

Research Article

Tuning of Activated Carbon for Solvent-Free Oxidation of Cyclohexane

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Activated carbon (AC) was prepared from carbonization of phosphoric acid soaked peanut shell at 380°C under inert atmosphere followed by activation with hydrogen peroxide. The AC was characterized by SEM, EDX, FTIR, TGA, and BET surface area and pore size analyzer. The potential of AC as a catalyst for solvent-free oxidation of cyclohexane to cyclohexanol and cyclohexanone (the mixture is known as KA oil) in the presence of molecular oxygen at moderate temperature was investigated in a self-designed double-walled three-necked batch reactor. The effect of different reaction parameters/additive was optimized. The maximum productivity value (2.14 mmol g⁻¹ h⁻¹, without base, and 4.85 mmol g⁻¹ h⁻¹, with 0.2 mmol NaOH) of the desired product was achieved under optimal reaction parameters: vol 12.5 mL, cat 0.4 g, time 14 h, oxygen flow 40 mL/min (pO₂ 760 Torr), stirring 1100 rpm, and temp 75°C. The AC shows recyclability for multiple runs without any significant loss in activity. Thus, the AC can be an efficient catalyst, due to low cost, ease of synthesis, easy recovery, nonleaching, and recyclability for multiple uses for the solvent-free oxidation of cyclohexane.

1. Introduction

Activated carbon (AC) was reported as an effective catalyst for the first time in the beginning of 19th century [1]. In early nineteenth century, AC was prepared commonly by thermal activation method from different agricultural raw materials and investigated as a catalyst for the degradation of hydrogen peroxide. The catalytic activity of the AC for the decomposition of hydrogen peroxide was very good but persisted only for short duration. The most probable reason for the vanishing of catalytic activity being used for decomposition of hydrogen peroxide may be deactivation of oxygenated groups on the surface of activated carbon [2, 3]. The major issue related to durability of AC was successfully

addressed by researchers in recent decades. Through physical, physicochemical, chemical, and chemothermal activation, the AC was tuned to show a good catalytic activity [4] in production of phosgene, sulphur halides, hydrogenation, polymerization, halogenation [5–7], removal of SO₂ and NO_x [8, 9], and oxidation of benzyl alcohol [10]. This performance of AC was attributed to its porosity, active sites, and high surface area. Thus, by controlling these parameters, AC can be tuned as an effective catalyst for a selected organic transformation.

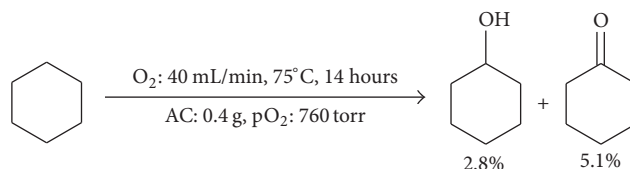
The oxidation of cyclohexane to cyclohexanol and cyclohexanone (KA oil) has paramount importance due to their applications in the synthesis of Nylon-6,6 and Nylon-6, as solvent lacquers, varnishes and shellacs, and as homogenizer

and stabilizer in soaps and detergents [11, 12]. The industrial scale production of KA oil was carried out in two-consecutive-step process: the noncatalytic autoxidation of cyclohexane to cyclohexyl hydroperoxide (CHHP) in the presence of oxygen, followed by the conversion CHHP to KA oil using a homogeneous cobalt (Co(II)) catalyst. This process has limitations of low cyclohexane conversion of 3–4% with selectivity of 60–70% to CHHP [13], high operation cost of recycling of unreacted cyclohexane, partial recovery of Co(II) catalyst due to its easy discharge with the salts leaving the process, and use of 180 Kg of NaOH to produce a single Kg of KA oil; this in turn generates 1100 Kg of alkaline waste [14]. The environmental and economical shortcomings of the industrial scale selective oxidation of cyclohexane to KA oil were reduced by using a heterogeneous catalyst. The catalytic system involving noble metals supported on oxides, zeolites, and aluminophosphates has afforded high activities and selectivity for KA oil. However, the high cost and leaching tendency of these catalysts make them unsuitable for their large scale applications. Besides, other catalytic formulations based on transition metals such as Cr, Co, Cu, Ta, and Nb have displayed only modest yields. Moreover, most of these catalysts have been utilized in the presence of a solvent [15, 16] and an expensive oxidant [17]. Several catalytic systems, such as FeRu, FeCo nanoclusters, supported Co catalyst, polymer supported cobaltous palmitate, and Co-salen complex immobilized on silica [18], Au/MCM-41 [13], gold nanoparticles immobilized upon mesoporous silica [19], Au nanoclusters on hydroxyapatite [17], metallophthalocyanines supported on γ -alumina [20], and chromium containing silicate [21], have been devised in solvent-free condition and presence of molecular oxygen. These catalysts in general have limitations of poor catalytic activity, loss of sensitivity, low selectivity, and high cost. The catalytic oxidation of hydrocarbons with AC in the presence of molecular oxygen (AC/O₂) has been considered one of the most challenging tasks in the field of catalysis [22]. The development of catalytic processes with nonmetal catalysts for the selective functionalization of alkane (C-H) is a goal of modern chemistry that has long been pursued [23]. Thus, the use of a tuned AC for solvent-free oxidation of cyclohexane to KA oil will be an interesting issue.

