International Journal of Basic and Applied Chemical Sciences ISSN: 2277-2073 (Online)
An Online International Journal Available at http://www.cibtech.org/jcs.htm
2013 Vol. 3 (4) October-December, pp.69-78/Merajuddin et al.
Research Article

CYCLOHEXANE OXIDATION –SYNTHESIS OF 1, 10 PHENANTHROLINE Cu (II) COMPLEXES BY CLASSICAL, MICROWAVE AND HYDROTHERMAL METHODS AND THEIR CATALYTIC ACTIVITY EVALUATION

***Merajuddin S. Ahmed, Ahmed Mubarak T., Ahmed Fouda M., Mujahid Alam M. and Saeed Sabr A.**
Department of Chemistry, King Khalid University, P. O. Box 9004, Abha 61413, Saudi Arabia
**Author for Correspondence*

ABSTRACT
1, 10-Phenanthroline was complexed with $CuCl_2.XH_2O$ in 1:1, 1:2 and 1:3 ratios. The complex of 1:2 ratio was further subjected to microwave radiations and hydrothermal treatment to get the nano-particles or dispersed complexes of micro size. The complexes and their nano-parcticals and coated catalyst were characterized by UV, IR, NMR, XRD and SEM studies. The complexes and their nano-particles were encapsulated on zeolite, clay and silica to enhance their catalytic activity. The classical method synthesized complexes and microwave and hydrothermally synthesized complexes were subjected for cyclohexane oxidation to evaluate their catalytic activity. The complexes and nano particles were subjected for oxidation in solvent system, without solvent system and in autoclaves using aerial oxygen and H_2O_2, Na_2O_2, KIO_4 and TBHP as oxidants.

Key Words: *1, 10-Phenanthroline, Microwave Radiations, Hydrothermal Treatment, Nano-particles and Cyclohexane Oxidation*

INTRODUCTION
Oxidation of cyclohexane is still a challenging task as it is one of the important bulk process for the production of polyamide fibers and plastics, such as nylon 6 and nylon 6, 6' (Tian, 2004). Cyclohexane oxidation reactions catalyzed by metallic complexes have been reported and the typical cyclohexane oxidation procedures are given in literature (Suresh *et al.,* 2000; Tao *et al.,* 2001; Detoni *et al.,* 2009; Canhota *et al.,* 2007; Silva *et al.,* 2007).

From the perspective of Green-chemistry, environmentally-friendly manufacturing of organic compounds has been re-examined in recent years and many new methodologies have been devised (Zhou *et al.,* 2005; Fan *et al.,* 2008; Biswas *et al.,* 2009; Thakurta *et al.,* 2009). It is with this view our efforts are continued to coup up with the challenging task of cyclohexane oxidation with an environmentally friendly easy method using a solid catalyst.

For this we applied the prepared complexes for oxidation of cyclohexane as such with atmospheric oxygen and also the complexes are been applied with different oxidants. In a modified method the complexes were re-synthesized for their nano-structures using hydrothermal and micro wave methods. Further to this the synthesized complexes were inserted into inorganic solids, which could offer an attractive route to their nano-hybrids in which complementary properties of the two components are expressed in a single material.

Micro porous solids or the layered solids in which the guest species can access by their encapsulation or intercalation process provide best system for the oxidation in presence of oxidants. To apply this methodology we encapsulated some complexes and their nano-structured complexes on molecular zeolites and some complexes were intercalated on clay materials.

The successfully coated catalysts, their nano-complexes by the hydrothermal, micro wave methods and coated catalysts were fully characterized before their application to oxidation of cyclohexane using different oxidants.

MATERIALS AND METHODS

The copper (II) chloride hydrate, phenanthroline, 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 and aluminum silicate were supplied by Sigma Aldrich. All chemicals and reagents used in the present study were of analytical grade.

FT-IR spectra were obtained on a Shimadzu Jasco-IR 450 spectrometer with samples prepared as KBr pellets or as neat using NaCl cells. UV Absorption spectra were taken on a Shimadzu UV 2100 spectrophotometer. Gas chromatographic analysis was performed on Shimadzu 2014 GC system equipped with silica column chromosorb 60/80 using FID detector. SEM results were recorded on JEOL-JSM 6360 LA and ISM 6700F microscope. ^{1}H NMR and ^{13}C NMR were recorded on Brucker 500 MHz spectrophotometer.

