

Oxidation of cyclohexane with molecular oxygen using macrocyclic homonuclear Cu complex catalyst

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Abstract

Binuclear monometallic macrocyclic complexes of copper with two different ligand environments (ligands L1 and L2) were synthesized and a general scheme for bonding the complexes ionically on acidified montmorillonite clay was evolved. The two catalysts CuCuL1-montmorillonite (denoted as catalyst1) and CuCuL2-montmorillonite (denoted as catalyst 2) were stable up to 600 °C and 438 °C respectively. These were then used in the oxidation of cyclohexane using molecular oxygen in the absence of initiators, promoters and coreactants. Experiments show that catalyst 1 gives much higher rate of reaction (most of the reaction is over in 50 minutes) compared to catalyst 2 and because of this the focus of our study has been on catalyst 2. Different product distributions were obtained with these two catalysts (170 °C, 30 minutes residence time) with the major product in both cases being cyclohexanone (8.8% overall conversion, 49% selectivity for cat1 and; 6.9% overall conversion, 74.7% selectivity for catalyst 2) and the byproducts formed were cyclohexene (3% selectivity for catalyst 1 and 3.2% selectivity for catalyst 2) and cyclohexanol (27.6 % selectivity for catalyst 1 and no cyclohexanol for catalyst 2). The experimental data were analyzed against different kinetic scheme proposed and the best scheme and the rate constants were determined using Genetic Algorithm. From experiments carried out at different temperatures, we found that for every rate constant, an Arrhenius type relation could be established.

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1. Introduction

Cyclohexanone and cyclohexanol are important intermediates in the manufacture of caprolactam (serving as a monomer for nylon 6 polymer formation) and adipic acid (serving as a monomer for nylon 66 polymer formation) [1]. The oxidation of cyclohexane is carried out industrially at a temperature of 423 – 453 K and pressure of 1.0 – 1.6 MPa in presence of Co salts (naphthenate, stearate, oleate) as catalyst. The cyclohexane conversion is kept low (about 3 - 4% per pass) as the cyclohexanol and cyclohexanone formed are more susceptible for further oxidation to CO₂. At the industrial condition, the products such as adipic, succinic and oxalic acids and their cyclohexyl esters are always formed which need to be separated first [1, 2]. Experiments have shown that water formed during the reaction has a retarding effect due to phase separation [3]. The mechanism suggested in the literature assumes that cyclohexyl hydroperoxide (CHHP) is the intermediate formed in the presence of transition metal salts and sometimes a small quantity of this has been detected in the product stream [3]. The main products of its decomposition are cyclohexanol and cyclohexanone and are always present in the product stream approximately in equimolar ratio. The primary effect of dissolved

metal salts on the oxidation is to increase the rate of reaction by catalyzing the homolytic decomposition of hydroperoxides [4].

These chemicals can also be produced by hydrogenation of phenol but the process economics still favors direct oxidation of cyclohexane [5]. To overcome the problem of separating the catalyst from the reaction mass, many heterogeneous catalysts have been developed for this reaction. Generally these catalysts are either oxides or metal cations incorporated in inorganic matrices such as silica, alumina, zirconia, active carbon, zeolites [7] or aluminophosphates [8]. The activity of these systems also depends on the correct choice of the solvent, which determines the polarity of the medium and the size of the active metal that needs to be adsorbed on the surface of the support. For example, during the oxidation of cyclohexane in presence of CoAPO-5 catalyst, the use of carboxylic acids (except formic acid) as the solvent is necessary and the use of propionic acid gives the highest reaction rate [9]. The other problems encountered in heterogeneous catalysis are leaching of active metal ions, extreme reaction conditions (2MPa pressure and 177° C temperature) and low activity [10]. An induction time is generally observed in the case of air oxidation of cyclohexane and is reduced by adding promoters or co-reactants such as acetaldehyde, cyclohexanone, cyclohexanol and azobiz(isobutyronitrile) (AIBN) [11]. Coreactants also help in increasing the rate of cyclohexane oxidation (by decreasing the overall activation energy) and selectivity of the target products (a mixture of cyclohexanone and cyclohexanol).