In the current work, AC from peanut shells was utilized as a metal-free catalyst for the solvent-free oxidation of cyclohexane to KA oil in the presence of oxygen under mild reaction conditions. The reaction parameters were optimized and the catalytic efficiency was found in terms of productivity. The ease of preparation, sufficient activity, low cost, recyclability, nonleaching, and ecofriendly nature make AC a useful catalyst for solvent-free oxidation of cyclohexane.

2. Experimental

2.1. Materials. Milled peanut (*Arachis hypogaea*) shell (local market), phosphoric acid (H₃PO₄, Sigma-Aldrich), sodium hydroxide (NaOH, Sigma-Aldrich), cyclohexane (C₆H₁₂, Sigma-Aldrich), cyclohexanol (C₆H₁₂O, Sigma-Aldrich), and cyclohexanone (C₆H₁₀O, Sigma-Aldrich) were used as received. Hydrogen, oxygen, and nitrogen gases were supplied by BOC Pakistan and were further purified with



SCHEME 1: Cyclohexane to KA oil conversion in the presence of AC.

appropriate filter. Triple distilled water (TDW) was used for preparation of catalyst.

2.2. Synthesis of the Catalyst. The raw materials (200 g) were purified and dried overnight at 105°C in an oven. The sample was soaked in H₃PO₄ (15%) for 24 hours, in the 1:1 ratio (g of peanut shell/mL of acid solution), washed in a modified soxhlet apparatus until reaching neutral pH, and subsequently carbonized in a tube furnace (reactor: quartz, diameter of 4 cm, length 50 cm) at 380°C under inert atmosphere in 1 hour. The precursor weight was reduced to 22 g, after carbonization. The sample was activated with H₂O₂ in a sonicator (ks 300, KUM SUNG ultrasonic, Korea) for 30 minutes. Finally the AC was washed in a modified soxhlet apparatus, dried, and meshed (US standard sieves). Furthermore the thermal treatment of sample was performed at 580°C with a ramp of 5°C/min and held for 2 h under N₂, in order to tune the surface of AC for desired functional group (quinone). The weight of the sample was 16.3 g after activation and high temperature treatment, which shows 91.8% weight loss.

2.3. Characterization of the Catalyst. The surface morphology of the AC was investigated by using scanning electron microscopy (SEM, JSM5910, Jeol, Japan). The elemental composition of AC was recorded by using Energy Dispersive X-ray Spectroscopy (EDS, I17 INCA200/Oxford instruments, UK). The X-ray analysis was performed by X-ray diffractometer (XRD, Rigaku D/Max-II, Cu Tube, Japan). The functional groups on the surface of AC were examined by Fourier Transform Infrared Spectrometer (FTIR, 120 Prestige, Shimadzu, Japan). The percent weight loss with heat was carried out by a TGA thermal analyzer (PerkinElmer, Thermal Analysis, Japan) in a temperature range of 0–1000°C under the N₂ flow at a rate of 10°C/min. Surface area of the AC was measured by using Quanta chrome (Nova 2200e) surface area analyzer.

2.4. Catalytic Test. The cyclohexane (12.5 mL) and AC (0.4 g) were loaded to a self-designed double-walled three-necked batch reactor. The mixture was stirred in the presence of molecular oxygen (40 mL/min) at 75°C for 14 hours (Scheme 1). The reaction was also performed in the presence of base NaOH: 0.2 mmole in the same set of reaction parameters. The conversion of cyclohexane to KA oil was analyzed by gas chromatography (GC, Clarus 580, Perkin Elmer, USA) using cross-linked methyl siloxane capillary column (30 m, 0.32 mm internal diameter, and 0.25 μ m film thickness), connected with flame ionized detector (FID).

