Oxidation of Cyclohexane in presence of Cu complex supported on zirconium pillared clay catalyst using oxygen

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Abstract

A binuclear monometallic macrocyclic Cu Cu complex has been prepared starting with 2,6-diformyl-4-methyl-phenol and 1,2-phenylenediamine and this complex was bonded on zirconium pillared montmorillonite through ionic bonding to obtain a heterogeneous catalyst. We have developed a general procedure of heterogenizing complexes on a zirconium modified montmorillonite and using the elemental analysis (done using scanning electron microscopy) we showed that the final complex loading was 1.65 % weight. The thermogravometric analysis showed that the final catalyst is stable up to 600º C while the complex broke down at 250 º C. This catalyst was used to carry out oxidation of cyclohexane using oxygen as the oxidant in the absence of intiator, promoter and solvent. A total conversion of 19% was obtained at 180º C and cyclohexanone was the major product while cyclohexanol and cyclohexene were formed in minor amount. The metal complex was found not to leach under the reaction conditions studied. A kinetic model was proposed and optimal curve fitting (using Genetic Algorithm) of the experimental data yielded the various rate constants.

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1. Introduction

The oxidation of cyclohexane is an important reaction from the industrial point of view because its oxidation products cyclohexanone and cyclohexanol, serve as intermediates in adipic acid for nylon 66 and caprolactam for nylon 6 industries respectively [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, stereate, oleate) as catalyst. The conversion is kept about 3 - 4% per pass as the cyclohexanol and cyclohexanone formed are more susceptible for further oxidation to CO_2. 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 on the reaction as it causes a 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 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].

The alternate route to cyclohexanol and cyclohexanone involves hydrogenation of phenol, a reaction that gives a selectivity of more than 97% at 99% conversion but the process economics still favors direct oxidation of cyclohexane [5]. In view of increasing the selectivity of the target products (cyclohexanone for production of nylon-6 or adipic acid for the production of nylon 66) under mild reaction conditions, studies have been conducted using oxidants (other than molecular oxygen) such as hydrogen peroxide, *t*-butyl hydrogen peroxide (TBHP) etc [6].

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 and complexes 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 177^0 C temperature) and low activity [10]. An induction time which is generally observed in the case of air oxidation of cyclohexane 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 is a multistage, free radical chain reaction, comprising of initiation, chain propagation and chain termination step. Two models available in literature [12, 13, 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 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^*. Poherecki et al. [15] suggested a catalytic model for cyclohexane oxidation following a few guidelines. As it is practically impossible to use too many reactions in the model as suggested by earlier researchers, which require the determination too many rate constants simultaneously, they suggested lumped kinetic models in which the rate constants are of the order of 10. They also suggested a universal scheme which can be modified depending upon the catalyst used and to eliminate the concentrations of intermediates which cannot be directly measured by assuming quasi-steady state approximation.

In our present work we have developed a macrocyclic binuclear monometallic copper complex and bonded it through ionic bonding on zirconium pillared montmorillonite. We have studied the oxidation of cyclohexane with this catalyst at different temperatures and reaction times. The products formed are identified by Gas Chromatography Mass Spectroscopy (GCMS) analysis and unlike other catalysts (forming cyclohexanol and cyclohexanone in equimolar amount) the major product formed for our catalyst was cyclohexanone with small amounts of cyclohexanol and cyclohexene.

2. Experimental

Preparation of the complex

The 2,6-diformyl-4-methylphenol needed for cyclic complexing agent is 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].

CuCuL': To 50 ml of N, N-dimethylformamide at 50º C, 2,6-diformyl-4-methylphenol (0.95g, 0.012) and 1,2-phenylenediamine (0.65g, 0.006mol) are added to. To this solution equivalent amount of cupric acetate is added and the precipitate of CuCuL' complex formed is filtered, washed with diethyl ether and dried. The FTIR spectrum shows the presence of functional groups C=N at 1690 cm^{-1} and C=O at 1614 cm^{-1} and C_6H_5O at 1223 cm^{-1}.

CuCuL: The CuCuL' (2g) is 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 (fig. 1) shows only C=N at 1512 cm^{-1} and no C=O peak appears as it forms C= N with 1,2-phenylenediamine.

