

Selective Catalytic Oxidation Of Toluene Using Fronds Of *Cocus Nucifera* Activated Carbon As Catalyst

V.J. Agnus Nivetha¹, T. Kasilingam², M. Sivachidambaram³, S.K. Jesudoss⁴, R. Sudhakaran⁵, Namitha Lekshmi⁶, R. Meenakshi⁷, S. Chitra⁸

^{1,2,3,6,7,8}Department of Chemistry, Theivanai Ammal College for Women, Villupuram, TamilNadu, India – 605 401

⁴Department of Chemistry, Sri Meenakshi Vidiyal Arts and Science College, Trichy, TamilNadu, India – 621 305

⁵Department of Chemistry, Govt. Arts College, Trichy, TamilNadu, India – 620 022

Abstract:

*Activated carbon (AC) was successfully synthesized by a chemical activation method using as the source of fronds of *Cocus nucifera* (*C. Nucifera*). The formation of fronds of *C. Nucifera* activated carbon (CNF-AC) and its physicochemical properties were investigated systematically. The morphology, surface area and porosity, of the synthesized materials were investigated using X-ray diffraction studies (XRD), HR-SEM, N₂ adsorption-desorption (BET) analysis. The excellent catalytic activity of CNF-AC (800 °C) was revealed in the selective oxidation of toluene to the corresponding benzaldehyde with 85% conversion and 87% selectivity. The material was evaluated for the oxidation of toluene in the presence of tert-Butyl hydroperoxide (tBHP) as the oxidizing agent and tetrahydrofuran (THF) solvent. Hence, the obtained results noted that the material was highly active, stable and can be recycled at least four times without a loss of catalytic efficiency. The CNF-AC was carried out in a sealed graphite crucible maintained at a temperature of 800 °C for the transformation of *C. Nucifera* into porous activated carbon to achieve the excellent catalytic activity.*

Keywords: *Cocus Nucifera*, Activated carbon, N₂ Adsorption-Desorption, Toluene, Catalytic Activity.

1. INTRODUCTION

Activated carbon (AC) is a carbonaceous material with high porosity. AC offers large surface area, high conductivity, flexible pore size, and durable chemical as well as physical inertness [1] due to their high specific surface area [2-3]. Activated carbons derive their outstanding properties from the extended surface area and their porosity. Such properties are the function of precursor and scheme of preparation. They not only determine the porosity but also the chemical nature of their surfaces, which consequently establishes their adsorptive as well as catalytic characteristics.[4]. On carbons with relatively higher surface area, the catalytic sites will be widely distributed [5]. The catalytic activity of activated carbon was assumed to be a result of the graphitic structure of the carbon as well as its surface functionalities [6]. Thus, it is used to replace with the toxic oxidising agents by more environmental friendly processes and to open up the possibility of using renewable biomass-derived feedstocks [7-9]. The oxidation reactions of organic compounds have been carried out, since it has industrial significance and produces eco-friendly products, particularly to

avoid toxic reagents such as organic peroxides and solvents [10]. The selective oxidation of toluene into the corresponding aldehyde is always a useful and elemental organic transformation in organic reactions, because such aromatic aldehydes and their derivatives are the main building blocks for the synthesis of fine chemicals and pharmaceuticals.

However, environmental concerns have motivated the development of carbon materials from various forms of biomass waste. Biomass wastes are in abundance and cheap. They are thus suitable raw material for synthesis of porous carbons. Over current years, a substantial amount of biomass, including tobacco stems, pea skin, coal liquefaction residue, cow dung, rotten carrot, cellulose, plant leaves, coffee residue, tea waste, orange peel, nut shells, cotton stalk, coconut shell have been selected as the starting material for synthesis of AC [11-18].