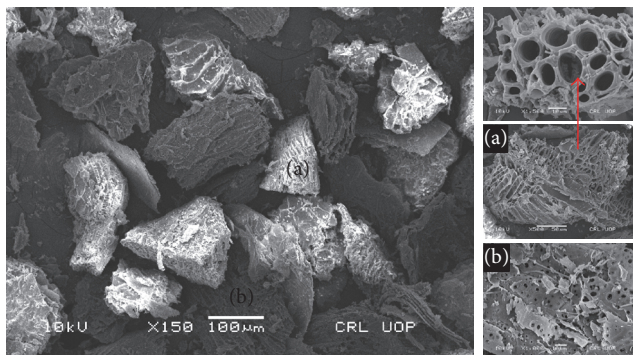


FIGURE 1: SEM images of the AC at different magnification. (a) and (b) represent the magnified area marked in large image.

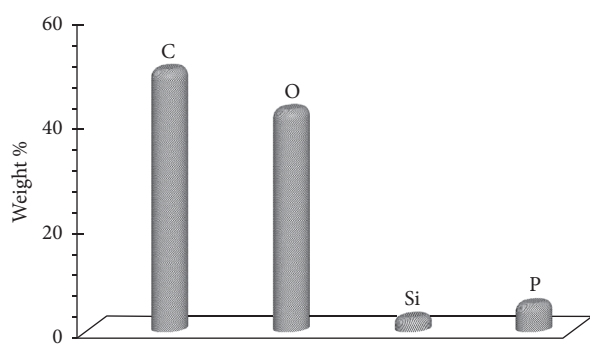


FIGURE 2: Elemental analysis of AC.

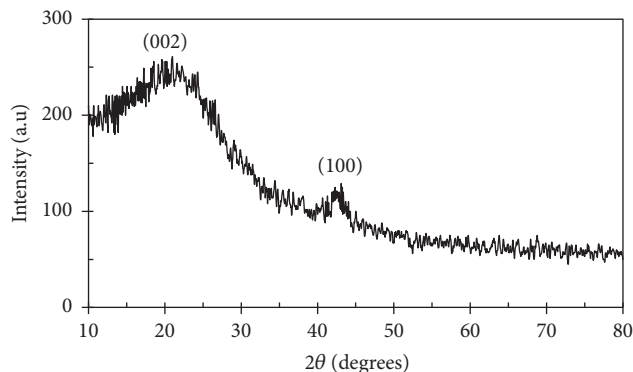


FIGURE 3: XRD pattern of AC.

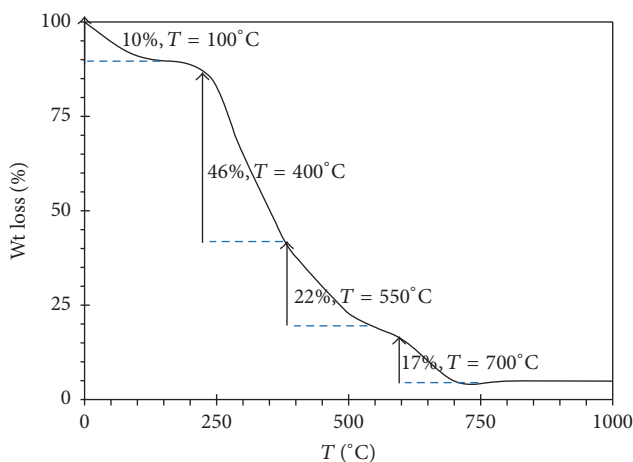


FIGURE 4: Thermogram of AC obtained at $T = 25\text{--}1000^\circ\text{C}$.

3. Results and Discussion

3.1. Characterization of the Catalyst. The surface morphology of AC was analyzed by SEM. SEM images reveal the porous structure, blend of micro-/mesopores with cross link channels connected with the internal surface of AC as shown in Figure 1. High magnification shows the presence of cavity ranging from 2 to 10 μm , which provide easy access to internal micro- and mesopores [22]. Furthermore, the EDX analysis (Figure 2) shows traces of phosphorus and silica; those are the major contents of peanut shells.

BET surface area of AC (1195 m^2/g) was investigated by N_2 adsorption/desorption, -196°C , with particle size ranging from 75 to 106 μm . Chen et al. have reported that the surface area does not play a major role in catalysis through activated carbon. Although the oxygen containing surface functional group plays a crucial role in catalysis [25].