The Elemental analysis of the final complex was done using Scanning Electron Microscope (SEM) and it was found that the complex contained 5.83 % (At%) copper. The thermogravimetric analysis of this complex was been done using a Perkin – Elemer instrument in N_2 atmosphere. The sample was heated from 40º C to 900º C at the rate of 10º C /min and it was found that the complex is stable upto 250 º C (fig. 2)

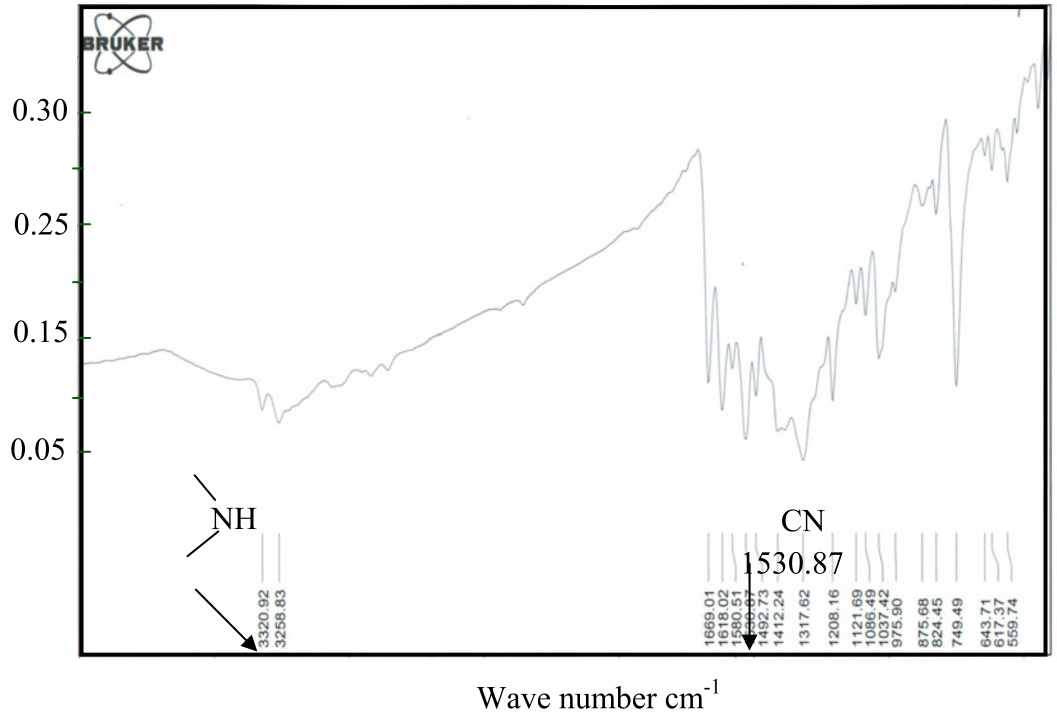

Figure 1: FT-IR spectra of the final homonuclear macrocyclic copper complex

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Preparation of the Heterogeneous catalyst

The complex thus prepared was heterogenized using acid treated montmorillonites as the support. The acid (using HCl) treated montmorillonites was procured from Ashapura Minechem Ltd., Mumbai, India and is first pillared using zirconium species and is followed by the

