Synthesis and Catalytic Activity of Polymer-Anchored Metal Complex for Oxidation of Cyclohexane

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ABSTRACT: Catalytic oxidation of cyclohexane was investigated over polymer-anchored Co(II) catalyst prepared by modification of polymer surface by NO_x and subsequent functinalization by amination. The catalyst characterized by various techniques, such as elemental analysis, atomic absorption spectroscopy, Fourier transform infrared spectroscopy (FT-IR), thermo-gravimetric analysis, and scanning electron microscopy confirmed the modification of polymer surface and bond formation between functionalized resin and metal ion. The oxidation of cyclohexane using molecular oxygen (O_2) as an oxidant was studied in the temperature and pressure range of 373–413 K and 1.0–1.4 MPa, respectively. The maximum cyclohexane conversion of 18.4% was obtained at 413 K and 1.2 MPa pressure. Cyclohexanone and cyclohexanol were found as the main reaction products with 93.0% selectivity. No appreciable change in catalytic activity and on product selectivity was observed after the catalyst recycled three times. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2013

INTRODUCTION

The oxidation of cyclohexane is an important reaction from the industrial point of view.[1,2] The oxidation products, cyclohexanol and cyclohexanone, are valuable chemical intermediates for the preparation of adipic acid and caprolactam, which are further used in the manufacture of nylon-6,6 and nylon-6 polymers. Literature studies have revealed the formation of several minor products (valeric acid, butyric acid, cyclohexene) along with main reaction products.[3–5] Industrially, cyclohexane is oxidized at 423–453 K and 1–2 MPa air pressure using cobalt naphthenate as catalyst with a low conversion (3–4%) and moderate selectivity (70–85%) to reaction products, cyclohexanol and cyclohexanone. The reaction is conducted at high temperature and pressure, therefore this causes increase in both operating and installation costs and making the complete process uneconomical. It is therefore desirable to develop an effective catalytic process with relatively high conversion and selectivity keeping the safety of the process in concern as well.

Various researchers have worked on homogeneous catalysts for various oxidation reactions.[6–8] However, to overcome the problem of recovery of catalyst from the reaction products and disposal of solid waste in homogeneous catalysts, researchers have developed more efficient and environment friendly heterogeneous catalysts.[9–12]

Heterogeneous catalysts are highly active, selective, recyclable, and can be easily recovered from the reaction mixture.[13,14] They are nontoxic and generate less solid waste compared to unsupported catalysts; therefore they have emerged as "green" technology. The commonly used heterogeneous catalysts comprise metal oxides, metal cations, and complexes incorporated in inorganic supports such as carbon, silica, alumina, zirconia, and zeolites.[15–18]

Since last two decades, researchers have tried to use polymers as a support because of easy recyclability and tailor-made properties, which can be changed according to the application. Though the researchers have shown the application of polymeric supports for various reactions like epoxidation, hydrogenation of alkenes, olefins,[19–21] few studies were conducted on oxidation of cyclohexane using polymeric supports at high temperature and pressure.[22,23] The support that has been used most extensively for the synthesis of polymer supported catalysts are macroporous polystyrene beads cross linked with divinylbenzene. Jayaswal et al.[24] studied the oxidation of cyclohexane using polymer-anchored cobaltous palmitate schiff base catalyst and reported cyclohexanone as major product (57% selectivity) with maximum conversion of 20.48% in 10 h using O_2 as oxidant. Few researchers used biopolymers such as chitosan based on schiff base for cyclohexane oxidation.[25,26] Loncarevic et al.[27] studied the oxidation of cyclohexane using Co(II) and Cr(II)

ions supported on poly(4-vinylpyridinium-*co*-divnylbenzene). Chromium catalyst showed high selectivity to cyclohexanone, whereas cobalt catalyst showed higher catalytic activity.

In this article, we report the synthesis of polymer support based on styrene and divinylbenzene by suspension polymerization technique. The resin is further modified with gas phase nitration using NO_x and subsequent functionalization with hydrazine hydrate as reported by Jayaswal et al.[24] The traditional method of chemical modification of styrene-divinylbenzene copolymers by immobilization of chloromethyl groups is the first step in most of the routes used for functional copolymers preparation. Different chloromethylation methods are described in literature. However, these methods suffer from the use of chloromethyl methyl ether, which is a carcinogenic reagent with rigorous reaction conditions, long reaction time and high cost.[28,29] Therefore we have reported the use of nitrated resin and subsequent functionalization of resin by amination as a precursor for the preparation of heterogeneous catalyst. This method increases the mechanical stability of the resin, reduces the reaction time (8 h) and forms complex with metal salt, which prevents the leaching of the metal during the catalytic reaction. In this article, cobalt metal is loaded on the functional polymer and used for the catalytic activity of cyclohexane oxidation in a batch reactor. The effect of various reaction parameters, i.e., temperature, pressure, and catalyst amount were optimized for maximum conversion and selectivity. The recyclability of the polymer-anchored complex was also evaluated.

EXPERIMENTAL

Materials

Styrene (Sigma Aldrich, Germany, $\geq$ 99%), divinylbenzene (Merck, Mumbai; India, 60%, technical grade), azobis-isobutyonitrile (SAS Chemicals, Mumbai; India), cobaltous chloride (Himedia, Mumbai; India, 99.0%), cyclohexane (Rankem, Mumbai; India, 99.5%), tert-butylhydroperoxide (TBHP) (Acros, USA, 70% in water) were used as obtained. Other chemicals and solvents were of analytical grade.