Figure 3 shows the XRD pattern of AC. The broad peak observed around $2\theta = 24^\circ$ corresponding to the reflection of (002) plane is due to the amorphous structure of AC while weak and broad peak $2\theta = 42^\circ$ due to the reflection of (100) plane is attributed to graphite-like structure [28, 29].

To investigate the weight loss of AC with rise in temperature until reaching 700°C is presented in Figure 4. First weight loss of AC was observed (10%, range $28\text{--}100^\circ\text{C}$) due to evaporation of water from the surface. Second and apparent weight loss (46%, range $100\text{--}400^\circ\text{C}$) may be due to the loss of bulk water and decomposition of hemicellulose. In this region

AC was deprived from carboxylic functional group [30]. The third and crucial weight loss (22%, range $400\text{--}550^\circ\text{C}$) was attributed to carbonization process. In this region most of the functional groups were converted to CO and CO_2 [31]. The final weight loss (17%, $550\text{--}700^\circ\text{C}$) most probably due to the conversion of AC to graphite-like structure and ethereal functional group disappeared. After 700°C the weight loss became flattened till reaching 1000°C ; in this region the quinonic functional group was also stable [32, 33]. The catalytic activity of AC in the oxidation reaction mainly depends on oxygen containing surface functional groups. The thermal stability of oxygen containing functional groups on the surface of AC at higher temperature was investigated widely [34]. Thus, the presence of quinonic groups on the surface of AC could play an effective role in catalysis.

The FT-IR spectra, in Figure 5(a), show peaks at 3430 cm^{-1} (NH stretching), 1616 cm^{-1} , (NH bending), 2925 cm^{-1} (C-H stretching), 2380 cm^{-1} (CO_2 asymmetric stretching), 1516 cm^{-1} (stretching of N=O), 1516 (asymmetric stretching N=O), 1386 cm^{-1} (CH_3 bending), 1251 (C-C Skeletal), 1082 cm^{-1} (C-N stretching), and 820 cm^{-1} (N-H out-plane bending) vibrations, while the spectra in Figure 5(b) present peaks at 3772 cm^{-1} (isolated O-H group), 3677 cm^{-1} (Si-OH), 3440 cm^{-1} (OH), 2532 cm^{-1} , 2365 cm^{-1} ,

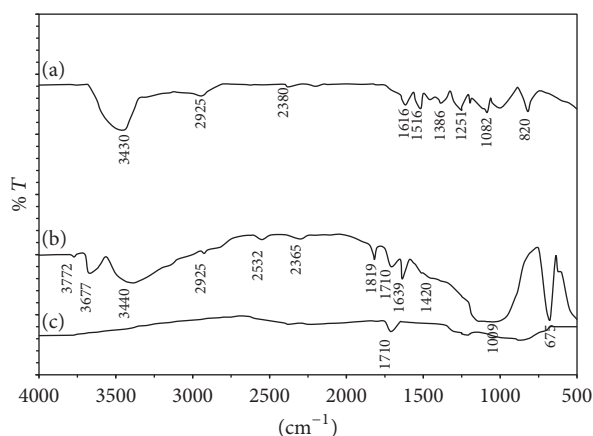


FIGURE 5: FTIR spectra of (a) carbonized carbon, (b) activated carbon (H_2O_2), and (c) thermally activated carbon.

1819 cm^{-1} , and 1639 cm^{-1} ($\text{C}=\text{O}$, stretching), 1420 cm^{-1} ($\text{C}-\text{O}$ and $\text{C}=\text{O}$ highly conjugated stretching), 1009 cm^{-1} ($\text{C}-\text{O}$), and 675 cm^{-1} ($\text{Si}-\text{O}-\text{Si}$) vibrations. Figure 5(c) shows that activated carbon treated at high temperature (580°C) lost almost oxygen containing functional group except quinonic functional group. Figueiredo et al. [24] reported that with continuous thermal treatment the oxygen containing functional groups decompose to CO and CO_2 at different range of temperature. Among these functional groups quinone decomposes to CO at high temperature, $700\text{--}1100^\circ\text{C}$, which is in close agreement with the result of current studies.

3.2. Optimization of Reaction Parameters. The oxidation of cyclohexane to KA oil in solvent-free condition was carried out under different reaction parameters for optimization of reaction parameters. The effect of time was investigated in the range of 2–16 hours at constant temperature of 75°C . Figure 6(a) shows almost linear increase in conversion as time progressed which saturated at time 14 hrs, while the selectivity of product decreased because of the deep oxidation of reactant to adipic acid.