The mechanism of cyclohexane oxidation proposed in literature is a multistage, free radical chain reaction, comprising of initiation, chain propagation and chain termination step. Tolman developed a reaction scheme consisting of 154 reactions which is impractical to analyze as it requires the determination of as many number of rate constants simultaneously with high accuracy. Hence lumped kinetic models which require lesser rate constants have been developed and the models available in literature [12, 13, and 14] are discussed below. In the first model, cyclohexane forms a hydroperoxide which is then converted into cyclohexanone and cyclohexanol and unidentified products (D) and in the second model, the formation of hydroperoxide is not considered, but further oxidation of cyclohexanol is terminated by the reaction with boric acid forming boric esters. Kharkova et al. [14] suggested an exhaustive model for non-catalytic oxidation which consisted of 19 reactions and 10 species based on literature and experimental data. They estimated the rate constants and the concentration of the intermediate free radicals RO_2^* , RO^* , R^* and OH^* . Pohorecki et al. [15] suggested a lumped kinetic model for the catalytic oxidation of cyclohexane. The reaction scheme consisted of 7 irreversible reactions and applied the quasi steady state hypothesis for the estimating the free radicals RO_2^* , RO^* and R^* . The reactive byproducts in the liquid phase and the non reactive byproducts in the gas phase were also incorporated in their model. The catalyst was thought to influence the initiation and the propagation steps but only the principal pathways were considered for global kinetics of oxidation. The role of the catalyst was introduced into the model by assuming certain forms of dependency of the reaction rate constants on the catalyst concentrations for specific pathways. In our work, we assumed a similar lumped kinetic model and shown that the rate constants (with Arrhenius type temperature dependence) can be determined.

Study of literature indicates the use of multimetallic catalyst to improve the catalytic activity and selectivity and this study is an effort in this direction. We further observed that using multimetallic catalyst, the heat of mixing ΔH_m , for different salts determines the state of the metal on the support (as ideal solution, solid solution, ordered solution, mono or biphasic solution or surface alloys) and this way affecting the performance of the catalyst. The use of multimetallic complexes is a step towards developing a system which is independent of ΔH_m . Even though complexes have been known in the early development of modern chemistry, their application in catalysis has been limited due to low thermal stability and literature has mainly focused on their preparation and properties. If these are used in catalysis these complexes are expected to provide new reactivity patterns because the interaction between the metals and the ligand would help in promoting reaction due to the unique charge distribution around it.

In our present work we have developed macrocyclic binuclear monometallic copper complexes with two different ligand environments. These complexes were ionically bonded to the zirconium pillared montmorillonite clay. We have studied the oxidation of cyclohexane with these catalysts at various temperatures in the temperature range 145 – 200 °C. The products formed are identified by Gas Chromatography Mass Spectroscopy (GCMS) analysis and unlike other catalysts (which form cyclohexanol and cyclohexanone in almost equimolar amount) the major product formed for our catalyst was cyclohexanone with small amounts of cyclohexanol and cyclohexene. In this paper we show that the Cu – Cu homonuclear complex serves as an effective catalyst for the oxidation of cyclohexane and does not require co-catalyst, solvent, promoters and initiators. The catalysts described in literature forms cyclohexanone and cyclohexanol in equimolar ratio and in contrast to this our catalyst gives cyclohexanone in considerably large amount. We have proposed a new ligand centered reaction mechanism and determined the rate constants by optimization using Genetic Algorithm. Our study shows that for the temperature range studied the rate constants can be expressed in the usual Arrhenius form and are independent of the concentrations of the species in the reaction mass.