RESULTS AND DISCUSSION

Synthesis of Cupper-Phenanthroline Metal Complex

General procedure for the preparation of the Cupper-phenanthroline metal complex ($CuCl_2.2H_2O$ with phenanthroline in 1:1, 1:2 and 1:3 ratio)

In a general procedure the $CuCl_2.2H_2O$ (2gm) was dissolved in 50 ml of ethanol and kept stirred on heat. Then the hot solution of 1, 10-phenanthroline in (1:1, 1:2 and 1:3) ratios as (2.11, 4.23 and 6.34 gm) was added drop wise to the hot solution of the metal salt. Changes in the colour of the reaction mixture were observed. Progress of the reaction was monitored by TLC. On completion the solvent was cooled and the crystals of the complex were separated and washed thoroughly, and then recrystallized again using ethanol. The elemental analysis found was in agreement with the calculated one and reported as follows.

Elemental analysis: 1:1 ratio, C (45.80%), H (2.56%), Cu (20.20%), N (8.90%), Cl (22.53%).

1:2 ratio, C (62.75%), H (3.51%), Cu (13.83%), N (12.20%), Cl (7.72%).

1:3 ratio, C (71.57%), H (4.00%), Cu (10.52%), N (13.91%).

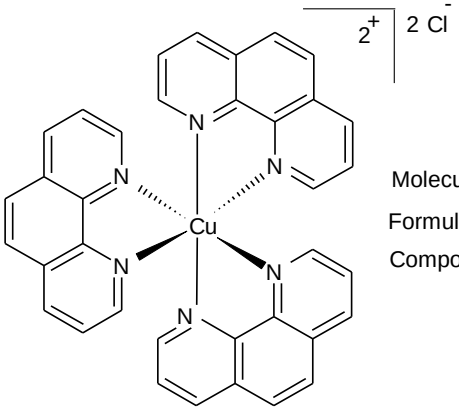
IR (KBr disc, υ_{max} cm^{-1}): 1:1ratio: 3055, 1606, 1585, 1494, 1423, 1145, 1107, 1047.

1:2 ratio: 2983, 1584, 1428, 1223, 1092, 644, 428.

1:3 ratio: 3368, 1625, 1428, 1104, 896, 723, 428.

On the basis of the data obtained the structure of the complexes can be proposed as follows in Figure 1.

The synthesized cupper-phenanthroline metal complex SEM image was shown in Figure 2 and its EDX data magnified at 5000 also shown in Figure 3.

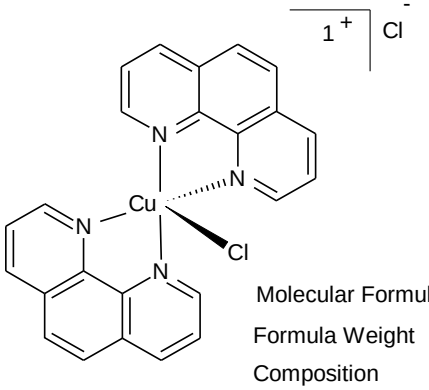


1,10 - Phenanthroline

Molecular Formula = $C_{36}H_{24}CuN_6$
Formula Weight = 604.16196
Composition = C(71.57%) H(4.00%) Cu(10.52%) N(13.91%)

$[Cu(phen)_3]Cl_2$

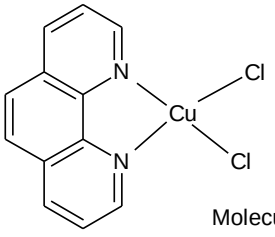
3 : 1



Molecular Formula = $C_{24}H_{16}ClCuN_4$
Formula Weight = 459.40964
Composition = C(62.75%) H(3.51%) Cl(7.72%) Cu(13.83%) N(12.20%)

$[Cu(phen)_2Cl]Cl$

1 : 2



Molecular Formula = $C_{12}H_8Cl_2CuN_2$
Formula Weight = 314.65732
Composition = C(45.80%) H(2.56%) Cl(22.53%) Cu(20.20%) N(8.90%)