Preparation of (R_1) Resin for Polymer Support

Polystyrene-divinylbenzene (PS-DVB) copolymers (R_1) were prepared by conventional suspension polymerization technique using azobis-isobutyronitrile (AIBN) as initiator. Toluene was added as diluent (porogen agent). In this article, the organic phase was prepared by mixing styrene (280 g, 3.04 mol), divinylbenzene (80 g, 0.62 mol), azobis-isobutyronitrile (4 g, 0.02 mol), and toluene (200 mL). This organic phase was suspended in an aqueous solution containing distilled water (900 mL), sodium sulfate (48 g, 0.034 g mol), calcium carbonate (8 g, 0.08 mol), and gelatin (0.028 g).[24,30]

The suspension copolymerization was carried out in a 2+L reaction flask fitted with a variable mechanical stirrer. The copolymerization was performed at 600 rpm for 4 h in a thermostatically controlled water bath. After this time, the temperature of the reaction mass was increased to 90°C in half an hour, and then it is kept constant for the next 2 h. After the reaction period, the resulting copolymer resin was washed with hot water and methanol to remove the diluents and residual

Table I. Physical Properties of the PS-DVB Resin

Property	
Shape	Spherical
DVB (%)	2.2
Resin size (mm)	0.1–1.0
Cross link density (%)	18.0
BET (m^2/g)	22.6
Pore Volume (cm^3/g)	0.022
Pore size (Å)	34.7
Temperature stability (°C)	$\sim$ 150

monomers. Excess calcium carbonate was removed by treating with $0.1N$ HCl. Finally, the resin was dried in an oven at 60°C for 12 h. The resins, obtained as spherical beads were separated by sieving. The physical properties of the PS-DVB resin are shown in Table I.

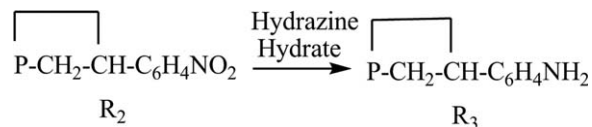### Gas Phase Nitration of PS-DVB Resins using $NO_x(R_2)$

Direct gas phase nitration of PS-DVB resin using mixture of NO and NO_2 (called NO_x) is already reported in the literature.[24]

$$P\text{-}CH_2\text{-}CH\text{-}C_6H_5 \xrightarrow{\text{NOx}} P\text{-}CH_2\text{-}CH\text{-}C_6H_4NO_2$$
$$R_1 \qquad\qquad\qquad R_2$$
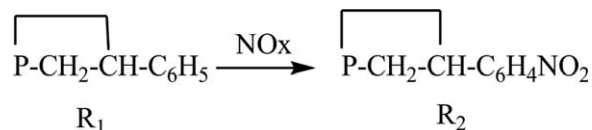
The amount of NO_x consumed in the reaction was determined after nitration at 100°C and unreacted NO_x was determined by adding distilled water (100 mL) in remaining mixture and titrating with $0.1N$ NaOH. After calculation it was found that 90% NO_x was consumed in the reaction.

Amination of Nitrated Resin (R_3)

The NO_2 functional group was reduced to amine groups by reacting the resin with hydrazine hydrate. Resin R_2 (2 g) was placed in a round bottom flask with 50 mL of hydrazine hydrate and the reaction mass was refluxed at 60°C for 4 h in an oil bath. After refluxing was over, the resin was filtered, then properly washed with distilled water and dried. The color of the resin changed from pale yellow to golden yellow.

$$P\text{-}CH_2\text{-}CH\text{-}C_6H_4NO_2 \xrightarrow[\text{Hydrate}]{\text{Hydrazine}} P\text{-}CH_2\text{-}CH\text{-}C_6H_4NH_2$$
$$R_2 \qquad\qquad\qquad\qquad R_3$$

Preparation of Catalyst

The R_3 resin (2.0 g) was allowed to swell in methanol (20 mL) for 30 min and a methanol solution (50 mL) of $CoCl_2.6H_2O$ (1% w/v) was added to resin mixture and the resulting solution was heated at 60°C in a thermostated oil bath for 18 h with continuous stirring. The liquid mixture was then cooled down to room temperature. The catalyst was filtered, washed several
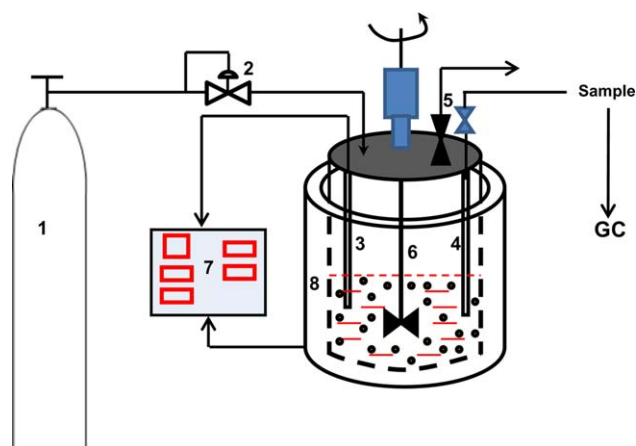
Figure 1. Schematic diagram of reactor setup: **1.** O_2 cylinder, **2.** gas inlet valve, **3.** thermocouple, **4.** sample outlet, **5.** pressure release valve, **6.** stirrer, **7.** control panel, and **8.** heater. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

times with methanol and deionized water to remove excess of cobalt metal and dried in an oven at 80°C for 12 h.
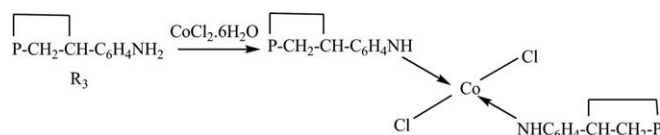
Characterization Techniques