2. Experimental

Reaction Procedure

Preparation of the macrocyclic complexes

The 2,6-diformyl-4-methylphenol needed for the macrocyclic complex was prepared following the procedure given in literature [16]. The NMR Spectrum of the dialdehyde we prepared shows singlets at 11.42 (phenolic), 10.2 (aldehydic), 7.74 (aromatic) and 2.36 ppm (methyl) and is consistent with that of the assigned structure and matches with that given in literature [16]. The complexes prepared by reacting 2,6-diformyl-4-methylphenol with 1,2-phenylenediamine and 1,3 diaminopropane to form the macrocyclic ligand are denoted as *CuCuL1* and *CuCuL2* respectively.

Synthesis of CuCuL1(CH₃COO)H₂O macrocyclic complex

CuCuL1': To 50 ml of N, N-dimethylformamide at 40° C, 2,6-diformyl-4-methylphenol (1.95g, 0.012) and 1,2-phenylenediamine (0.65g, 0.006mol) were added. To this solution equivalent amount of cupric acetate is added and the precipitate of *CuCuL1'* complex formed is filtered, washed with diethyl ether and dried. The FTIR spectrum shows the presence of functional groups C=N at 1510cm⁻¹ and C=O at 1614 cm⁻¹.

CuCuL1: The CuCuL1' (2g) was dissolved in 30ml of methanol and equivalent amount of 1,2-phenylenediamine is added. The crystals that appear are collected by filtration and washed with diethyl ether and dried. The FTIR spectrum shows only C=N at 1512 cm^{-1} and the C=O peak disappears as it forms C= N bond on reaction with 1,2-phenylenediamine.

Synthesis of CuCuL2 macrocyclic complex

CuCuL2': To 50 ml of N, N-dimethylformamide at 40° C , 2,6-diformyl-4-methylphenol (1.95g, 0.012) was added first, followed by the drop wise addition of 0.5 ml of 1,3 diaminopropane with stirring. To this solution equivalent amount of cupric acetate was added and the solution was stirred till all the turquoise crystals of copper acetate had dissolved. The precipitate of CuCuL2' formed was olive green in color and it was collected in 30 minutes then filtered, washed with diethyl ether and dried. The FTIR spectrum shows the presence of functional groups C=N at 1532 cm^{-1} and C=O at 1614 cm^{-1} .

CuCuL2: The CuCuL2' (2g) was dissolved in 30ml of methanol and equivalent amount of 1,3 diaminopropane was added drop wise with stirring. Within 10 minutes olive green crystals appeared and were collected by filtration and washed with diethyl ether and dried. The FTIR spectrum shows only C=N at 1532 cm^{-1} and the C=O peak does not appear as it forms C= N bond on reaction with 1,3 diaminopropane.

Preparation of the Heterogeneous catalyst

The acid (using HCl) treated montmorillonite was procured from Ashapura Minechem Ltd., Mumbai, India and was first pillared using zirconium ions and then was intercalated with the complex. The clay (20 g) is subjected to swelling by adding water (1 liter) to the clay and stirring it for 5 hours and the mixture was finally centrifuged and dried. In the next step, the clay was treated with NaCl solution (1 M) and this was aged for 24 hours. The clay was separated, dried and then refluxed with freshly prepared zirconium oxychloride (0.1 M) solution for 24 hours at 100° C to obtain zirconium pillared montmorillonite. The final step is the intercalation of the complex in the clay layers and is shown in this figure. The clay from the previous step was taken and refluxed with the complex dissolved in acetonitrile for 24 hours at 80° C and the final catalyst thus obtained was separated, washed with acetone and dried. The catalysts synthesized using CuCuL1 and CuCuL2 complex are denoted as Catalyst 1 and Catalyst 2 respectively.

Reaction Procedure

The oxidation reactions were performed in a high-pressure stainless steel reactor. An autoclave-rocking reactor having capacity of 250 ml with gas delivery system, and sampling line was employed for the reaction. The reactor was initially charged with 100 ml cyclohexane and 1g of catalyst, then heated to the required temperature for the desired residence time using oxygen as the oxidant. An on/off controller was used for controlling the temperature with a chrome alloy thermocouple for temperature sensing. The products obtained after reaction were analyzed by gas chromatography (GC) using a fused silica capillary column $0.25\text{ mm} \times 50\text{ m}$ film thickness 0.25 micron with flame ionization detector and the gas chromatography mass spectroscopy (GC-MS) was carried out using a Shimadzu QP-2000 instrument.