$[Cu(phen)Cl_2]$

1 : 1

Figure 1: Cupper-phenanthroline metal complexes in 1:1, 1:2 and 1:3 ratio

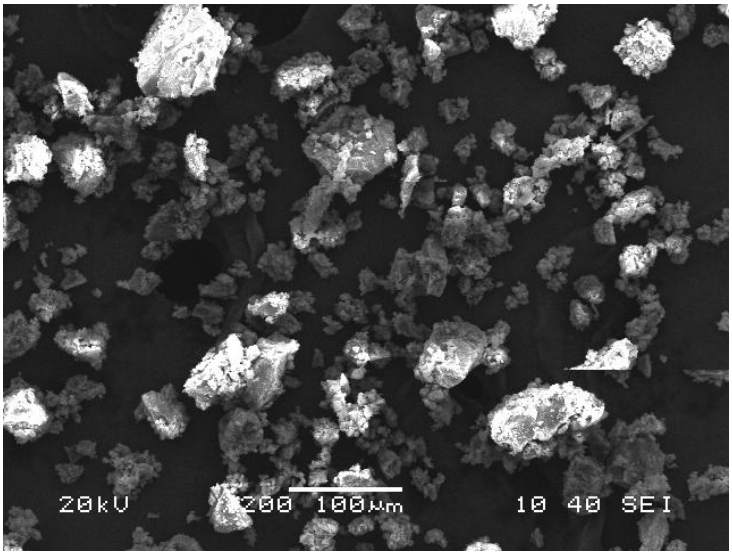


Figure 2: SEM Micrographs for [Cu(phenan)$_2$Cl$_2$] complex magnified at X 200

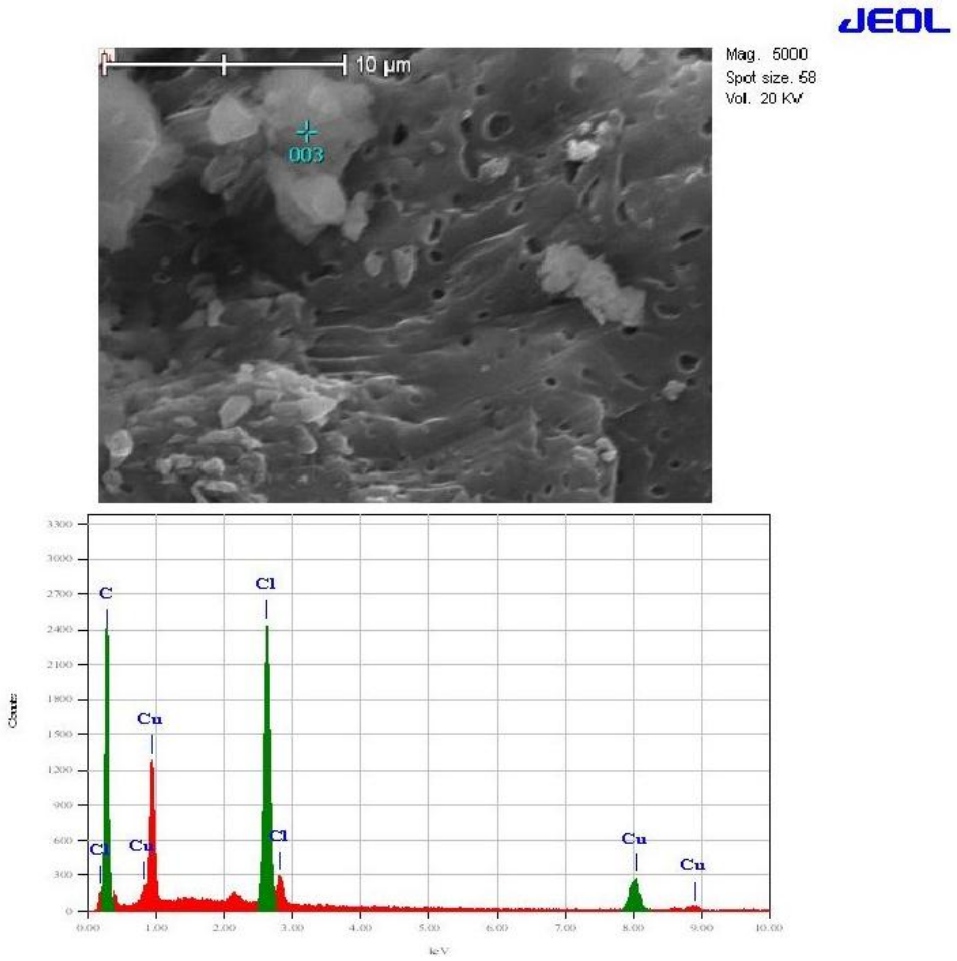
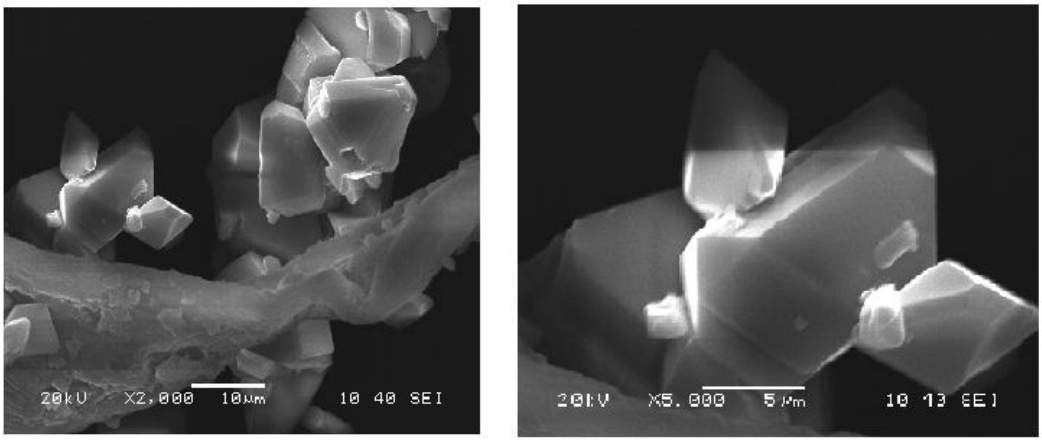