Elemental analysis of the functionalized resin and complex were determined by an Elementar model Vario-EL-III, USA. Metal content of the polymer-anchored complex was estimated by atomic absorption spectroscopy (AAS) (GBC Avanta atomic absorption spectrophotometer, Australia). Typically, 0.1 g of the catalyst sample was digested with 10 mL concentrated HNO_3. The solution was diluted to 50 mL in a volumetric flask using distilled water and analyzed by AAS. The BET surface area was determined by N_2 adsorption/desorption measurement at 77 K on ASAP 2020 (Micromeritics, USA). The samples were degassed at 90°C for 8 h prior to adsorption analysis. The total pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure (P/P_0) of 0.99. Fourier transformed infrared spectroscopy (FT-IR) was used to identify the interactions of the transition metals with the functional groups
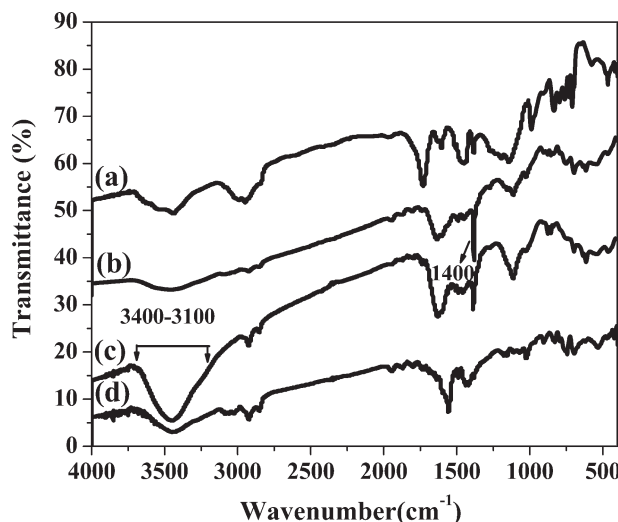

Figure 2. FT-IR spectrum of (a) unmodified resin (R_1), (b) nitrated resin (R_2), (c) aminated resin (R_3), and (d) polymer-anchored catalyst.

present on polymer support. The spectra were recorded using Nicolet (NEXUS Aligent 1600, USA) from KBr pellets in the range of 4000–400 cm^{-1}. The morphology of the samples was recorded by Scanning Electron Microscopy LEO 435 VF, England. The samples were coated with a thin film of gold to prevent surface charging. The thermal stability of functionalized resin and the catalyst was determined by thermogravimetry in Perkin Elmer (Pyris Diamond, USA) equipment with an accuracy of 1 μg. For each run, 10 mg catalyst was heated from room temperature to 800°C, at a heating rate of 10°C min^{-1}. α-Al_2O_3 was used as a reference.

Oxidation of Cyclohexane

The oxidation of cyclohexane was carried out in a 300 mL batch stainless steel Parr reactor (4843, USA) using O_2 as oxidant. The reactor was initially charged with 100 mL cyclohexane, 100 mg of catalyst, and 1.0 MPa oxygen pressure and then heated to the required temperature for the desired reaction time. The O_2 gas absorption was noted by observing the decrease in the reactor pressure. The schematic diagram of the experimental set up is shown in Figure 1.

The products were analyzed by gas chromatograph (Netel, India) equipped with SGE capillary column (0.25 mm i.d., 30 m long, 0.25 μm thickness) and a flame ionization detector using N_2 as carrier gas. The oven temperature was programmed

Table II. Physical and Analytical Data of Polymer-Anchored Resin at Various Modification Stages and of Polymer-Anchored Metal Complex

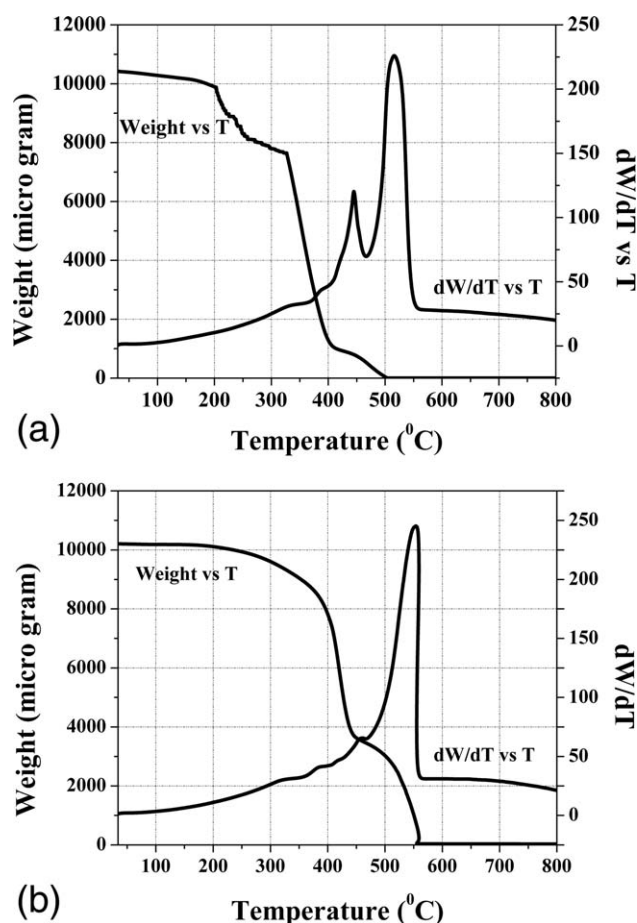|	Colour	Elements (%)			Metal loading (wt %)	S_{BET} (m²/g)	Pore volume (cm³/g)	Pore size (Å)
		C	H	N				
PS-DVB Resin (R_1)	White	80.5	10.9	0.4	-	22.6	0.0224	34.7
Nitrated Resin (R_2)	Pale Yellow	78.3	6.7	4.4	-	15.8	0.0187	32.6
Aminated Resin (R_3)	Golden Yellow	76.7	8.3	6.8	-	11.4	0.0123	31.7
Polymer anchored Co Complex	Brown	75.2	7.2	5.6	1.7	9.3	0.0096	28.3