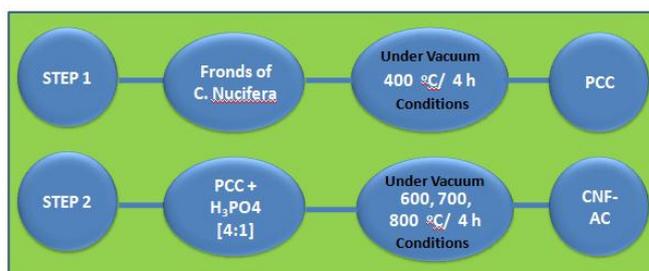
Coconut (*C. nucifera*) is a versatile palm tree that belongs to the Arecaceae family with widespread use as a source of food, fuel and raw materials. [19]. In India, coconut is the most important industrial crop after oil palm, rubber and paddy. However, large amounts of coconut waste materials are produced. The utilization of coconut waste by-products such as husks, shells and dregs [20-24] as potential precursors for the production of AC have been studied. Coconut leaves (CNF) have been used as roofing material for huts, household purposes and the wastes were often left to decompose on the fields. Thus, there is an interest to use these materials as a precursor for AC. The properties of AC depend on its preparation method along with the nature of the activation method, physical or chemical processes. Physical activation involves carbonization followed by activation of the resulting char in the presence of activating agents such as CO₂ or steam. In the chemical activation, the raw material is impregnated with activating agents such as K₂CO₃, ZnCl₂, H₃PO₄, KOH; then the impregnated material is heat-treated in an inert atmosphere at various temperatures [25-30]. Activation with phosphoric acid is a well-established method for the preparation of activated carbons [1, 32, 33]. H₃PO₄ is considered as low-cost materials which promotes the decomposition of the cellulosic precursor at relatively low activation temperatures [34].

The aim of present work is to investigate the catalytic applicability of our prepared activated carbon derived from the waste fronds of *C. Nucifera* (CNF) for the selective oxidation of toluene. H₃PO₄ was used as an activating agent and the as-prepared AC shows better surface characteristics. It was further characterised by XRD for structure, pore texture, surface area (BET).

2. EXPERIMENT PART

2.1 Preparation of AC from Chemical method.

CNF as the precursor material was collected from Pukkiravari village, Kallakurichi district, Tamil Nadu, India. The AC was prepared from the precursor material (CNF) by a two stage process. The pre-carbonization process, the CNF was washed with distilled water to remove dust, impurities and then dried in an oven for 24 h at 110 °C to reduce the moisture content. The resulting CNF was heated at 400 °C at a rate of 5 °C min⁻¹ for about 4 h under vacuum conditions and cooled to room temperature at the same rate. This is labelled as pre-carbonized carbon (PCC). Chemical activation was performed by mixing 40 g of dried PCC and agitated with 200 g of aqueous solution containing 85% H₃PO₄ by weight. The impregnation ratio of chemical activating agent/PCC was fixed as 4:1 and it was homogeneously mixed at 85 °C for 4 h. The slurry was dried in an oven for at least 24 h at 110 °C.



Scheme 1 Schematic representation for the preparation of CNF-AC

The resulting samples were then heated in a muffle furnace to prepare AC at four different temperatures 600, 700, 800 °C at a heating rate of 5 °C min⁻¹ for 2 h under vacuum conditions. After the heat was reduced, the activated carbon was washed several times with cold water to maintain a neutral pH. The washed activated carbon samples were dried under vacuum at 110 °C for 24 h and stored in desiccators. The final samples were labelled as CNF-AC6, CNF-AC7 and CNF-AC8 according to the activation temperatures 600, 700, 800 °C, respectively. Scheme 1 shows the schematic representation for the preparation of chemically treated CNF-AC.

2.2 Characterization techniques

The crystalline compounds in the samples were identified by qualitative X-ray powder diffractometry (XRD) using a Siemens D5000 X-ray powder diffractometer. Surface morphology studies and EDX elemental analysis of the BFF pre-carbonized and activated carbon sample were performed mutually by using a Quanta 200 FEG high resolution scanning electron microscope (HRSEM). Nitrogen adsorption/desorption isotherms were used to measure the specific surface area, pore width, pore volume and pore diameter of the AC samples. The boiling point of liquid nitrogen (196 °C) was used in the instrument Micromeritics ASAP 2020 BET analyzer device.