Figure 3: SEM Micrograph of [Cu(Phenan)$_2$Cl$_2$] complex magnified at 5000 with its EDX data

Research Article

Conversion of Cu-Phenanthroline (1:2) Complex to their Nano-particals using Microwave

200 mg phenanthroline copper metal complex was added in a 12 mL Teflon vessel of double-walled digestion vessel (Milestone-Micro SYNTH) system and then dissolved in 3 mL deionized water, After sealing the vessel, it was placed in a microwave oven chamber to react for 5 and 10 min at 120, 140, 160°C, respectively using a microwave digestion system. The sample temperature was monitored by a built-in thermocouple immersed in a solution.



A). **B).**

Figure 4: SEM Micrographs of $[Cu(phen)_2Cl_2]$ nano-particle complex synthesized by microwave method and magnified at A). X 2000 and B). X 5000

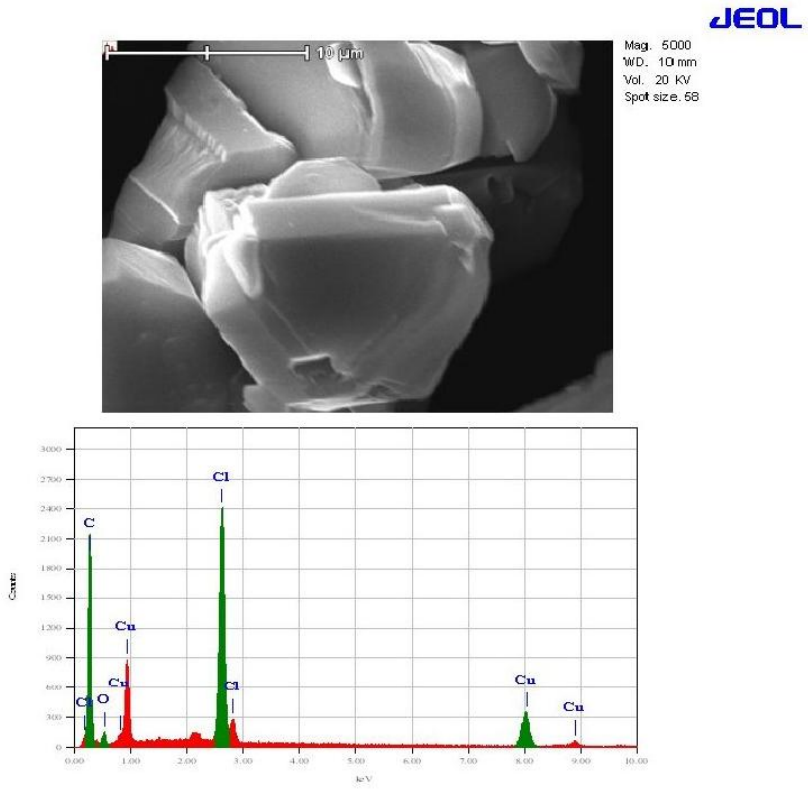


Figure 5: SEM micrograph of $[Cu(phen)_2)Cl_2]$ nano-particle complex, magnified at 5000 with its EDX data