Figure 3. Thermo-gravimetric analysis and DTA profiles of (a) aminated resin (R_3) and (b) polymer-anchored catalyst.

at 80°C for 1 min and then raised to 180°C at a ramp rate of 10°C/min. The injector and detector temperatures were 220°C and 260°C, respectively. The products were further confirmed by GC-MS (Perkin-Elmer Clarus 500, USA).

RESULTS AND DISCUSSION

Catalyst Characterization

The physiochemical data of the resin prepared at different stages (R_1, R_2, R_3) and polymer-anchored complex was determined by elemental analysis. The metal content of the polymer complex was determined by AAS and the results are shown in Table II. The low content of metal (1.7%) is because of limited availability of reactive functional groups during metal anchoring.[31] The BET surface area of unmodified PS-DVB was 22.6 m^2/g, which after subsequent modification and anchoring of metal onto the support, decreased, which may be because of pore blocking. The pore sizes and pore volume were found in the range of 34.7–28.3 Å and 0.0224–0.0096 cm^3/g, respectively.

The FT-IR spectrum of unmodified resin, functionalized resin, and metal complex is shown in Figure 2. The sharp peaks appeared at 700 and 1400 cm^{-1} for the R_2 resin confirmed the presence of NO_2 group on it [Figure 2(b)]. The decrease in the intensity of peaks at 1400 cm^{-1} in the aminated R_3 resin confirmed the presence of NH_2 group [Figure 2(c)]. A broad band

in the 3100–3400 cm^{-1} range may be assigned to the combined mode of the stretching vibration of adsorbed water molecule and NH_2 group [Figure 2(c)].[24] The band appeared in the range of 2700–2900 cm^{-1} in all spectra correspond to (–CH_2) groups.

The stability of polymer-anchored complex was determined by thermo-gravimetric analysis and DTA analysis in the temperature range of 100–800°C as shown in Figure 3. The decomposition behavior of the functionalized resin (R_3) and polymer-anchored metal complex has been compared in order to understand the effect of polymer anchoring [Figure 3(a,b)]. The characteristic weight losses related to physisorbed water were detected between 90°C and 110°C. The weight losses in the temperature range of 200–700°C correspond to the splitting of the functional group (aminated group). The aminated resin decomposed in the temperature range of 320–380°C. After complexation of metal ion on functionalized polymer, thermal stability of the metal complex was improved by 20–40°C. At temperatures higher than 700°C, some residue was found, may be because of the formation of metal oxides.

DTA curve for polymer support as well as polymer-anchored catalyst indicates that all weight loss steps are exothermic in nature.

Scanning electron micrographs for unmodified resin, functionalized resin, and polymer-anchored metal complexes were recorded to observe morphological changes occurring at the different stages of the modification. Figure 4 presents some of the images at different magnifications. Figure 4(a) shows the image of unmodified resin at 17× magnification, whereas Figure 4(b) shows the image at higher magnification (2000×). As expected unmodified resin (R_1) has smooth surface, whereas nitrated [Figure 4(c)], aminated [Figure 4(d)], and polymer-anchored metal complex [Figure 4(e)] showed slight roughening of the top surface. This is possibly because of the interaction of the metal ions with the polymer support that resulted in the formation of the complex.

Catalytic Activity

The catalytic activity of cyclohexane was evaluated using polymer-anchored Co(II) catalyst and molecular oxygen (O_2) as an oxidant. No reaction occurred in the absence of catalyst, indicating the absence of any homogeneous reaction. The reaction was carried out by varying different parameters, such as reaction temperature, pressure, and catalyst amount to optimize the reaction products.

Cyclohexanone, cyclohexanol, and cyclohexyl hydroperoxide (CHHP) were the main reaction products detected during the reaction and the product distribution is shown in Figure 5. The CHHP, an intermediate in the reaction product, on further oxidation converted to cyclohexanol and cyclohexanone.

Elimination of the Effects of the External and Internal Mass Transfer Resistances