Catalyst Characterization

(1) FTIR Analysis of the complex:

Examination of the FTIR spectra was useful in showing that the formation of the complex and its various intermediates are complete and this is determined based on the frequencies of the C=N and C=O bond. The C=O bond frequency which is present till the metal binds to the second position disappears in the final step of the complex synthesis when **CuCuL1'** is reacted with 1,2-phenylenediamine (or **CuCuL2'** is reacted with 1,3 diaminopropane).

(2) CHN analysis of the complex

The CHN analysis was carried out in an elemental analyzer (CE 440 Leimann Labs Inc.). Helium was used as the carrier gas and 3-5 mg of the sample was required. The percentage of Carbon, Hydrogen and Nitrogen present in the complexes were determined and the experimentally obtained values were matched with the values that were calculated theoretically. Close agreements was observed between the experimental (Exp) and the theoretical (Cal) values and are given in Table 1.

Table 1: CHN Analysis of the complexes

Complex	Carbon		Hydrogen		Nitrogen	
	Exp	Cal	Exp	Cal	Exp	Cal
CuCuL1(CH₃COO)H₂O	57.6	56.9	3.9	4	6.9	8.3
CuCuL2	55.7	54.4	3.5	4.9	9.7	10.6

(3) Thermogravimetric Analysis (TGA)

The TGA analysis has been done using a Perkin – Elemer instrument in N₂ atmosphere. The CuCuL1 complex was heated from 40° C to 900 °C at the rate of 10° C /min and it was found that the complex is stable upto 250 ° C. The CuCuL2 complex was heated from 50° C to 700° C at the rate of 10° C /min and it was found that the complex is stable upto 300 ° C. Similarly the TGA of the final catalysts done by heating it at the rate of 10° C /min showed that Catalyst 1 was stable till 600 °C (heating from 50 to 800 °C) while Catalyst 2 was stable till 438 °C (heating from 50 to 900 °C).

(4) Energy Dispersive X-ray Analysis (EDAX)

The EDAX analysis was carried out using FET QUANTA 200 Scanning Electron Microscope (SEM) and for this the samples were first coated with gold under vacuum. It was found that the catalyst 1 contains 4.66 wt % copper and 6.54 wt % zirconium while catalyst 2 contains 1.3 wt % copper and 6.2 wt% zirconium

(5) Small Angle X-Ray Diffraction Analysis

X-ray diffraction measurements were done on ARL X'TRA X-ray diffractometer (Thermo Electron Corporation) equipped with Cu-K α ($\lambda=0.154$ nm) radiation. The voltage and current

applied to the X-ray tube were 45 kV and 20 mA respectively. The sampling width was set at 0.05 ° and the scanning speed was 3 °/minute ($2\theta = 2^\circ - 30^\circ$). The d-spacing was calculated from the 2θ value of the peak corresponding to (001) and it was found that the d-spacing of the original montmorillonite was 16.35 Å ($2\theta = 5.4^\circ$) while the d-spacing of the catalyst 1 was 30.84 Å ($2\theta = 2.86^\circ$). From this we can conclude that after the complex was loaded on montmorillonite there is an increase in its d-spacing and hence the complex has been intercalated between the layers of the clay.