The ramping rate in this study was set at 10 °C/min. The applied power was controlled via a temperature feedback module. After irradiating 5 or 10 min (Power 600 W), the phenanthroline copper complex nanoparticles was obtained and the reactor device was then taken out, cooled at room temperature and then as-obtained product was filtered off, washed with water for several times and dried naturally in air. The structure of the final product was characterized by X-ray diffraction method, using Shmidazu XRD-6000 and target is Cu using α particle. The particle size and shape was visualized by scanning electron microscopy (SEM) and magnetic properties were identified by a vibrating sample magnetometer (VSM). The size and the shape of phenanthroline copper metal complex nanoparticles have been shown in Figure 4 and its EDX data at magnified 5000 was also shown in Figure 5. After getting encouraging results, we applied the scope and generality of this method for various metal complexes such as Cu-quinoxalin, pyrazine and bipyridine. These metal complex nanoparticles were synthesized by the similar microwave-assisted solvothermal method.
The XRD data of this complex has shown in Figure 6.

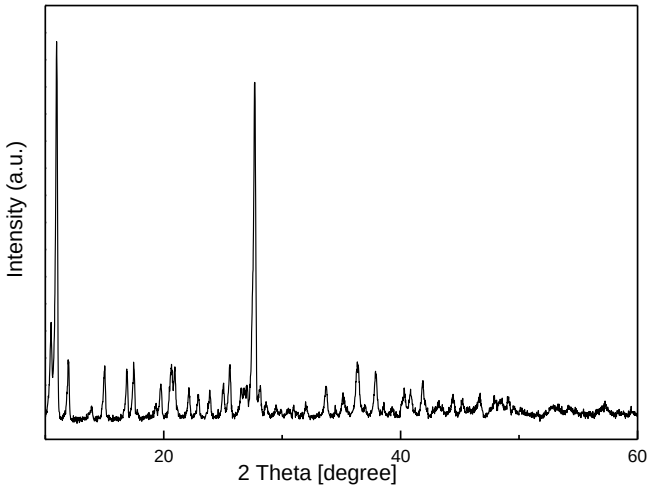
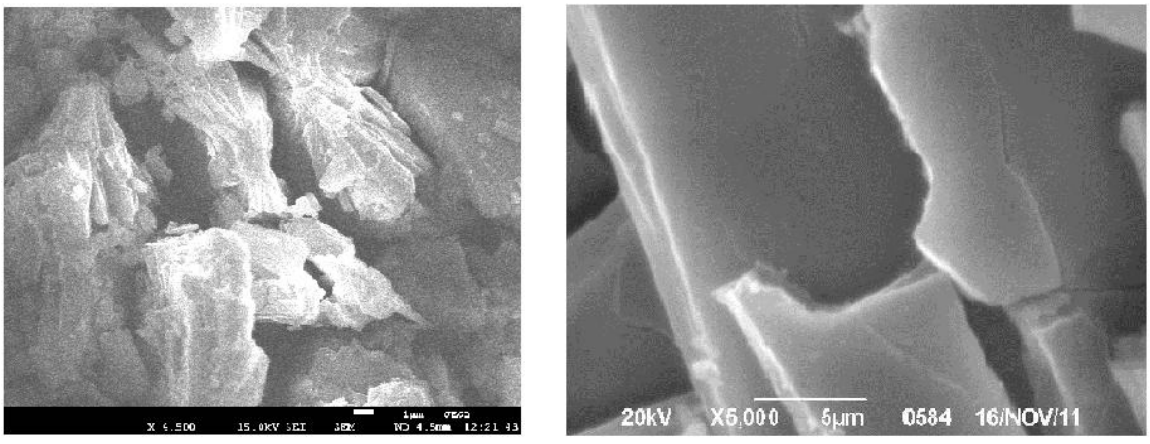


Figure 6: XRD diffractometer for the [Cu(phen)$_2$)Cl$_2$] nano-particle complex



A). B).