For interpretation of kinetics, it was first necessary to ensure that the data obtained were in the kinetic regime. The reaction is under kinetic control regime if both internal and external mass transfer resistances are negligible. Therefore effects of the external and internal mass transfer resistance on cyclohexane oxidation were investigated by varying the stirring speed and the catalyst particle size as shown in Figure 6. Experiments were
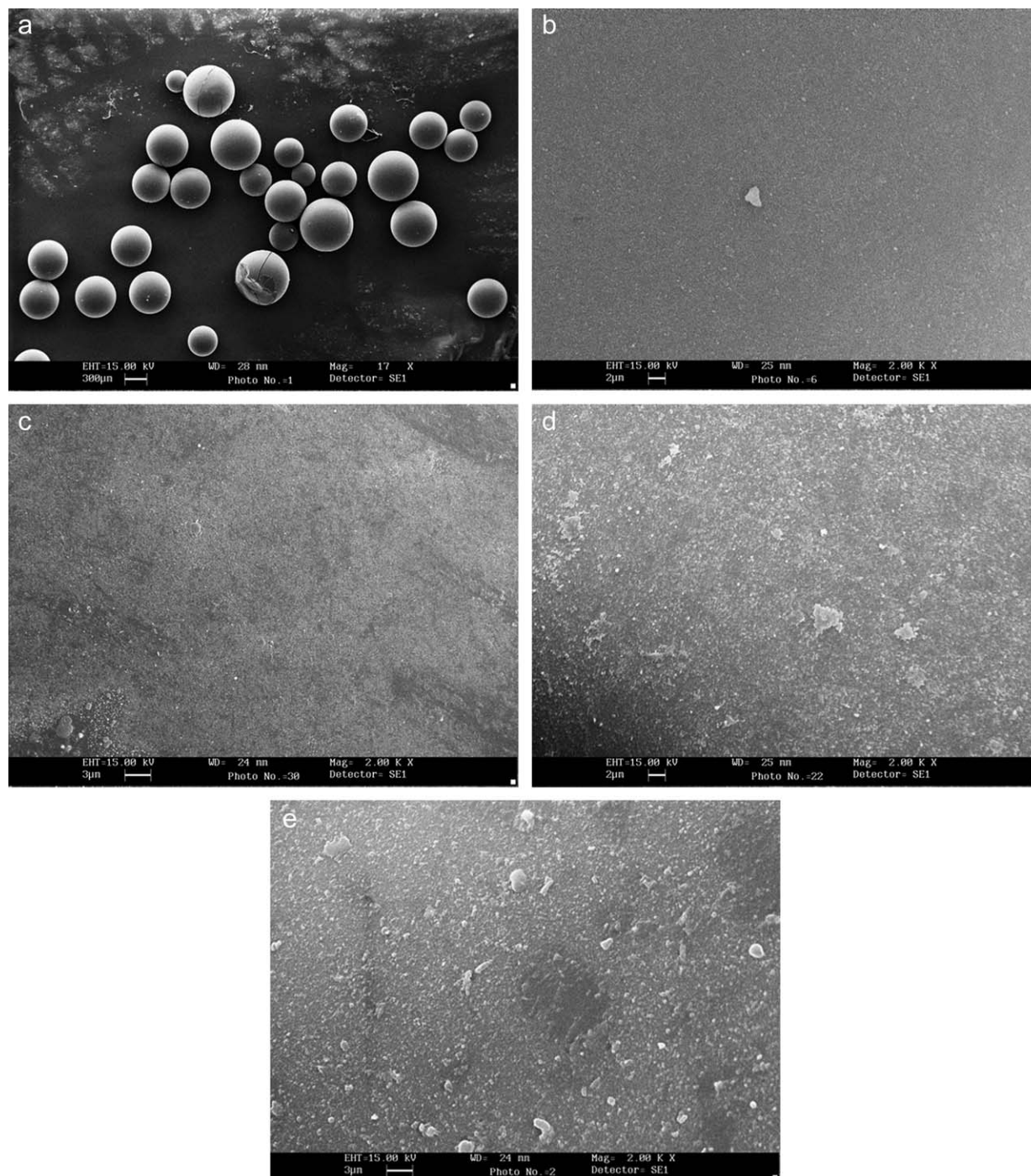
Figure 4. Scanning electron microscopy images of (a) unmodified resin (Magnification 17X), (b) unmodified resin (magnification 2000×), (c) nitrated resin, (d) aminated resin, and (e) polymer-anchored catalyst.

first carried out at 393 K and 1.2 MPa at different stirring speeds to study the effect of external mass-transfer resistance on cyclohexane oxidation. From the experimental data [Figure 6(a)], it was observed that there is no significant effect of stirring speed on cyclohexane oxidation after 600 rpm. All further experiments were, therefore, conducted at 600 rpm.

The catalysts were sieved to different particle sizes: 0.25, 0.6, and 1.0 mm and the cyclohexane conversion obtained with different size catalyst particles are shown in Figure 6(b). The results suggested that internal mass transfer resistance was not present when catalyst particle size was varied. Thus, the catalyst with 0.6 mm particle size was used for further experiments.