2.3. Catalytic Performance

Liquid phase oxidation of toluene was carried out in a batch reactor, under the reaction conditions at atmospheric pressure. In a typical procedure, 0.04 g of the CNF-AC8 zeolite catalyst (catalyst with better properties), 20 mmol of toluene (C₆H₅CH₃, 20 mmol of tBHP (30%) and 10 mmol of THF were placed in a round-bottom flask equipped with the reflux condenser and the thermometer. The resulting mixture was heated at 70 °C for 4 h and then cooled to room temperature. About the tBHP selection, it is the commonly used oxidant in literature. The others oxidants like NaOCl and H₂O₂ suffer from poor solubility in the chosen organic substrate and catalytic system and hence not used in the present study. The oxidized products after the catalytic reaction were separated by centrifugation. The products were analyzed by the gas chromatograph with a flame ionization detector, using an SGE BPX70 capillary column (70% Cyanopropyl Polysilphenylene-siloxane, 30 m × 0.53 mm × 0.50 μm) and N₂ as a carrier gas. GC technique was carried out to analyze the conversion and selectivity of the products.

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction studies of CNF-AC

Fig. 1 shows the XRD patterns of the CNF-AC catalysts prepared by the chemical activation method from CNF by using different activation temperatures of 600 °C, 700 °C, and 800 °C. All CNF-AC samples showed broad peaks around 23° and 43° and related to

(100/101) Bragg reflections, which also matches with the JCPDS card number 75-2078 [35, 36]. In addition, AC samples exhibit certain broader peak at 43° , it clearly explains that the CNF-AC 8 has appears in high amount of porous structure is formed. The high porosity increases the catalytic ability of the CNF-AC samples.

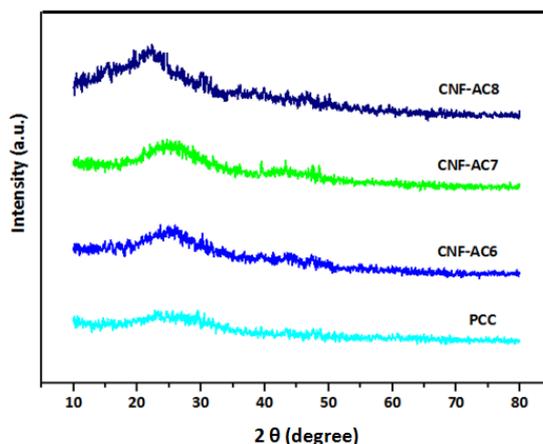


Fig. 1. X-ray diffraction (XRD) studies of (PCC, CNF-AC6, CNF-AC7, CNF-AC8)

3.2. Morphological studies of CNF-AC

Fig. 2(a–d) shows the SEM pictures of CNF-AC samples prepared at various activation temperatures (600 to 800 °C) and Fig. 2a is PCC does not show any specific porous nature due to non activated carbon. The right sideview images of Fig. 2(b, c and d) clearly show micro holes presence in the porous nanosurfaces. The formation of CNF-AC samples are relatively uniform micro and mesoporous-like nanosurfaces and high porosity of about 200–100 nm is observed.

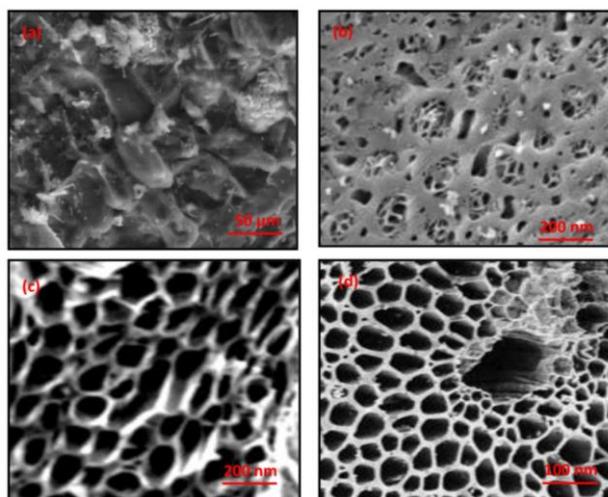


Fig. 2. SEM images of (a) PCC (b) CNF-AC6 (c) CNF-AC7 (d) CNF-AC8

Moreover, some macropores will appear in the images are due to the agglomeration with sizes in the range of 15–25 nm. The surface morphology of CNF-AC nanosurfaces was slightly rough and might be attributed to the primary hierarchical ordered CNF-AC nanosurfaces with high porosity. The depth size of the holes ranges from tens to several hundred nanometers. The morphology of porous nanosurfaces is composed of numerous holes and tiny nanoporous of primarily CNF-AC framework, as implicit by the HR-SEM results.

