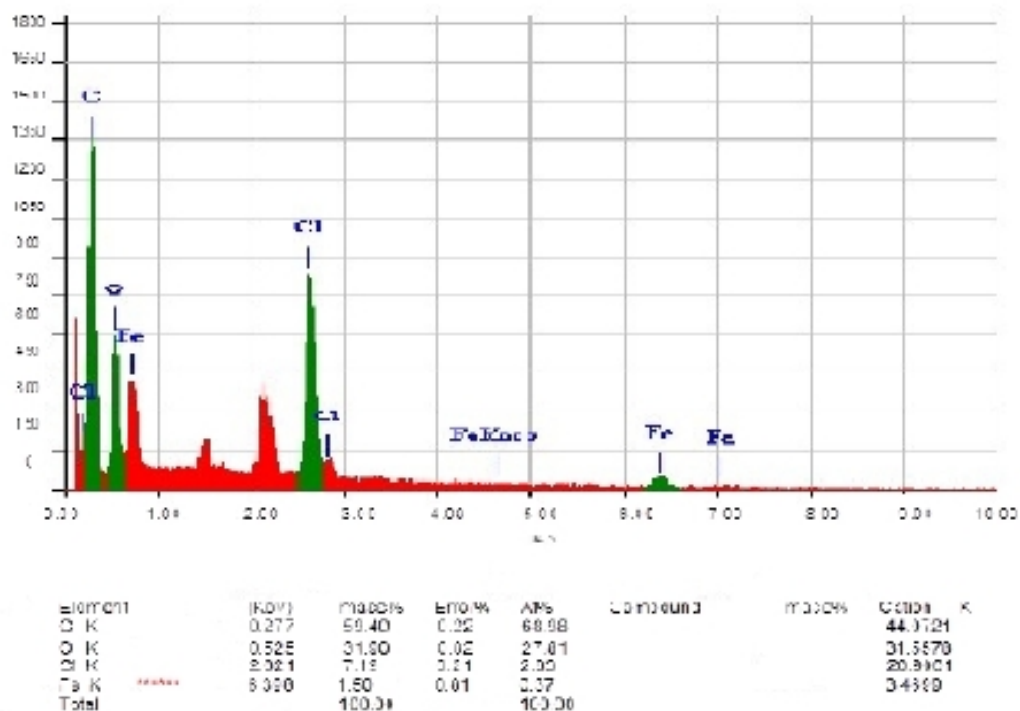
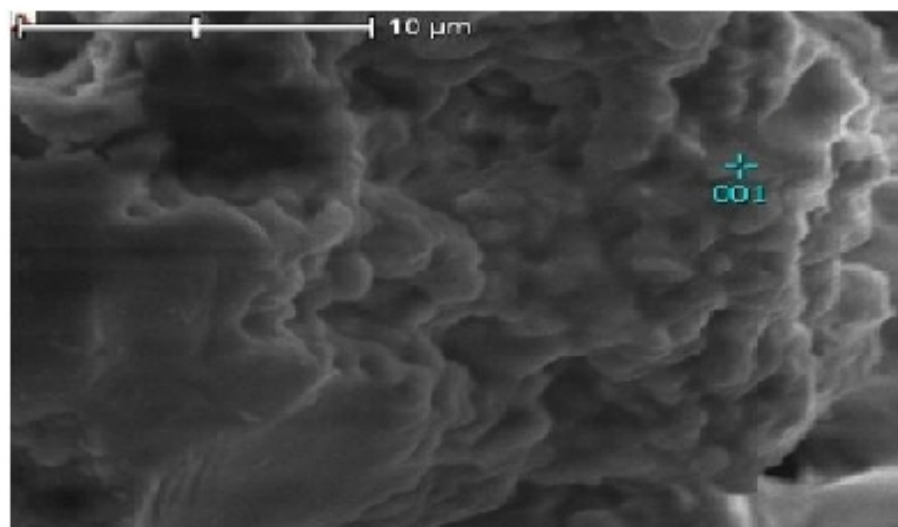


Fig. 5a. SEM and EDX images for the Fe-alanine Schiff base complex

**Table 4. Oxidation of cyclohexane using oxidant (H<sub>2</sub>O<sub>2</sub> & TBHP) with Schiff bases catalyst after two hours**

Compound	Matrix	Oxidant with product <i>i.e.</i> , cyclohexanone formation	
		H <sub>2</sub> O <sub>2</sub>	TBHP
Fe-Ala-Sal	Zeolite	10%	12%
Fe-Phe-Sal	Zeolite	8%	10%
Fe-Ala-Sal	Montmorile clay	3%	5%
Fe-Phe-Sal	Montmorile clay	5%	8%

From the above studies, it is clear that TBHP oxidant found good for this oxidation reactions than the other oxidants interms of cyclohexanone yield.