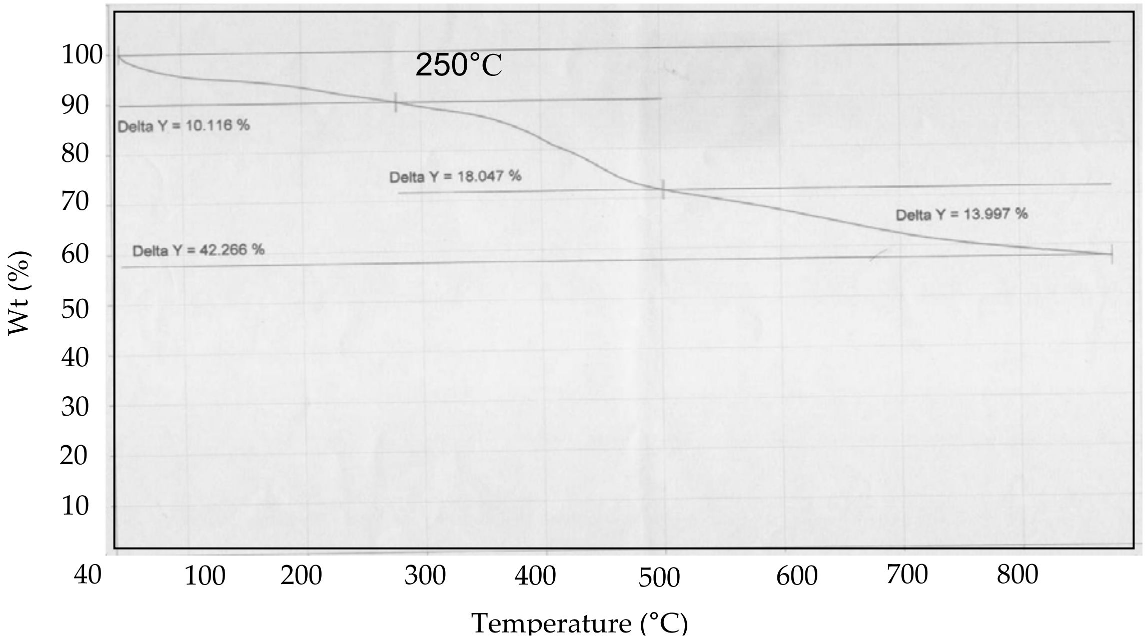


Figure 2: Thermogravimetric analysis of the final homonuclear macrocyclic copper complex

intercalation of the complex as shown in fig 3. 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 is finally centrifuged and dried. In the next step, the clay is treated with NaCl solution (0.1 M) and this is aged for 24 hours. The clay is separated, dried and then refluxed with freshly prepared zirconium oxychloride (0.1 M) solution for 24 hours at 100º C to obtain zirconium pillared montmorillonite. The final step is the intercalation of the complex in the clay layers and is shown in fig 3. The clay from the previous step is taken and refluxed with the complex dissolved in acetonitrile for 24 hours at 80 º C. The catalyst thus obtained is separated, washed with acetone and dried to obtain the final catalyst. The elemental analysis was done using (SEM) of the Cu homobinuclear complex on montmorillonite after coating the sample with gold. It was found that 2.14 wt% Cu and 5.86 wt% Zr was present. The thermogravimetric analysis of this final catalyst in N_2 atmosphere showed that it was stable upto 600 º C (fig. 4).

Reaction Procedure

The cyclohexane used in our study was obtained by fractionating the LR grade chemicals (Ranbaxy Chemicals, India).The oxidation reactions were performed in a high-pressure stainless steel batch reactor. An autoclave-rocking reactor having capacity of 250 ml, 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 in the presence of molecular oxygen. 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 mm × 50 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.