Figure 7: SEM Micrographs of [Cu(phen)$_2$Cl$_2$] complex synthesized by hydrothermal method and magnified at A). X 4500 and B). X 5000

Research Article

Conversion of Cu-Phenanthroline (1:2) Complex for Dispersed Micro-particles using Hydrothermal Method

Nano-particles of the complexes were synthesized by using an alternate method hydrothermally. For this we used PAAR INSTRUMENT, Model 4848, USA, where the metal salt $CuCl_2$ and phenanthroline in the ratio of (1:2) was used in ethanol as a solvent. The internal temperature for the reaction was 94^{o}C and the external temperature was 112 ^{o}C and at 120 RPM. The reaction mixture was kept under this condition for 2 hours. The reaction mixture was brought to room temperature and the resultant complex was filtered off, washed with cold ethanol to remove the unreacted lig and, dried under vacuum. The SEM image of the complex synthesized by this method has shown in Figure 7.

Coating of Catalyst

The synthesized complexes were coated on Montmorile Clay, Molecular Seives powder with Zeolite Y "Na" and Aluminium Silicate. Prior to coating the materials were dried under vaccum at 200 ^{0}C.

In a procedure, separately the materials to be coated i.e., Montmorile Clay (2 gm), Molecular Sieves powder with Zeolite Y "Na" (2 gm) and Aluminium Silicate (2 gm) were taken in the specially designed catalyst coating reactor heated at 200 ^{0}C under nitrogen atmosphere for 1 hr. Then it was allowed to cool and THF was added and kept under stirring at 80 ^{0}C and filtered to wash. After washing fresh THF was added and the complex to be coated was taken in dissolved THF and added under nitrogen with cannula. Heating and stirring was continued for another 3 hrs. Later, the reactor was brought suddenly to 0 ^{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 XRD data for the coated complexes converted to catalyst has shown in **Figure 8.**

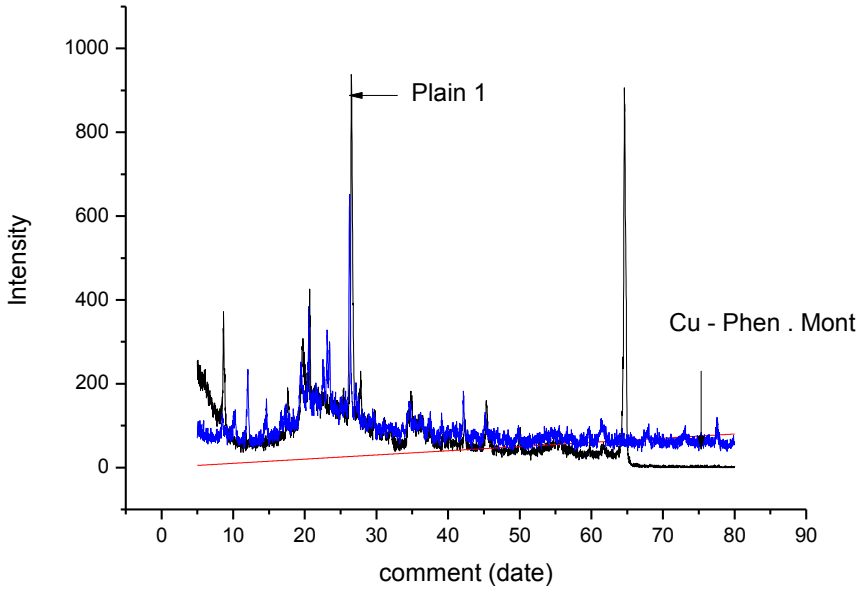


Figure 8: XRD diffractometer for the Cu-1, 10-phenanthroline complex coated on Montmorillonite K 10

The chemistry of Cu-phenanthroline complexes is well understood due to the interest in photochemistry, photocatalytic chemistry and in oxidation reactions. Copper-phenanthroline complexes give different geometries like tetrahedral roughly square plane, square pyramidal and distorted trigonal bipyramidal. The idealized geometry assumes to be square pyramidal. This is evident by the SEM-micrographic analysis of the complexes prepared by different methods.