3. Results and Discussion

The reaction in the presence of catalyst 1 was conducted in the 145°C to 190°C temperature range. The above temperature range was chosen because below 145°C the conversion was very low while above 190°C, though the conversion was high a large amount of undesired products were formed. The overall conversion increases from 9% to 23.6 % when the temperature was increased from 145°C to 190°C (480 minutes residence time). At 145 °C only cyclohexanone was formed as the product and after 480 minutes the conversion was 9 % and the selectivity towards the formation of cyclohexanone was 90.5%. When the temperature was increased to 160 °C cyclohexanol and cyclohexene were formed in small amounts along with cyclohexanone which was the major product. With increase in temperature the selectivity towards the formation of cyclohexanone and cyclohexanol decreases. Cyclohexene was formed only in small amounts and its selectivity was below 10 % in the temperature range studied. The yield of cyclohexanone and cyclohexanol increases with increase in temperature so the decrease in the selectivity can be attributed to the increase in rate of formation of the undesired product (D). The conversions of cyclohexane as well as the yield of the products were found to approach a steady state value with increase in time at all reaction temperatures. The reaction was conducted for 8h and a drastic change in conversion and yield were observed during the first 2.5h of reaction. To confirm that the metal complex is not leaching at the reaction conditions studied, we carried out the following experiments.

- I. The oxidation reactions were carried out using the spent catalyst and the conversion was

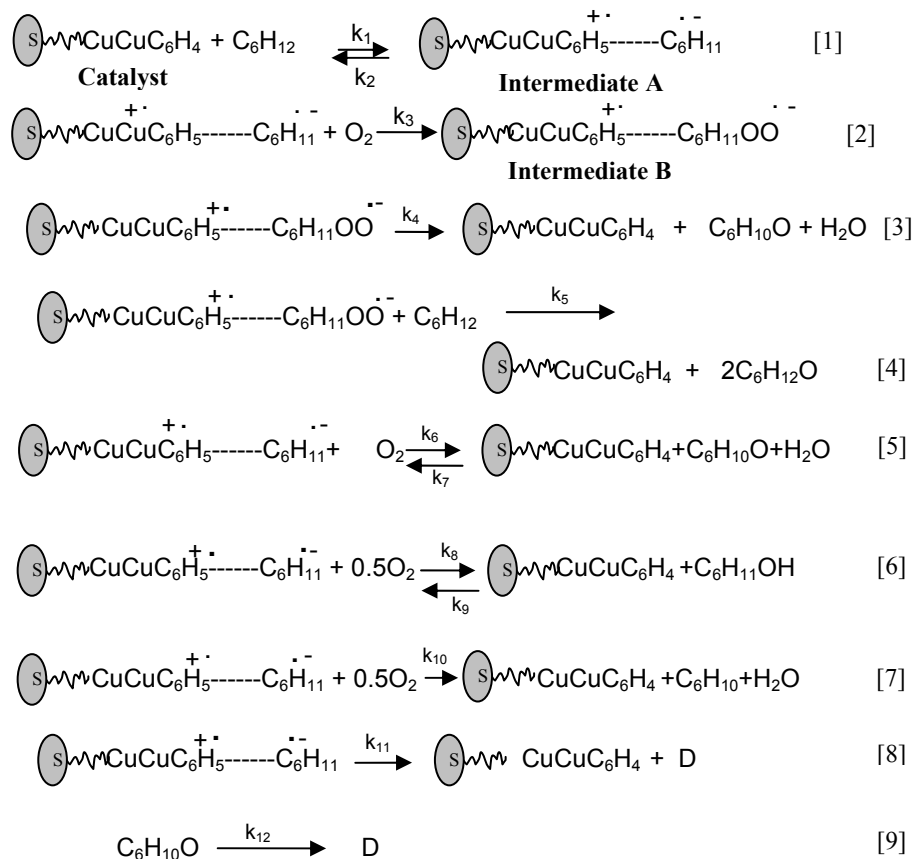


Fig 1: A plausible ligand centered reaction mechanism for the oxidation of cyclohexane in presence of catalyst 1

found to be the same as in the case of the fresh catalyst.

- II. From the product, the catalyst was filtered and the product mixture was once again subjected to the same temperature and pressure. The overall conversion was measured before and after the catalyst was filtered and found to be unchanged indicating that there is no leaching of the active species.