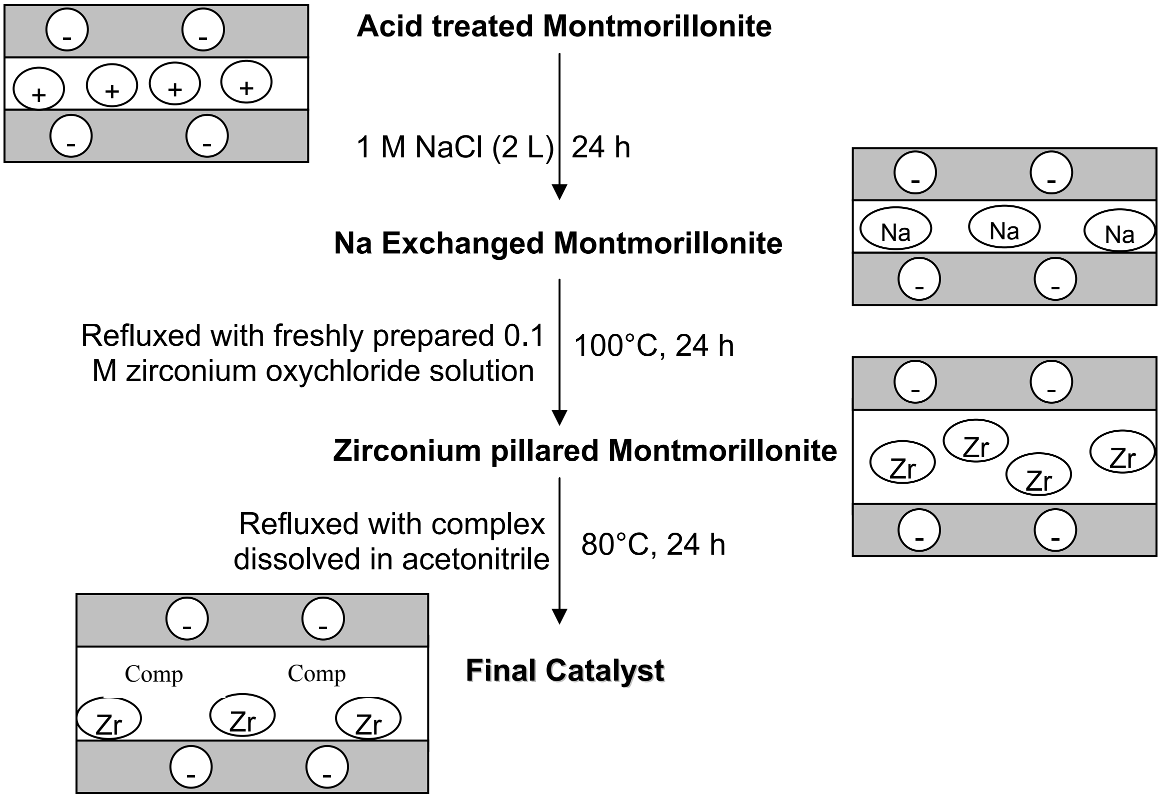


Figure 3: Catalyst preparation scheme