3.3. N₂ Adsorption–Desorption Isotherms of CNF-AC

The nitrogen isotherm studies of the hierarchical ordered CNF-AC samples are displayed in Fig. 3. All the CNF-AC samples show type IV isotherm. The samples of CNF-AC6 (600 °C), CNF-AC7 (700 °C) and CNF-AC8 (800 °C) showed a broader hysteresis loop from P/P₀ = 0.45 to P/P₀ = 1, which is due to the presence of both micropores and mesopores in the CNF-AC nanosurfaces. The adsorption at low relative pressure (P/P₀ = 0.02) points out the presence of micropores.

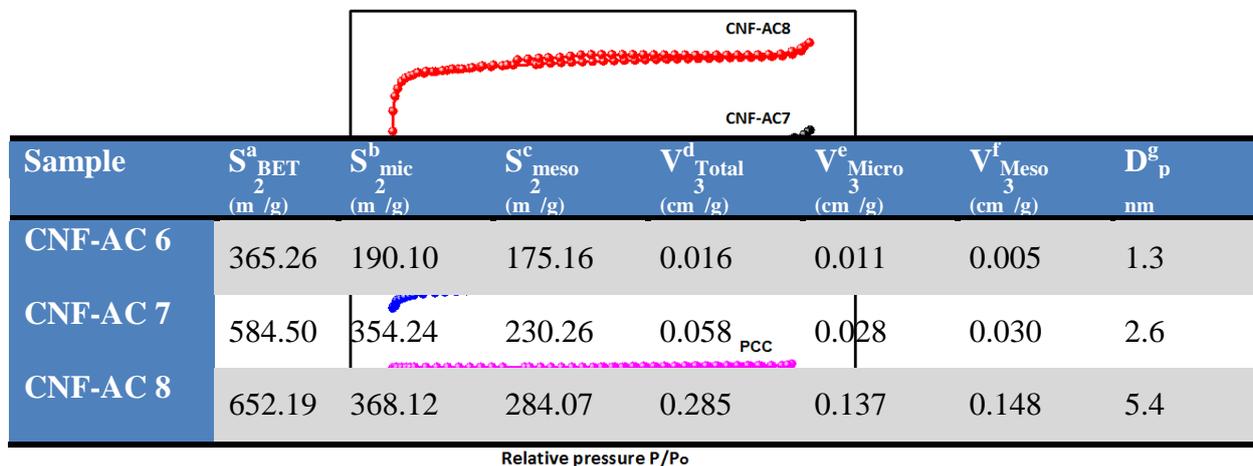


Fig. 3. Nitrogen adsorption/desorption isotherms of (PCC, CNF-AC6, CNF-AC7, CNF-AC8)

Normally, the catalytic activity increases by the mesoporosity presence in the CNF-AC nanosurfaces. The textural properties of the CNF-AC samples are presented in Table I. As seen in Table 1, the BET surface area and the total pore volume increases from 175.16 m²/g and 0.016 cm³/g, 230.26 m²/g and 0.058 cm³/g, 284.07 m²/g and 0.285 cm³/g respectively with increasing the activation temperatures. Finally, the above results clearly point out the extra mesoporosity has been created without affecting the microporosity and therefore it should help in superior accessibility of the catalytic sites in CNF-AC by the reactant molecules [37] As a result, the N₂ adsorption results confirmed the formation of the hierarchical CNF-AC and these hierarchical structures play a key role in the catalytic performance [38].

Table 1 Sample code, BET surface area, pore volume and average pore diameter of CNF-AC samples

^a BET surface area, ^b Micropore surface area, ^c Mesopore surface area, ^d Total pore volume, ^e Micropore volume, ^f Mesopore volume, ^g Average pore diameter.

3.4. Catalytic activity of *C. nucifera* activated carbon catalyst under optimum condition

The catalytic activities of the as-synthesized CNF-AC8 catalysts were determined by the selective oxidation of toluene at optimum reaction conditions. CNF-AC8 is chosen for the reason of high micro and mesoporous nature which increases the catalytic ability to the conversion of toluene. In general, toluene oxidation gives to the final products of benzaldehyde and benzoic acid. In order to find the optimized catalyst (CNAC) performance in the selective oxidation of toluene, the reaction conditions were altered by studying the effect of catalyst loading (0.01–0.05 g), reaction temperature (30–80 °C), solvent (1,4-dioxane, ethyl acetate, chloroform, THF (tetrahydrofuran), n-hexane), oxidant (H₂O₂, tBHP, NaOCl), tBHP/C₆H₅CH₃ molar ratio (0.50–1.50), time (1 to 5 h) and reusability of the catalyst.