A reaction mechanism has been proposed (Figure 1) based on the product distribution obtained from the experiments that were conducted and some of the pathways leading to the formation of the products were taken to be reversible in nature as the concentration of the products approached almost steady state values. The cyclohexane molecule in presence of the catalyst first forms a cyclohexyl radical anion intermediate, A (step1). Intermediate A reacts with oxygen molecule forming a peroxy radical anion intermediate, B with the catalyst (step2). This intermediate B forms cyclohexanone as shown in step3 of Fig 1. This also can react with another molecule of cyclohexane forming cyclohexanone and cyclohexanol (see Step4). The intermediate A reacts with oxygen forming cyclohexanone in step 5 and cyclohexanol in step 6 and cyclohexane in step 7. Unidentified side products (D) are also formed from intermediate A (step 8) and cyclohexanone (step 9).

Following the reaction mechanism, we can write a mole balance equations for each component of the reaction. Using these equations, we carried out simulation employing Runge-Kutta 4 method (as needed for the Genetic Algorithm(GA) in this specific code for optimal curve fitting) with $\Delta t = 0.01$ min for numerically stable solution and calculated the concentrations of each component for 8h of reaction time. The results were optimized with the experimental values by using GA code and for this the objective function OF (given below) was written as the sum of squares of the

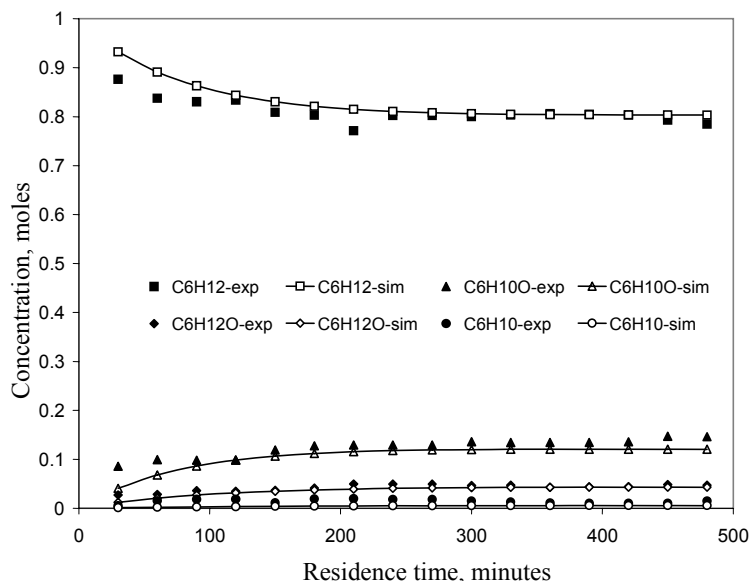


Fig 2: Comparison of the simulated and the experimental results

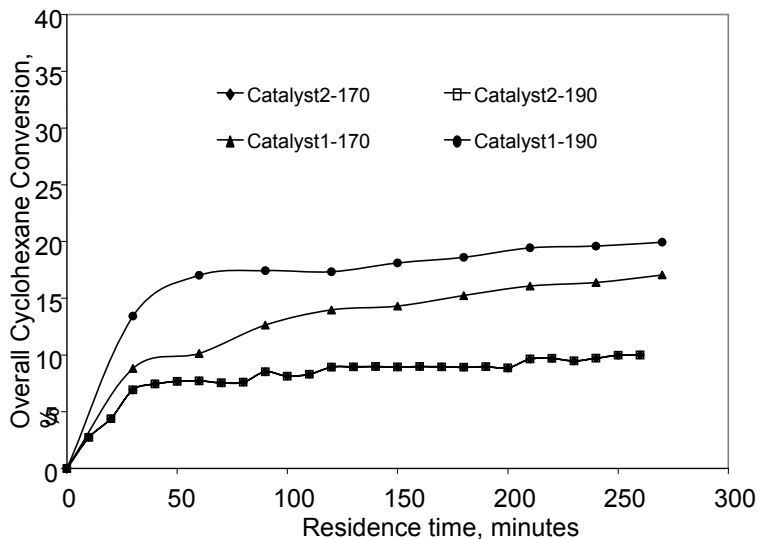


Fig 3: The variation of overall cyclohexane conversion with residence time. Comparison of the results obtained in presence of catalyst1 and catalyst2

difference of simulated and experimental values of cyclohexane, cyclohexanone cyclohexanol and cyclohexene.