Effect of Temperature and Pressure. To study the effect of temperature and pressure on cyclohexane oxidation with O_2 oxidant, both the temperature and pressure were varied simultaneously. The temperature was varied from 373 to 413 K and
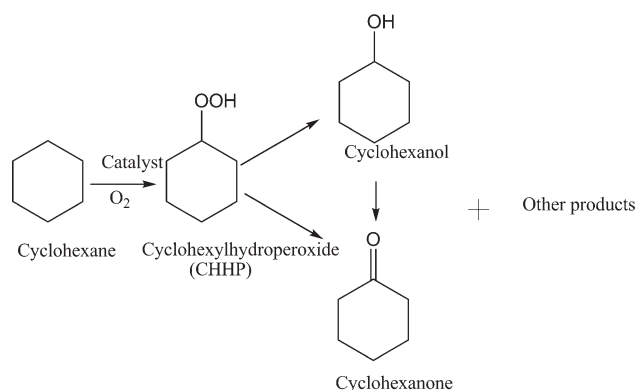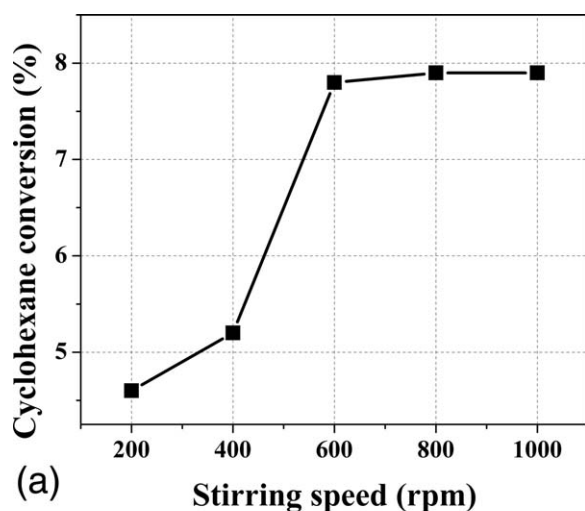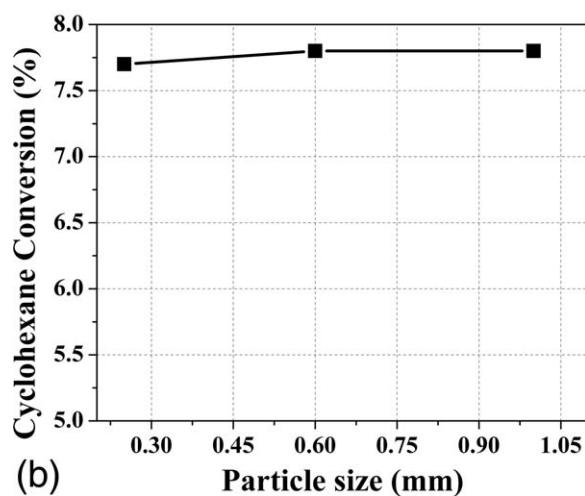
Figure 5. Reaction products from catalytic oxidation of cyclohexane.

pressure from 1.0 to 1.4 MPa using 100 mL cyclohexane and 100 mg catalyst to find the optimal conversion and product selectivity. Initially very low conversion was obtained (~2.0%) in the temperature range of 363–373 K at 1.2 MPa pressure.

Figure 6. (a) Effect of stirring speed on cyclohexane conversion and (b) effect of particle size on cyclohexane conversion. Reaction conditions: cyclohexane: 100 mL, temperature: 393 K, pressure: 1.2 MPa, catalyst: 100 mg.
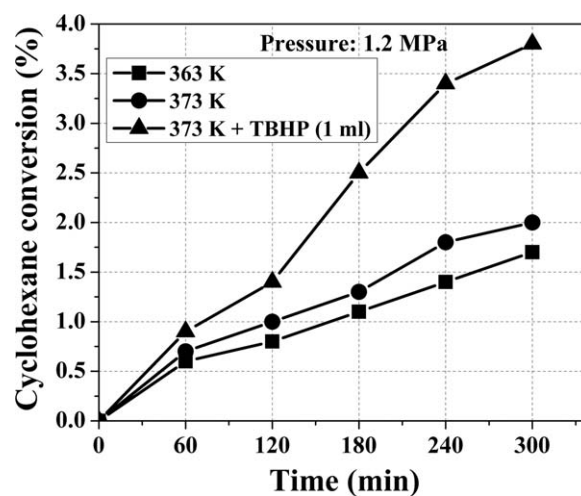

Figure 7. Cyclohexane conversion at low temperatures in the presence and absence of TBHP.

Therefore small amount of TBHP, 1 mL was added as an initiator to remove the induction period and to increase the cyclohexane conversion. As shown in Figure 7, in the absence of TBHP initiator, catalytic activity of catalysts was low. Therefore, all the further experiments were conducted in the presence of TBHP initiator. As the temperature was increased (the pressure also increased), conversion of cyclohexane increased. The results are shown in Figure 8. This phenomenon may be because of that at lower temperature, the energy was not sufficient to activate the oxygen molecules. The conversion increased from 4.0% to 16.8% as temperature was raised from 373 to 413 K and the corresponding pressure increased from 1.0 to 1.4 MPa. Above 413 K, various side products were formed and as a result the color of the reaction mixture changed to dark brown. As a result of this, the reactions were conducted only upto 413 K. Maximum conversion of cyclohexane (16.8%) was obtained at 413 K and 1.2 MPa pressure.

Figure 9 shows the effect of temperature on the selectivity of cyclohexanol, cyclohexanone and CHHP products at 1.2 MPa
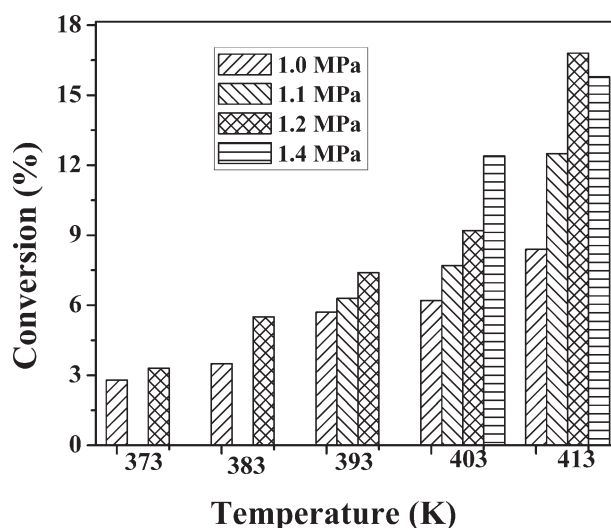