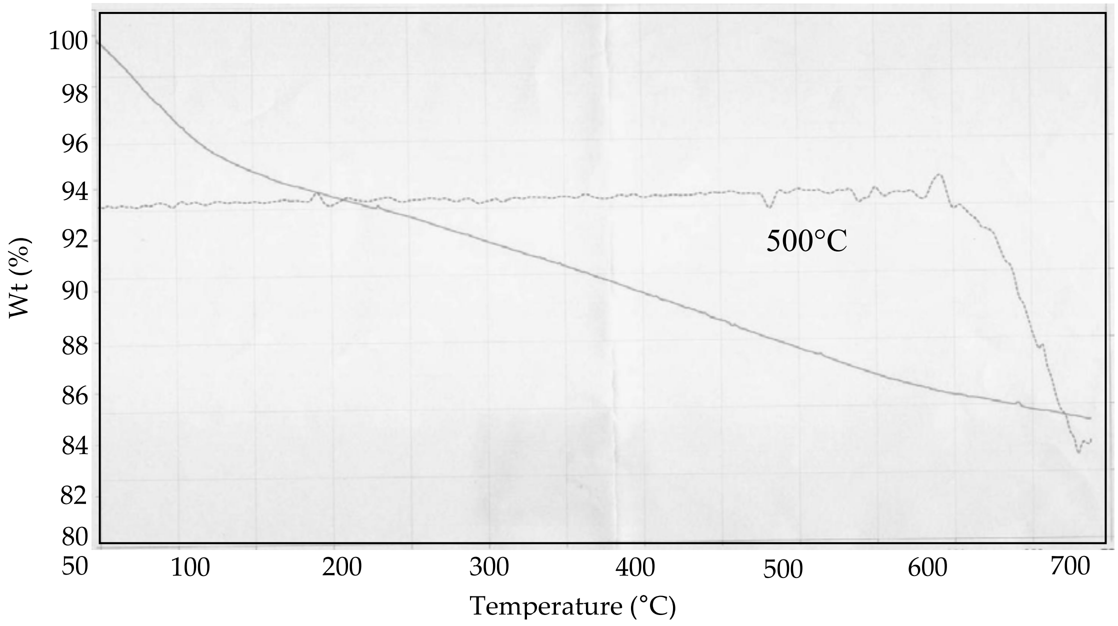
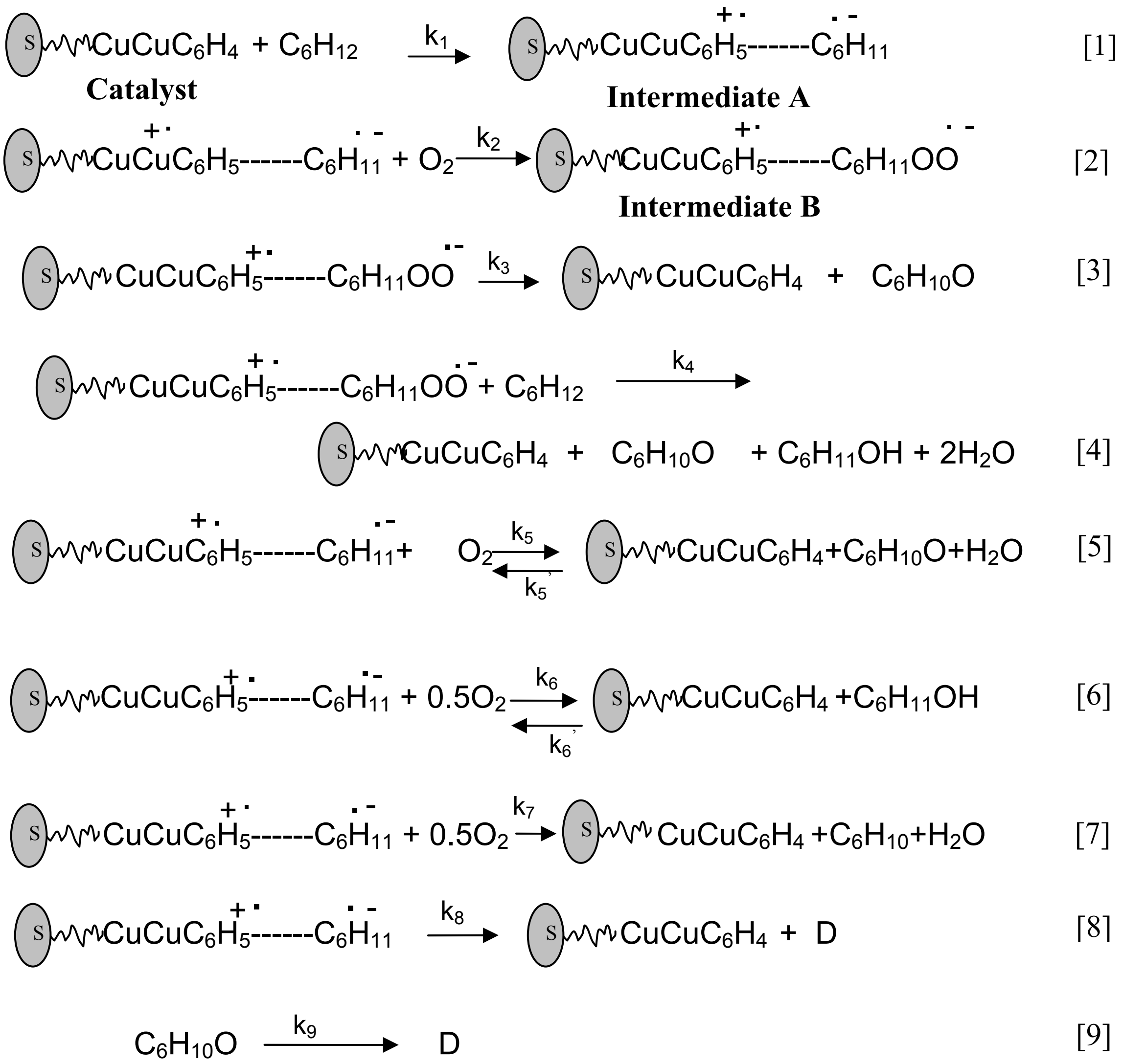