3.4.1. Effect of the catalyst loading

The activity of the catalyst amount on the production of benzaldehyde by the oxidation of toluene was investigated with the variation of CNF-AC8 catalysts from 0.01 g to 0.05 g, while maintaining the other parameters as constant as shown in Fig. 4, since the catalytic activity is directly proportional to the catalyst amount. In the absence of the catalyst in the oxidation reaction, the conversion achieved was 5% only. Hence the CNF-AC8 catalyst shows better activity and good yield conversion and selectivity in the oxidation reactions. The conversion has marked its level from 30% to 85% with increased catalyst amount from 0.01 g to 0.04 g. This increased level is due to the presence of more active sites on the catalyst surfaces. Furthermore, the catalyst amount was increased, there are no significant changes arisen in the conversion and benzaldehyde selectivity is also reduced, due to the additional level oxidation of toluene to benzoic acid in the presence of excess CNF-AC8 catalyst. [38, 39] The experimental results conclude that the optimized catalyst amount is fixed as 0.04 g.

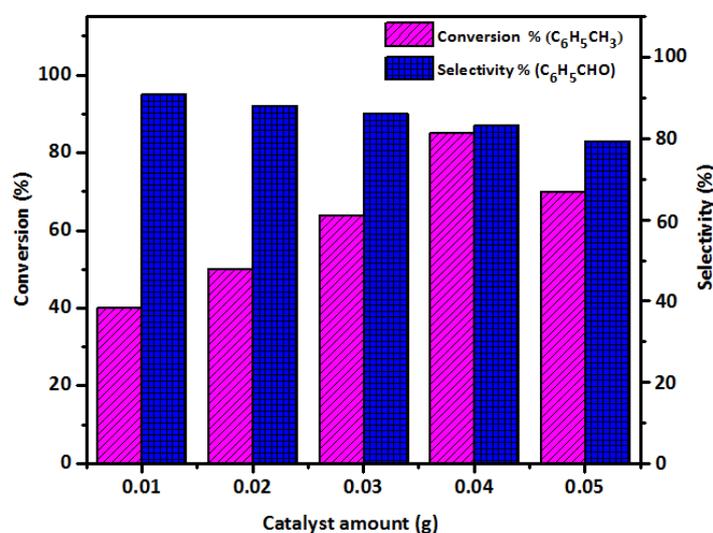


Fig. 4. Effect of the catalyst loading on the oxidation of toluene

3.4.2. Effect of reaction temperature

The major impact of reaction temperature on the oxidation reactions of toluene using CNF-AC8 catalyst was analyzed at five different temperatures from the range of 30–70 °C in the presence of the THF solvent and tBHP oxidant. The results are displayed in Fig. 5 and reveal that the conversion increased from 30% to 85% when the temperature is increased from 30–70 °C with no effect on the selectivity of benzaldehyde. Since the reaction can be affected by the thermal effect on the kinetics, at 30 °C, the conversion of toluene will be lower [40]. But at higher temperature, (<30 °C) the conversion will be greater, as it favours the reaction. When the temperature is increased to 80 °C, there are no more changes in the conversion and the selectivity of benzaldehyde is decreased. The selectivity is decreased due to the swift decomposition of TBHP at the high temperature and also further oxidation of toluene to benzoic acid. The optimum temperature is fixed as 70 °C in favour of the further reaction balanced between the toluene conversion and benzaldehyde selectivity.