#### 4. CONCLUSION

In summary, we synthesized the complexes and their Schiff bases and immobilized them on different inorganic substrates to create a nano reactor system for larger biomimetic activity. The conducted experiments using different conditions to evaluate a better process to enhance the product formation suggest that further studies in this direction is required.

Thus it is concluded that this preliminary studies, helps for further modifications in catalytic system to enhance the activity.

#### ACKNOWLEDGEMENTS

We sincerely extend our heart full thanks to King Khalid University, College of Science, Department of Chemistry for providing facilities and the financial support under *The Long-term Comprehensive National Plan for Science, Technology and Innovation-KACST* program is greatly appreciated for the project No. 08-NAN152-7.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

#### REFERENCES

1. Absi-Halabi M, Stanislaus A, Qabazard H. Trends in catalysis research to meet future refining needs. *Hydrocarbon Processing*. 1997;76:45-55.
2. Waddams AL. *Chemicals from Petroleum*, 4ed. Houston: Gulf Pub. Co., Book Division; 1980.
3. Weirauch W. *Hydrocarbon Processing*. 1997;23.
4. Guibet JC. *Fuels and Engines Volume Rev ed*. Institute Francais Du Petrole Publications: Paris. 1999;1:55-62.
5. Walker RW, Morlay C. Oxidation kinetics and auto ignition of hydrocarbons, in *Comprehensive Chemical Kinetics M*. Pilling Ed. Elsevier. 1997;35.
6. Bonnet D, Ireland T, Fache E, Simonato JP. Innovative direct synthesis of adipic acid by air oxidation of cyclohexane. *Green Chem*. 2006;8:556-559.

7. Guo CC, Huang G, Zhang XB, Guo DC. Catalysis of chitosan-supported iron tetraphenylporphyrin for aerobic oxidation of cyclohexane in absence of reductants and solvents. *Appl Catal A Gen.* 2003;247:261-267.
8. Shilov AE, Shul'pin GB. *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*, Kluwer Academic Publishers, Dordrecht, Netherlands; 2000.
9. Tian P, Liu ZM, Wu ZB, Xu L, He YL. Characterization of metal-containing molecular sieves and their catalytic properties in the selective oxidation of cyclohexane. *Catal Today.* 2004;93-95:735-742.
10. Günther A, Jensen KF. Multiphase microfluidics: From flow characteristics to chemical and materials synthesis. *Lab Chip.* 2006;6:1487-1503.
11. Suresh AK, Sharma MM, Sridhar T. Engineering aspects of liquid phase air oxidations of hydrocarbons. *Ind Eng Chem Res.* 2000;39:3958-3997.
12. Barton DHR, Martell AE, Sawyer DT. *The Activation of Dioxide and Homogeneous Catalytic Oxidation*, Plenum, New York; 1993.
13. Kilincarslan R, Karabiyik H, Ulusoy M, Çetinkaya B, Büyükgüngör B. The synthesis, electrochemical properties and structural characterization of *bis* (*N*-(4-dimethylaminophenyl)-3, 5-di-*tert*-butylsalicylaldiminato) copper (II). *J Coord Chem.* 2006;59:1649-1656.
14. Garnovskii AD, Nivorozhkin AL, Minkin VI. Ligand environment and the structure of Schiff base adducts and tetra coordinated metal-chelates. *Co-ord Chem Rev.* 1993;126:1-69.
15. Yousaf M, Pervaiz M, Sagir M, Zaman AU, Mushtaq M, Naz MY. Synthesis of tetradentate schiff base derivatives of transition bimetallic complexes as antimicrobial agents. *J Chin Chem Soc.* 2013;60(9):1150–1155.
16. Anupama B, Kumari CG. Cobalt (II) Complexes of ONO donor Schiff bases and N, N donor Ligands: Synthesis, Characterization, Antimicrobial and DNA binding Study. *Int J Res Chem Environ.* 2013;3(2):172-180.
17. Khalid MK, Muhammad T, Farzana, N, Salman S, Sajjad A, Fazal R, Shahnaz P, Choudhary MI. Acylhydrazide Schiff Bases: DPPH Radical and Superoxide Anion Scavengers. *Med Chem.* 2012;8:705-710.
18. Khalid MK, Karim A, Saied S, Ambreen N, Saleem M, Aryn A, Perveen S, Ahmad A, Choudhary MI. Synthesis, antioxidant and carbonic anhydrase inhibitory potential of Schiff bases of thiazoles. *J Pharm Res.* 2012;5:661-663.
19. Yousaf M, Ali KG, Chatha SAS, Ahmad HB, Khan KM. Polymerization of methylmethacrylate by tridentate schiff base derivative of indenyl and cyclooctatetraenyl lantheniod complexes along with Al(*i*-Bu)<sub>3</sub> catalytic system. *J Chem Soc Pak.* 2011;33:255-259.
20. Chohan ZH, Khalid MK, Claudiu TS. Synthesis of antibacterial and antifungal cobalt(II), copper(II), nickel(II) and zinc(II) complexes with bis-(1,1'-disubstituted ferrocenyl) thiocarbohydrazone and bis-(1,1'-disubstituted ferrocenyl) carbohydrazone. *Appl Organometal Chem.* 2004;18:305-310.
21. Yamamoto S, Akitsu, T. Fluorescence detection by photochromic dye of photoinduced electron transfer reactions between lysine and methionine derivative Schiff base copper (II) complexes and titanium oxide. *Asian Chem Lett.* 2011;15:203-209.
22. Nakayama T, Minemoto M, Nishizuru H, Akitsu T. Spectroelectrochemistry of photoinduced electron transfer reactions between leucine and serine derivative Schiff base copper(II) complexes and titanium Oxide. *Asian Chem Lett.* 2011;15:215-219.
23. Nishizuru H, Kimura N, Akitsu T. Photo-induced reduction of hybrid systems of phenylalanine and other derivatives of Schiff base Cu (II) complexes and titanium (IV) oxide. *Asian Chem Lett.* 2012;16:33-42.