Research Article

Application of Complexes for Oxidation

Method 1: Oxidation of Cyclohexane using Cupper-phenanthroline Metal Complex with Different Oxidants in Solvent System:

In a general procedure, the oxidation of cyclohexane was performed by using acetonitrile as a solvent and H_2O_2, Na_2O_2, KIO_4 and TBHP as oxidants. In a typical method the oxidants were subjected in acetonitrile (30 mL) in the molar ratio of 2:10, 5:10 (1:5, 1:2) with respect to cyclohexane (10 mL).

The oxidants and cupper-phenanthroline metal complex were taken in a two necked septa sealed flask fixed with reflux condenser in (30 mL) acetonitrile as a solvent system. Cyclohexane was added drop wise to the contents in flask using syringe and needle. Temperature was maintained at 80^{o}C and the reactants were kept under stirring for a period of 2 hrs. At each time intervals, the samples were collected, dressed and analyzed by GC. The results are summarized in Table 1.

Table 1: Oxidation of Cyclohexane using Metal Complexes with Different Oxidants in Acetonitrile Solvent System at 80 °C

Metal Complex	Oxidant Ratio	Oxidant with product formation			
		H_2O_2	Na_2O_2	KIO_4	TBHP
Phen: Cu	**1:10**	nil	nil	nil	-
Phen: Cu	**2:10**	trace	nil	trace	trace
Phen: Cu	**5:10**	trace	nil	5-8%	5-10%

Note: *Traces means less than 1%, Nil means no product formation was observed*

Method 2: Oxidation of Cyclohexane using Cupper-phenanthroline Metal Complex with Different Oxidants under Solvent Free System:

In a modified method the oxidants H_2O_2, Na_2O_2, KIO_4 and TBHP and the complex were taken together with cyclohexane itself and kept stirred at 80°C for 2 hrs. The samples were collected time to time at regular intervals and analyzed by GC. The results are presented in Table 2.

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

Metal Complex	Oxidant Ratio	Oxidant with product formation			
		H_2O_2	Na_2O_2	KIO_4	TBHP
Phen: Cu	1:10	trace	nil	trace	nil
Phen: Cu	2:10	3%	nil	5%	7%
Phen: Cu	5:10	3%	trace	5%	5-10%

Method 3: Oxidation of Cyclohexane using Different Oxidants with cupper-phenanthroline metal complex in Autoclaves without Solvent System:

In a more precise way, the complex was subjected for oxidation processes using different oxidants *i.e.*, H_2O_2, Na_2O_2, KIO_4 and TBHP with cyclohexane 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 ^{o}C and 100 ^{o}C for 2 hrs. The pressure in the autoclave was 1 bar and 2 bar, kept under well stirred. The autogenous pressure developed in the autoclave during the reaction was 1 bar and 2 bar. The samples were collected at regular time intervals and analyzed by GC and IR. The results are summarized in Table 3.

Table 3: Oxidation of cyclohexane using different oxidants with metal complexes in autoclaves under without solvent system

Metal Complex	Oxidant Ratio	Oxidant with product formation		
		H_2O_2	KIO_4	TBHP
Phen: Cu	2:10	5-8%	10-12%	15%
Phen: Cu	5:10	trace	trace	2-3%

Method 4: Oxidation of cyclohexane using different oxidants with metal complex's-Nano particles synthesized by microwave and hydrothermal method in Acetonitrile:

Cyclohexane oxidation studies were performed using oxidants and nano-particles synthesized by hydrothermal method microwave method to get some promising results of these complexes. For this the Nanoparticles of these complexes were taken in solvent free system in autoclave where the indigenously developed pressure was 1 to 2 bar and the oxidant ratio to the complex particles was changed and the reactions were performed for different time intervals. The study of this type is for the first time is reported by us and the results are given as below.