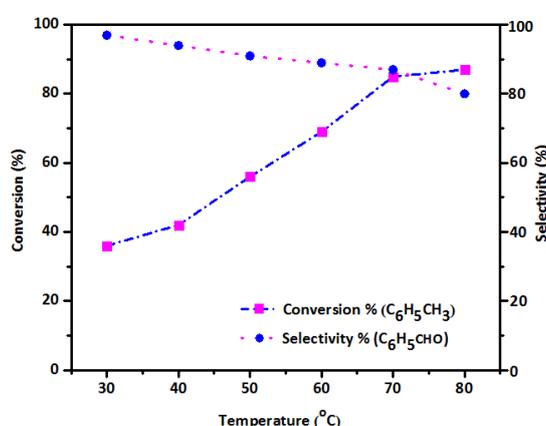


Fig. 5. Effect of the reaction temperature on the oxidation of toluene

3.4.3. Choice of the oxidant

The catalytic activity test has a strong impact on the oxidants [41]. In general, ecological tolerability of two essential oxidants like oxygen (O₂, air), hydrogen peroxide and TBHP makes them to have better performance in diverse applications. In the present study, the catalytic performance with three different oxidants, such as tBHP, H₂O₂ and NaOCl was investigated and the results are shown in Table 2. Absence of any oxidant in the reaction does not show any appreciable percentage of product since it involves only the lattice oxygen. In gas chromatographic techniques, the analysis of the reaction mixture is determined with a high conversion (85%) and selectivity (87%) of the products in tBHP medium, when compared to other oxidants. tBHP is strongly stable and most capable oxidant for the toluene conversion. When the same reaction was carried out in the other oxidizing agents like H₂O₂, the toluene conversion (77%) and selectivity (83%) was achieved and in the presence of NaOCl, the low toluene conversion (66%) and selectivity (80%) was achieved. The oxidizing agents illustrated that the enhanced conversion efficiency is in the order of tBHP, (85%) > H₂O₂ (77%) > NaOCl (66%). The results concluded that tBHP, was found to have better performance for the toluene conversion and benzaldehyde selectivity. H₂O₂ and NaOCl were found to be ineffective oxidants in the present work. Since, it is suffered by poor solubility nature. Due to the strong oxidizing power of NaOCl, toluene simply oxidized to benzoic acid, since toluene conversion and benzaldehyde selectivity was decreased [42]. Therefore, further oxidation reactions are carried out in the presence of tBHP, as an oxidant.

Oxidants	Conversion (%)	Selectivity (%)
TBHP	85	87
H ₂ O ₂	77	83
NaOCl	66	80

Table 2. Choice of the oxidants on the selective oxidation of toluene.

3.4.4. Effect of Solvents

The effect of the solvents in the conversion of toluene and selectivity of benzaldehyde is shown in Table 3. A variety of solvents were tried out for exploring the effect of solvents in the conversion process and five different solvents, 1,4-dioxane, ethyl acetate, chloroform, tetrahydrofuran (THF) and n-hexane were used. Our results have shown that THF exhibit maximum conversion of toluene up to 85% and the selectivity of benzaldehyde to 87%. Hence, THF is found to be utmost suitable for this reaction system, due to the high polarity index (4.8) of the solution. The toluene conversion was increased in the order by using the following solvents, THF (85%) > ethyl acetate (82%) > chloroform (71%) > 1,4-dioxane (67%) > n-hexane (61%). It is difficult to explain which property of the solvent influenced the reaction, because it does possess certain conditions. Example, it promptly dissolves in both the substrate and the oxidant. The oxidant should be most stable in the THF solvent. tBHP along with toluene was dissolved and thus direct the reactants, in such a way, that they are properly adsorbed on the catalyst surface. Other solvents (ethyl acetate, chloroform, H₂O₂, and n-hexane) in the oxidation process show lower efficiency in the conversion as shown in Table 3. Because above solvents have lower solubility in tBHP oxidant with a decrease in the order of polarity indexes (ethyl acetate (4.4) > chloroform (4.1) > 1,4-dioxane (4.0) > n-hexane (0.1)) than the THF solvent. Above all, the competitive adsorption between the solvents and toluene at the active sites of the catalyst decreases the toluene conversion.

Solvents	Conversion (%)	Selectivity (%)
THF	85	87
ethyl acetate	82	83
chloroform	71	79
1,4-dioxane	67	75
n-hexane	61	69

Table 3. Effect of the solvents on the selective oxidation of toluene.