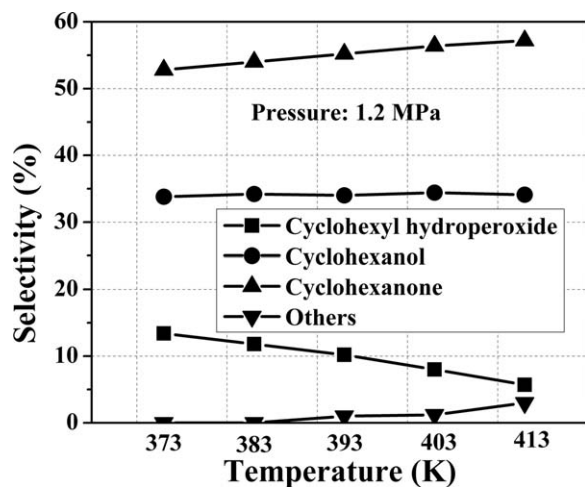Figure 8. Effect of temperature and pressure on cyclohexane conversion.

Figure 9. Effect of temperature on selectivities of CHHP, cyclohexanol, and cyclohexanone at constant pressure of 1.2 MPa.
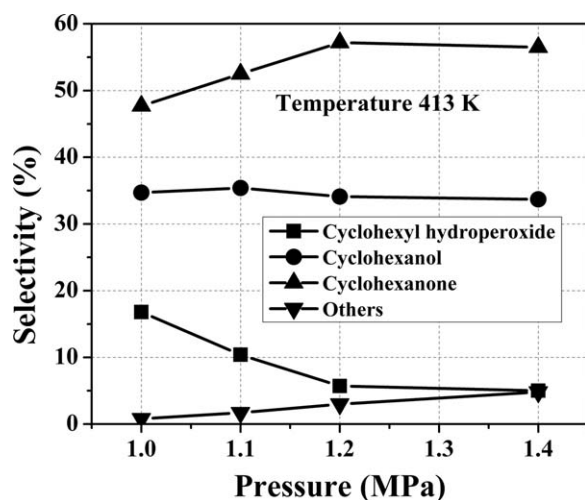

Figure 10. Effect of pressure on selectivities of CHHP, cyclohexanol, and cyclohexanone at a constant temperature of 413 K.
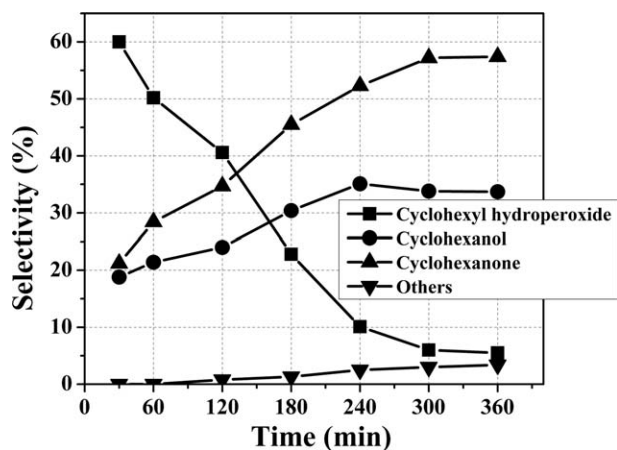

Figure 11. Effect of reaction time on selectivity of products. Reaction conditions: cyclohexane: 100 mL, temperature: 413 K, pressure: 1.2 MPa, catalyst: 100 mg.
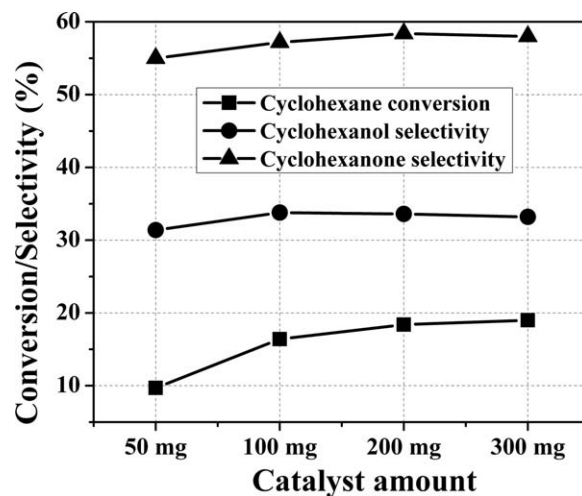

Figure 12. Effect of catalyst amount on cyclohexane conversion and products selectivity. Reaction conditions: cyclohexane: 100 mL, temperature: 413 K, pressure: 1.2 MPa.

pressure. The selectivity of CHHP was higher (13.4%) at 373 K and as the temperature was increased, CHHP selectivity decreased to 5.7% with the increase in selectivity of cyclohexanol and cyclohexanone to 34.1% and 57.2%, respectively.