Table 4: Oxidation of cyclohexane using different oxidants with metal complex's-Nano particles synthesized by microwave and hydrothermal method with Acetonitrile

Metal Complex	Oxidant Ratio	Microwave			Hydrothermal		
		H_2O_2	KIO_4	TBHP	H_2O_2	KIO_4	TBHP
Phen: Cu	5:10	5%	nil	10-	10%	5%	12%

Table 5: Oxidation of cyclohexane using different oxidants with metal complexes coated as catalysts in autoclaves under without solvent system

Metal Complex	Oxidant Ratio	Oxidant with product formation		
		H2O2	KIO4	TBHP
Phen-Cu: Zeolite	5:10	5-7%	7-10%	12-15%
Phen-Cu: Montomorile		3-5%	7-9%	10-12%
Phen-Cu: Aluminium silicate		trace	trace	2-3%

Method 5: Oxidation of cyclohexane using different oxidants with metal complexes coated as catalysts in autoclaves under without solvent system:

We further carried out cyclohexane oxidation with coated catalysts in autoclave without using solvent system and the results presented in Table 5.

Conclusion

In summary, we synthesized the $Cu(phen)_2]Cl_2$ complex with both classical and modified methods have shown a significant change on the morphology of the complex. The SEM and XRD data have revealed that the modified method applied by microwave has significantly enhanced the properties and homogeneity of complex, where nanoparticle size and shape with flowery crystallite morphology have been evidenced. The crystal sizes of the complex are estimated at the ranges of ~5 – 100 μm. This complex has been effectively used as catalysts for the oxidation of cyclohexane in the presence of different oxidants under solvent and solvent free conditions. The oxidized products of cyclohexane are cyclohexanol and cyclohexanone. The coated catalyst on various matrices has shown significant improvement in the yield. Our effort in this work is still in progress and we expect some contributory achievements as we continue in this direction.

ACKNOWLEDGEMENT
We sincerely extend our heart full thanks to King Khalid University, College of Science and 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.

REFRENCES

Biswas AN, Das P, Kandar SK, Agarwala A, Bandyopadhyay D and Bandyopadhyay P (2009). Chiral iron(III)-salen-catalyzed oxidation of hydrocarbons. *Catalysis Commununications* **10** 708-711.

Canhota FP, Salomão GC, Carvalho NMF and Antunes OAC (2007). Cyclohexane oxidation catalyzed by 2,2′-bipyridil Cu(II) complexes. *Catalysis Commununications* **9** 182–185.

Detoni C, Carvalho NMF, Aranda DAG, Louis B and Antunes OAC (2009). Cyclohexane and toluene oxidation catalyzed by 1,10-phenantroline Cu(II) complexes. *Applied Catalysis A: General* **365** 281-286.

Fan B, Li H, Fan W, Jin C and Li R (2008). Oxidation of cyclohexane over iron and copper salen complexes simultaneously encapsulated in zeolite Y. *Applied Catalysis A: General* **340** 67-75.

Malachowski MR, Dorsey BT, Parker MJ, Adams ME and Kelly RS (1998). Probing the catalytic properties of copper(II) complexes of appended cyclams: correlations between catalysis and stability constants or electrochemical properties. *Polyhedron* **17** 1289–1294.

Silva AC, Fernández TL, Carvalho NMF, Herbst MH, Bordinhão J, Horn JrA, Wardell JL, Oestreicher EG and Antunes OAC (2007). Oxidation of cyclohexane catalyzed by bis-(2-pyridylmethyl) amine Cu(II) complexes. *Applied Catalysis A: General* **317** 154–160.

Srabtree RH (1995). *Chemical Revives* **95** 987-1007.

Suresh AK, Sharma MM, Sridhar T (2000). Engineering aspects of industrial liquid-phase air oxidation of hydrocarbons. *Industrial Engineering Chemistry Research* **39** 3958.

Tao J, Tang D, Li Q, Yu Z and Min E (2001). *Journal of Natural Gas Chemistry* **10** 295.

Thakurta S, Roy P, Rosair G, Gómez-García CJ, Garribba E and Mitra S (2009). Ferromagnetic exchange coupling in a new bis(μ-chloro)-bridged copper(II) Schiff base complex: Synthesis, structure, magnetic properties and catalytic oxidation of cycloalkanes. *Polyhedron* **28** 695-702.

Tian P, Liu ZM, Wu ZB, Xu L and He YL (2004). Characterization of metal-containing molecular sieves and their catalytic properties in the selective oxidation of cyclohexane. *Catalysis Today* **93** 735-742.

Zhou L, Xu J, Miao H, Wang F and Li X (2005). Catalytic oxidation of cyclohexane to cyclohexanol and cyclohexanone over Co3O4 nanocrystals with molecular oxygen. *Applied Catalysis A: General* **292** 223-228.