24. Kurata M, Yoshida N, Fukunaga S, Akitsu T. Proposed mechanism of photo-induced reactions of chiral threonine Schiff base Cu (II) complexes with imidazole by TiO<sub>2</sub>. *Contem Engin Sci.* 2013;6:255-260.
25. Yoshida N, Akitsu T. Reaction of Hybrid Systems Composed of Cu (II) Complexes Having Chiral Schiff Base Amino-Acid Ester Derivatives and TiO<sub>2</sub>. Integrating Approach to Photofunctional Hybrid Materials for Energy and the Environment. Nova Science Publishers, Inc (NY, USA). 2013;5:111-124.
26. Yoshida N, Akitsu T. Comparison of Sm (III) and Cr (VI) Ions for Visible Light Induced Reduction in Methanol by Hybrid Systems of Chiral Schiff Base Cu (II) Complexes and TiO<sub>2</sub>. *Samarium: Chemical Properties, Occurrence and Potential Applications*, Nova Science Publishers, Inc. (NY, USA), in press; 2010.
27. Nagajothi A, Kiruthika A, Chitra S, Parameswari K. Fe (III) Complexes with Schiff base Ligands: Synthesis, Characterization, Antimicrobial Studies. *Res J Chem Sci.* 2013;3(2):35-43.
28. Merajuddin SA, Ahmed MT, Alam MM, Halima AAIH. Cyclohexane Oxidation: Synthesis and Characterization of Amino Acid Metal Complexes and Their Catalytic Activity Evaluation. *Int J B APP Chem Sci.* 2013;3(4):29-40.
29. Merajuddin SA, Ahmed MT, Ahmed FM, Alam MM, Saeed SA. Cyclohexane Oxidation–Synthesis of 1, 10 Phenanthroline Cu (II) Complexes by Classical, Microwave and Hydrothermal Methods and Their Catalytic Activity Evaluation. *Int J B APP Chem Sci.* 2013;3(4):69-78.

---

© 2014 Ahmed et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

*Peer-review history:*

*The peer review history for this paper can be accessed here:*  
<http://www.sciencedomain.org/review-history.php?iid=475&id=16&aid=4297>