Figure 4: Thermogravimetric analysis of the final catalyst

3. Results and Discussion

The variation of conversion and product distribution at three different reaction temperatures viz. 160º C, 180º C, 200º C were studied for 8 hours. The products were analyzed using GC and GC-MS analysis and it was found that cyclohexanone was the major product that has been formed while cyclohexanol and cyclohexane were formed in minor amount. The conversion increased from 9.5% to 19% (for 150 minutes) when the temperature was increased from 160 º C to 180 º C. The selectivity of cyclohexanol increased when the temperature was increased from 2.6% at 160 º C to 19.2% at 180 º C. As a result of this the selectivity of cyclohexanone decreased from 79.3% at 160 º C to 41.4% at 180 º C. The selectivity at 180 º C for cyclohexanone is still high since it is attained at a very high conversion (19%).



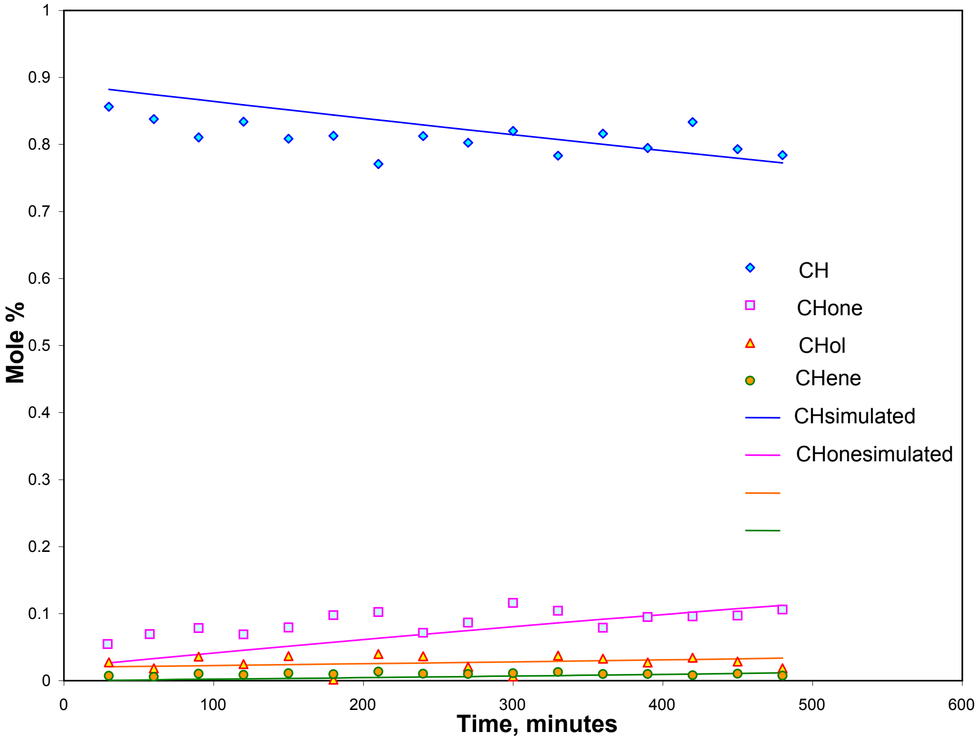


Figure 6: The variation of product stream concentration with time at 180º C (CH = Cyclohexane, CHone = Cyclohexanone, CHol = Cyclohexanol & CHene = Cyclohexene

Based on the product distribution a reaction mechanism has been proposed. The cyclohexane molecule in presence of the catalyst first forms a cyclohexyl radical anion intermediate, A (step1 of Fig 5). Intermediate A reacts with oxygen molecule forming a peroxy radical anion intermediate, B with the catalyst (step2 of Fig 5). This intermediate B forms cyclohexanone as shown in step3 of Fig 5. This also can react with another molecule of cyclohexane forming cyclohexanone and cyclohexanol (see Step4). The intermediate A reacts with oxygen forming cyclohexanone in step5 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).

Oxidation of cyclohexane catalyzed by transition metals is known to occur by free radical mechanism and CHHP is formed which decomposes to cyclohexanone and cyclohexanol [17]. The presence of CHHP in the product mixture can be detected by adding excess triphenylphospine to the product formed in the batch reactor. The increase in the intensity of the peak corresponding to the alcohol in the GC analysis of the reduced sample confirmed the presence of CHHP molecule [18-20]. In the presence of our catalyst, we have shown that on carrying similar experiments by adding triphenylphospine, peak intensity of the cyclohexanol in the GC analysis of the original product and the reduced sample remains unchanged. Thus, it was concluded that the there was no formation of CHHP.

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 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.

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. We have optimized the simulated results with the experimental values by using GA code for the reaction carried out at 180º C (see Fig 6). For this, we wrote an objective function, OF (given below) as the sum of squares of the difference of simulated and experimental values of cyclohexane, cyclohexanone and cyclohexanol.

$OF = \alpha_1([CH]_{sim}-[CH]_{exp})^2 + \alpha_2([CHone]_{sim}-[CHone]_{exp})^2 + \alpha_3([CHol]_{sim}-[CHol]_{exp})^2$

The optimal values for rate constants thus obtained are given as follows: k_1=2.0523E-04, k6 = $k_{2,}$ = 9E-01, k_3 = 9.782188E-01, k_4 = 7.5796E-04, k_5 = 9.916352E-01, k_5' = 5.343E-04, 9E-02, k_6' = 1.731E-05, k7 = 7.623892E-02

4. Conclusions

In the present work, a macrocyclic binuclear monometallic Copper complex has been prepared and this has been supported on zirconium pillared montmorillonite. The heterogeneous catalyst thus prepared was stable upto 600º C while the final complex was stable upto 250º C. 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. It was also found that the metal complex was not leaching under the conditions in which the reaction was conducted. Literature suggests that cyclohexanone and cyclohexanol are formed in equal amounts, but in presence of this catalyst cyclohexanone is formed with 79.3% selectivity at 160º C

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