The effect of partial pressure of oxygen in the range of 0–760 Torr was investigated. The conversion was increased with increase in $p\text{O}_2$ up to 570 Torr and beyond that the conversion was decreased because of the surface saturation with oxygen as shown in Figure 6(b). The effect of oxygen flow rate was determined on oxidation of cyclohexane to KA oil. The conversion increment was observed linearly with oxygen flow rate, shown in Figure 6(c). Thus, 40 mL/min was selected as optimum flow of oxygen for further reactions because at high flow rate the selectivity of product was declined.

The oxidation of cyclohexane was carried out at different temperatures, from 45 to 85°C for 14 hours. The conversion increased with an increase in temperature linearly up to 75°C and then separated at higher temperature. The selectivity of the reaction was strongly depending on the temperature and shows inverse relationship with temperature as shown in Figure 6(d). Effect of catalyst loading was determined by adding different amount of catalyst to the reaction mixture

at the same reaction conditions. Figure 6(e) shows that the oxidation of cyclohexane was increased with an increase in catalyst loading. The maximum conversion of cyclohexane was achieved by adding 0.4 g of catalyst at 75°C . Further loading of catalyst decreased the conversion of cyclohexane, which may be due to the less collision of reactant molecules and catalyst surface because there were more catalyst surface active sites available and reacting molecules almost remain constant. The effect of stirring on cyclohexane to KA oil conversion showed that the conversion has direct relationship with stirring while selectivity rapidly decreased with increase in stirring speed (Figure 6(f)). The optimum stirring speed was considered 1100 rpm for further studies. Figures 6(a)–6(f) show the optimization of reaction parameters, such as temp, 75°C ; time, 4 hrs; $p\text{O}_2$, 760 Torr; flow of oxygen, 40 mL/min; catalyst loading, 0.4 g; and stirring, 1100 rpm, which were used for all proceeding experiments otherwise specified.

3.3. Catalytic Activity of the Catalyst. Figure 7(a) shows the product distribution as a function of oxygen pressure. Liquid phase oxidation of cyclohexane to KA oil over AC in solvent-free condition in the presence of molecular oxygen shows maximum conversion of 10.35% and the productivity = $2.14\text{ mmol/g}\cdot\text{h}$ in the absence of any initiator, promoter, or base, while using NaOH in the reaction keeping other parameters constant; the conversion and productivity were 23.5% and $4.85\text{ mmol/g}\cdot\text{h}$, respectively (Figure 7(b)). The enhanced conversion with NaOH was due to the facilitation of the deprotonation. Furthermore the conversion of 3.5% and 2.3% was observed in the presence of air and nitrogen, respectively. The oxidation in nitrogen may be due to the oxygen functional groups on the surface of AC.

On the surface of AC, oxygen containing functional groups are responsible for the oxidation of cyclohexane to cyclohexanol and cyclohexanone [35]. It is widely reported that the surface of activated carbon has strong interaction with molecular oxygen through oxygen containing functional groups like carbonyl, ketone, and quinone [36–39]. Furthermore, Cao et al. show that oxidation reaction occurred through oxygen containing surface functional groups of AC while these functional groups were regenerated through molecular oxygen [36]. In the recent studies it was explored that, among other oxygen containing groups, quinonic group was the most stable and major source for the oxidation of cyclohexane. Fenton-like mechanism of quinone/hydroquinone system was the most probable route for propagation of cyclohexane oxidation. Quinone was regenerated from hydroquinone through continuous oxygen bubbling in reaction mixture [40]. The surface functional groups (variety/density) can be tuned through chemical/thermal treatment [35]. In the recent studies, generated oxygen functional groups on the surface of AC were tuned with thermal treatment as shown in TGA. The activated carbon was treated at high temperature 580°C ; therefore the only existing oxygen containing functional group would be quinone. Marchon et al. [33] have reported the stability of quinonic functional group at high temperature (700°C). Similarly Hoffman and coworkers show the stability of quinonic