The low yield percentage of conversion using hexane shows that the reaction possibly will not precede, due to its very lower solubility in tBHP [39]. The conversion of toluene is only 55% in a hydrous condition which is lower than that of other solvents. The dehydrogenation of toluene with water is less auspicious and also benzaldehyde could be oxidized to benzoic acid if water is used as a solvent which can bring down its selectivity.

3.4.5. Effect of molar ratio of tBHP/C₆H₅CH₃

The amount of tBHP oxidant is a key factor of the reaction and influence the catalytic performance of toluene oxidation. The effect of the substrate to oxidant molar ratios was studied and the results are shown in Fig. 6. Accordingly, the effect of five various molar ratios (0.50, 0.75, 1.00, 1.25 and 1.50) of the toluene to tBHP ratio was measured by keeping other reaction parameters as constant. Low conversion of the substrate was acquired, as the substrate to oxidant ratio is same or the stoichiometric ratio is low. It may be due to the lesser

amount of oxidant that reacts with the higher amount of toluene for coordination. As clearly seen in Fig. 6, when the substrate toluene to oxidant molar ratio value is increased from 0.50 to 1.50, the conversion of toluene was gradually increased. The above results also noted that the excess amount of oxidant significantly enhances the rate of conversion of toluene. Hence the availability of more oxygen on the decomposition of tBHP oxidizes toluene easily [43]. But high amount of oxidant will over oxidize the benzaldehyde to benzoic acid. Therefore, the higher amount of oxidant (tBHP has a negative effect on the benzaldehyde selectivity). With an increase in the amount of tBHP /C₆H₅CH₃ molar ratio is equal to 1.50 or more, there is no more increase in the toluene conversion and also decrease the benzaldehyde selectivity. The above statement clearly stated that the huge amount of oxidant is not a crucial condition for improving the catalytic performance of the catalyst. As a result, the optimum molar ratio of tBHP /C₆H₅CH₃ is taken as 1.25.

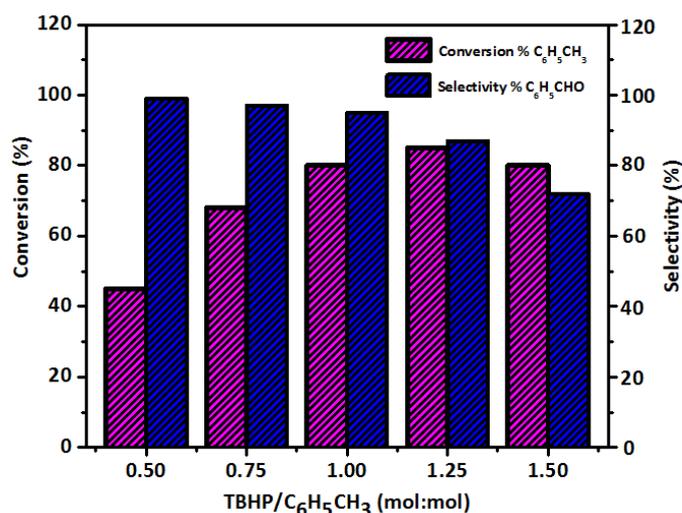


Fig. 6. Effect of tBHP/C₆H₅CH₃ molar ratio on the oxidation of toluene

3.4.6. Effect of reaction time

The conversion reactions of toluene and its selectivity towards benzaldehyde using CNF-AC8 catalyst at different reaction times are revealed in Fig. 7. While the reaction time is increased from 1 to 5 h, the initial conversion is increased and it is further increased to its maximum conversion of 85% when the reaction is carried out for 4 h. With further increased time, it remains gradually decreased and constant. Almost 77% conversion is reached within 3 h. The benzaldehyde selectivity is outstanding at 4 h of the reaction and it is further decreased as the benzaldehyde is converted into benzoic acid. Therefore, it is concluded that the 4 h was found to be the optimal reaction time for the maximum conversion with a high degree of solubility in benzaldehyde product.