$$OF = ([CH]_{sim}-[CH]_{exp})^2 + ([CHone]_{sim}-[CHone]_{exp})^2 + ([CHol]_{sim}-[CHol]_{exp})^2 + ([CHene]_{sim}-[CHene]_{exp})^2.$$

In this study the fitness function is taken as $1/(1+OF)$ and the fitness function's value of a string is known as the string's fitness which is evaluated to find the fitness value. The crossover and mutation probability were varied and finally taken at 0.9 and 0.05 respectively. The random population was created using a random number generator with a random seed equal to 0.887. The optimization was done for different temperatures and the results obtained for 180 °C are given in figure 2. The best fit rate constants were determined and are given in Table 2.

The reaction in presence of Catalyst 2 was studied at 170 and 190 °C and cyclohexanone was formed along with small amounts of cyclohexene and cyclohexanol was not formed as in the case of L1 ligand. The comparisons of the conversion obtained in presence of catalyst 1 are catalysts 2 are given in figure 3. At 170 °C and 260 minutes residence time a conversion of 10 % was obtained and the selectivity towards the formation of cyclohexanone and cyclohexene were 79 % and 7.5 % respectively. On increasing the temperature to 190 °C there was no major increase in conversion and it was 11% and the cyclohexanone and cyclohexene selectivity were 81% and 8% respectively. Thus it can be seen that the selectivity to cyclohexanone is higher in the case of catalyst 2 due to the low conversion obtained in the presence of this catalyst than that obtained in the presence of catalyst 1.

Table 2: Rate Constants at different temperature obtained by optimization using GA

Rate Constants (m ³ /(g catalyst)(mol).s)	T = 418 K	T = 433 K	T = 443 K	T = 453 K	T = 463 K
k ₁	8.0229E-03	1.1332E-02	1.3995E-02	2.5222E-02	2.8753E-02
k ₂	8.1867E-01	1.4612E+00	1.8335E+00	3.5720E+00	3.3627E+00
k ₃	1.4933E-01	3.0448E-01	6.0796E-01	1.4045E+00	2.3831E+00
k ₄	5.6242E-01	1.0406E+00	3.0898E+00	4.5345E+00	4.9754E+00
k ₅	0.0000E+00	1.5081E-01	8.7161E-01	1.1236E+00	1.4145E+00
k ₆	5.0659E-02	8.5732E-02	2.5259E-01	4.1331E-01	4.1310E-01
k ₇	2.4400E-06	4.8000E-06	9.3400E-06	1.0580E-05	2.3120E-05
k ₈	0.0000E+00	9.9404E-03	4.5223E-02	7.2765E-02	1.0295E-01
k ₉	0.0000E+00	3.7970E-05	6.0730E-05	8.1740E-05	9.9730E-05
k ₁₀	0.0000E+00	2.1574E-03	5.0993E-03	1.6927E-02	1.8292E-02
k ₁₁	2.3800E-06	2.0118E-04	2.0118E-04	4.2812E-04	5.3714E-04
k ₁₂	1.2000E-07	2.4000E-07	2.4000E-07	4.8000E-07	4.8000E-07

4. Conclusions

In the present work, a macrocyclic binuclear monometallic Copper complex has been prepared and this has been supported on zirconium pillared montmorillonite. From the small angle x-ray diffraction patterns we can conclude that the complex is intercalated in the layers of montmorillonite as there is an increase in the d-spacing (from 16.35 Å to 30.84 Å) after loading of the complex in the clay. The heterogeneous catalyst thus prepared was stable at high temperatures. This catalyst has been tested for its catalytic activity with the oxidation of cyclohexane, in which cyclohexanone was obtained as a major product and cyclohexanol and cyclohexane were formed in minor quantities. Copper complex with two different ligand environment was synthesized and it was seen that the catalyst activity and product distribution were different for both these catalysts. It was also found that the metal complex was not leaching under the conditions in which the reaction was conducted.

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