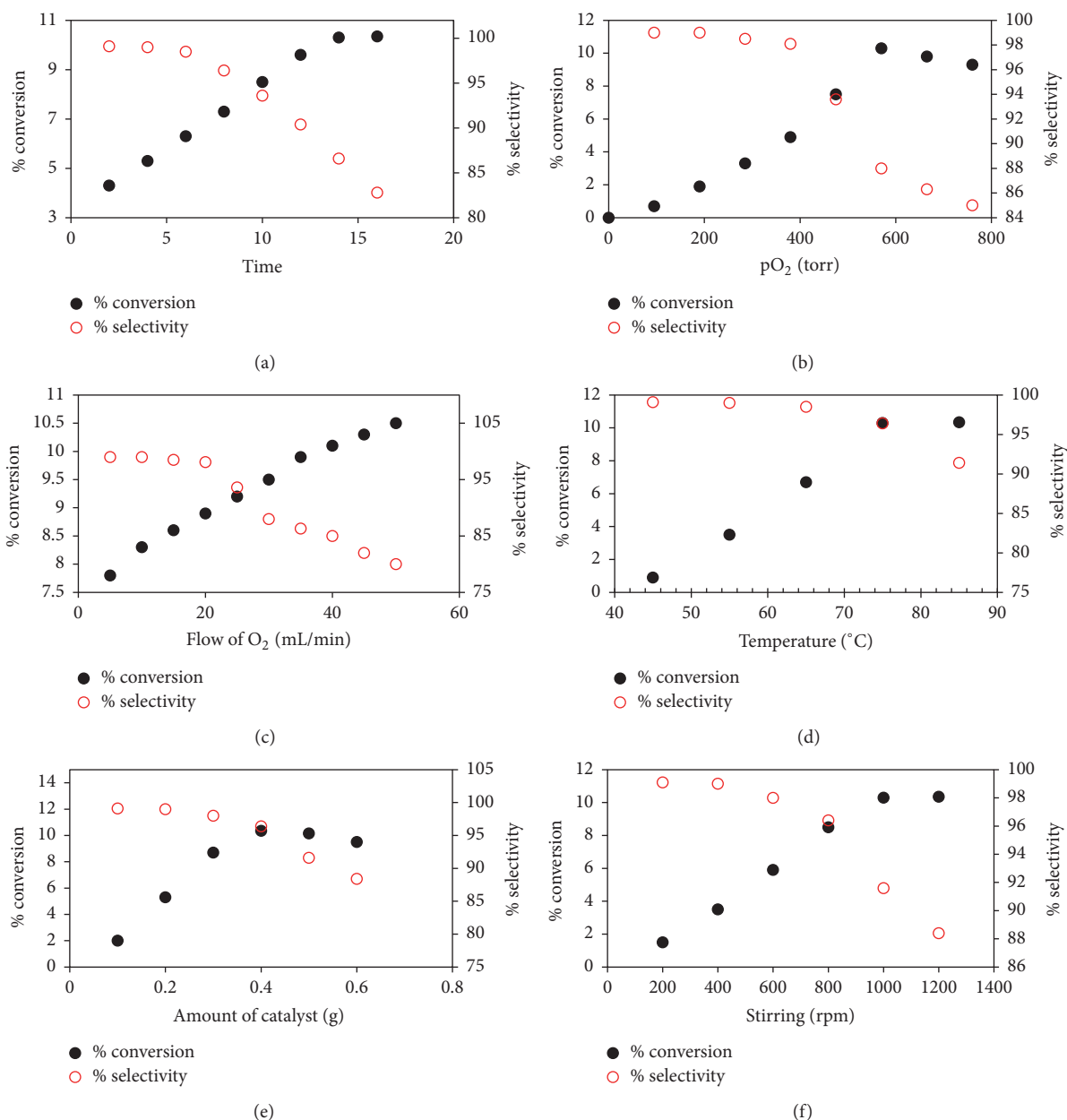


FIGURE 6: Reaction parameters: (a) time, (b) partial pressure of oxygen, (c) flow of oxygen, (d) temperature, (e) catalyst loading, and (f) stirring of cyclohexane to KA oil conversion.

functional group up to 800 $^{\circ}C$ [32]. Therefore, to sum up, the oxidation of cyclohexane to cyclohexanol and cyclohexanone follows the mechanism shown in Scheme 2.