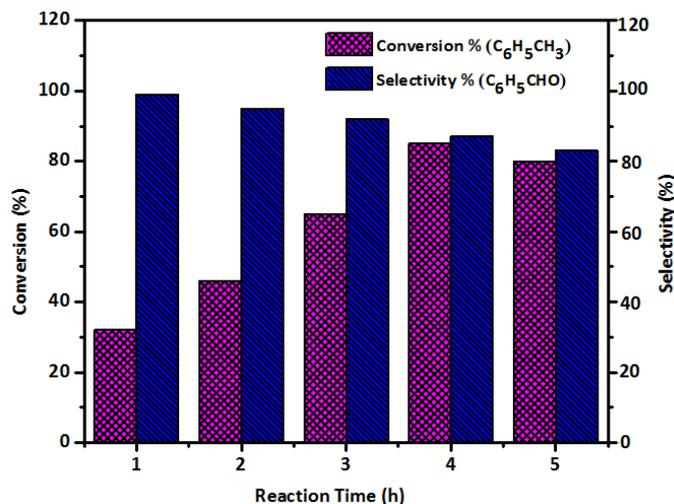


Fig. 7. Effect of reaction time on the oxidation of toluene

3.4.7. Reusability Studies

The recycling performance of the catalyst is more significant for the industrialized related applications. The reusability of the optimized CNF-AC8 catalyst was studied up to four runs and the results are shown in Fig. 8. The reusability studies were done by separating the catalyst by filtering from the reaction solution after the completion of the reaction, washed thoroughly with acetone and then dried at 120 °C for 2 h. The dried CNF-AC8 catalyst is used up for the next run under the same reaction conditions. The catalyst shows higher catalytic activity with high conversion and selectivity upon the initial use. The catalytic activity is not lost completely on further reactions but slightly reduced when they are used further and this may be owing to the blocking of the active sites, because due to the formation of strongly adsorbed by-products [44]. Therefore the results show that the catalyst can be used for four times. To be concise, the CNF-AC8 showed a better stable activity during the reusability studies.

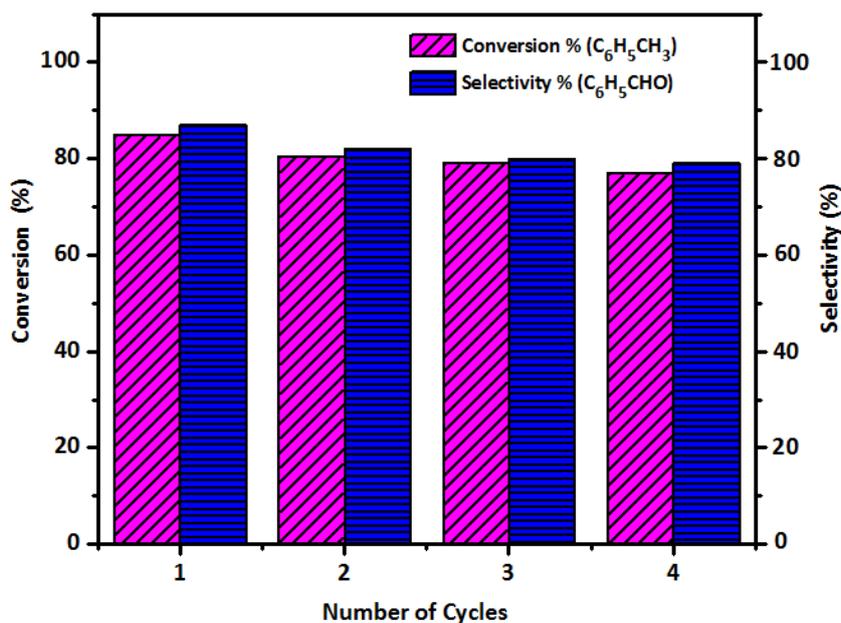


Fig. 8. Reusability studies on the CNF-AC8 catalyst

4. CONCLUSION

We have reported a novel and recyclable heterogeneous hierarchical ordered CNF-AC8 catalyst prepared by the chemical activation method and its catalytic activity for the selective catalytic oxidation of toluene for the first time. The characterization techniques employed in this work prove the formation of hierarchical ordered CNF-AC8 nanosurfaces. The HR-SEM analysis confirmed the porous like morphology with several tiny nano-sized particles obtained on the CNF-AC8 catalyst. The high porous, higher surface area, increased total pore volume are confirmed by XRD and BET techniques. The highly efficient optimal CNF-AC8 catalyst was investigated for its catalytic activity, stability and a superior catalytic oxidation performance of 85% toluene conversion and 87% benzaldehyde selectivity were achieved. Also, it is reusable up to four times without a significant loss in the catalytic activity.

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