Activated carbon as a catalyst was used in several studies for oxidation reaction of various alcohols and hydrocarbons. The catalytic activities of the AC in these studies were compared on the basis of productivity (mmol/g-h) value as presented in Table 1. Donnet used AC for aerobic benzylic oxidation of 2-benzylbenzo[d]imidazoles in reaction conditions: substrate, 2 mmol; AC, 60 mg; time, 12 hrs; temp, 80 $^{\circ}C$; and observed maximum productivity, 0.35 mmol/g-h [27]. Similarly AC was used as a catalyst for oxidation of benzyl alcohol in different studies with productivity

values (0.11 mmol/g-h and 0.506 mmol/g-h), respectively [2, 26]. Sun et al. [23] reported maximum productivity value (28.8 mmol/g-h) for AC used for oxidation of cyclohexane in acetonitrile with TBHP. Although in the study a high productivity value was observed, the use of TBHP makes the reaction impractical due to the concern of environmental hazard. In another study, Watanabe and coworkers studied the catalytic activity of activated carbon oxidized cinnamyl alcohol in ethanol (5 mL), substrate (1.1 mmol), AC (0.1 g), temperature (80 $^{\circ}C$), and time (15 h) which achieved the productivity value of 0.15 mmol/g-h [35].

3.4. Activation Energy. Figure 8 shows the activation energy of reaction measured for oxidation of cyclohexane at different

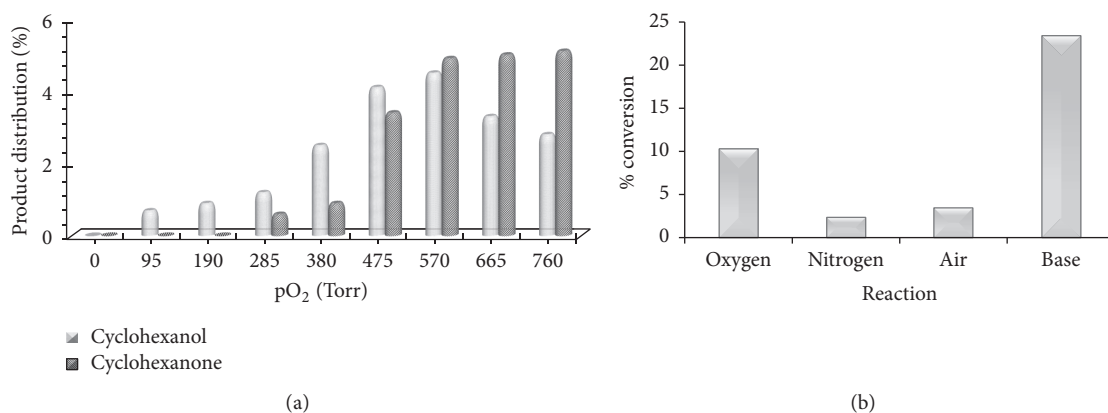
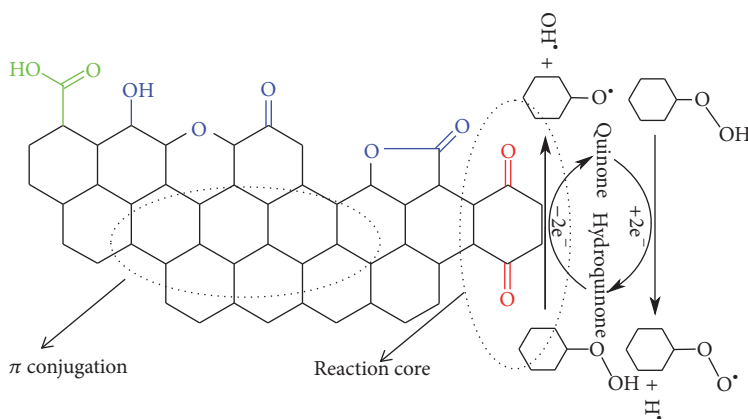


FIGURE 7: (a) Cyclohexanol and cyclohexanone formation as a function of oxygen. (b) Cyclohexane to KA oil conversion in oxygen, nitrogen, air, and base.

TABLE 1: AC-catalyzed organic substrates, with productivity and reaction conditions.

S. number	Oxidation reaction	Productivity*	Reaction condition	Ref
1	Aerobic benzylic oxidation of 2-benzylbenzo[d]imidazoles	0.35	Reactant: 2 mmol; AC: 60 mg; time: 12 hours; temp: 80°C	[24]
2	Aerobic oxidation of benzyl alcohol	0.11	Reactant: 0.184 mmol; AC: 0.1 g; time: 3 hours; temp: 80°C	[25]
3	Oxidation of cyclohexane	28.8	Reactant: 59 mmol; acetonitrile: 10 mL; TBHP: 5 mL; O ₂ : 30 mL/min, 70°C, 2 hours	[26]
4	Oxidation of benzyl alcohol	0.506	Reactant: 1.1 mmol; AC: 100 mg; ethanol: 5 cm ³ ; temp: 120°C; time: 5 hours	[27]
5	Oxidation of cinnamyl alcohol	0.15	Reactant: 1.1 mmol; AC: 100 mg; ethanol: 5 cm ³ ; temp: 80°C; time: 15 hours	[27]
6	Oxidation of cyclohexane	2.14	Reactant: 115.56 mmol; AC: 0.4 g; temp: 75; time: 14 hours; pO ₂ : 760 Torr	Current study
		4.85	Reactant: 115.56 mmol; AC: 0.4 g; temp: 75; time: 14 hours; pO ₂ : 760 Torr; NaOH: 0.2 mmol	

*Productivity (mmol g⁻¹ h⁻¹) = mmol of product/catalyst (g) × time (h).



SCHEME 2: Proposed mechanism for oxidation of cyclohexane with quinonic group of AC.

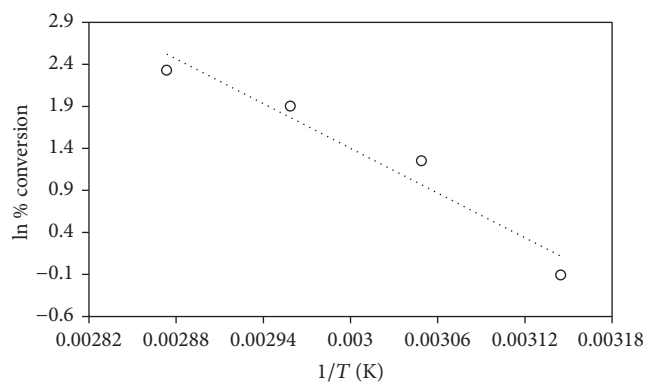


FIGURE 8: Arrhenius plot of AC-catalyzed conversion of cyclohexane to KA oil.

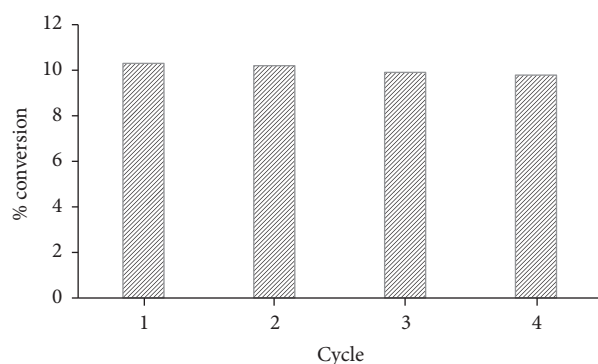


FIGURE 9: Recycling of AC for cyclohexane to KA oil conversion.

temperature (318–348 K) at standard reaction conditions: substrate, 115.56 mmol; AC, 0.4 g; temp, 75°C; time, 14 hrs; and p_{O_2} , 760 Torr. The activation energy was found to be 71.2 kJ/mol. This data was in agreement with effect of stirring discussed earlier suggesting that the reaction was in kinetic control regime.

3.5. Reusability of Catalyst. The activated carbon was used as a catalyst for oxidation of cyclohexane to KA oil in optimized reaction conditions (reactant, 12.5 mL; AC, 0.4 g; temp, 75°C; time, 14 hrs; p_{O_2} , 760 Torr; stirring, 1100 rpm) to investigate the lifespan of the catalyst. The catalyst was used four times for oxidation reactions after simple drying in an oven, under the same reaction condition, and the catalytic activity of activated carbon remained unaltered, shown in Figure 9.

4. Conclusion

Activated carbon was synthesized by chemothermal process and used for solvent-free oxidation of cyclohexane at low temperature with molecular oxygen. Activated carbon was tuned with thermal treatment for development of quinonic functional groups on the surface. Optimal reaction parameters were set up as follows: reactant, 115.56 mmol; AC, 0.4 g; temp, 75; time, 14 hours; p_{O_2} , 760 Torr; stirring, 1100 rpm. The catalytic activity of catalyst was compared with reported literature on the basis of productivity which shows

importance of current study. The catalyst was reused several times which shows durability of the catalyst. The mechanistic proposals of the studies show that the quinonic functional group is the best reaction core for oxidation of cyclohexane with regenerative nature with molecular oxygen. The AC was found as truly heterogeneous catalyst with extended lifespan.

Conflicts of Interest

The authors declare no conflicts of interest.

Acknowledgments

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