The effect of oxygen pressure (1.0–1.4 MPa) on products selectivity is shown in Figure 10. The increase in pressure resulted in the increase in selectivity of cyclohexanol and cyclohexanone and the maximum selectivity was found at 1.2 MPa. The result is consistent with the observation that with increase in pressure, the solubility of gas in liquid increases.[32,33] Above 1.2 MPa pressure, the selectivity of cyclohexanol and cyclohexanone remained almost constant, whereas the selectivity of CHHP decreased from 16.4% (1.0 MPa) to 5.0% (1.4 MPa). The decreased selectivity of CHHP was ascribed to the decomposition of CHHP at higher oxygen pressure, with simultaneous increase in selectivity to cyclohexanol and cyclohexanone.
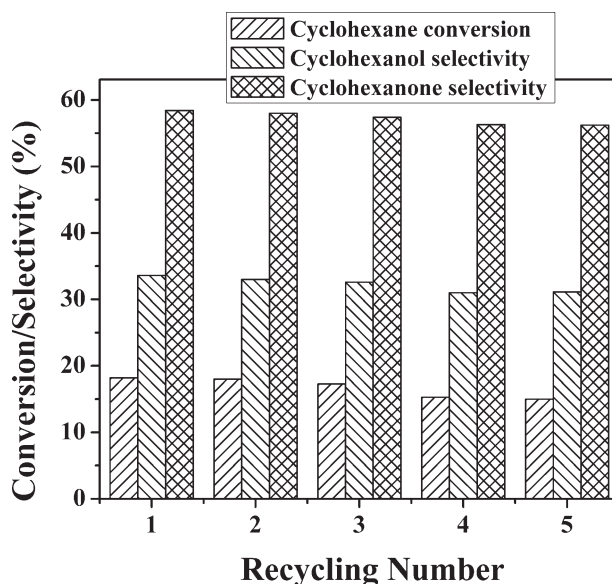

Figure 13. Recyclability of polymer-anchored cobalt catalyst.

Table III. Comparison of this Article with Published Literature

Support	Catalyst	Reaction Conditions	Conv (%)	Cyclohexanone selectivity (%) (K)	Cyclohexanol Selectivity (%) (A)	Combined selectivity (%) (K-A)	Combined yield (%) (K-A)	Reference
Zeolite	Cu(II) complex	Catalyst: 0.75 g, cyclohexane: 25 g, 373 K, 800 psi, 8 h, MeCN: 25 g, TBHP: 0.4 g	14.9	48.5	28.1	76.6	11.4	16
Chitosan (polymer support)	Co(II) complex	Catalyst:2 mg, cyclohexane: 7 ml, 418 K, 1.6 MPa, 4.5 h	10.7	86.2	10.0	96.2	10.3	26
Ti-Zr alloy	Ti-Zr-Co	Catalyst: 40 mg. cyclohexane: 8 ml, 413 K, 2.0 MPa, 6 h	6.8	50.2	40.2	90.4	6.14	6
SiO$_2$	Au nano particles	Catalyst: 50 mg, Cyclohexane: 20 ml, 423 K, 0.8-1.0 MPa	21.0	56.0	34.4	90.4	19.4	18
Polystyrene divinylbenzene (PS-DVB)	**Co(II) complex**	**Catalyst: 200 mg, cyclohexane: 100 ml, 413 K, 1.2 MPa, 5 h**	**18.4**	**58.4**	**33.6**	**92.0**	**17.0**	**Present work**

However, excessive oxygen pressure could lead to the formation of acids.

Effect of Reaction Time. The effect of reaction time (0–6 h) on cyclohexane oxidation was studied at 413 K and 1.2 MPa pressure. Figure 11 showed that CHHP is a predominant product in the first hour of the reaction. As the reaction progressed, selectivity to cyclohexanol and cyclohexanone increased, which showed the decomposition of CHHP to cyclohexanol and cyclohexanone. However after 5 h, the selectivity of CHHP decreased to 5.0% and selectivities of cyclohexanol and cyclohexanone did not change any more with a further prolongation of the reaction time.

Effect of Catalyst Amount. The effect of catalyst amount on cyclohexane oxidation was investigated by varying the catalyst amount in the range of 50–300 mg at 413 K and 1.2 MPa oxygen pressure. Figure 12 showed that cyclohexane conversion increased with increase in catalyst amount from 9.7% at 50 mg to 18.4% at 200 mg. With further increase in catalyst amount to 300 mg, conversion increased marginally to 19.0%. Therefore 200 mg catalyst was chosen as an optimal amount of catalyst. The combined selectivity of cyclohexanol and cyclohexanone increased from 86.4% to 92.0% by varying the catalyst amount from 50 to 200 mg.

Therefore, maximum conversion of cyclohexane oxidation (18.4%) was obtained at temperature 413 K, 1.2 MPa oxygen pressure with 200 mg of catalyst in 5 h. Cyclohexanone (58.4%) and cyclohexanol (33.6%) were obtained as main reaction products with CHHP as intermediate product. High TOF value (597.1 h^{-1}) was obtained for the reaction.

Catalyst Recycling

To study the stability of the catalyst, the polymer-anchored cobalt catalyst was recycled in the batch reactor at 413 K, 1.2 MPa oxygen pressure. In a typical experiment, the catalyst was filtered out after a reaction time of 5 h, washed thoroughly with acetonitrile and dried at 70°C. The catalyst was further analyzed under similar reaction conditions. The results (Figure 13) confirmed that there was no appreciable change in the catalytic activity as well as the product selectivity for three cycles. After three cycles, leaching starts to occur and a slight decrease in catalytic activity was observed. Therefore, the catalyst can be safely used upto three cycles.

Reaction Mechanism

Catalytic oxidation of cyclohexane generally follows the free radical mechanism and to determine whether reaction follows the free radical mechanism, hydroquinone, a free radical scavenger was added during oxidation reaction at optimized reaction conditions. It was found that hydroquinone had a strong inhibitory effect on the oxidation reaction and confirmed that reaction follows free radical chain mechanism.

Therefore, according to the reaction mechanism, TBHP in the presence of metal ions decomposes, generating tert-butoxy radicals that abstract a hydrogen atom from the cyclohexane, forming the cyclohexyl radical, which is the initiating step. The cyclohexyl radical then rapidly reacts with molecular oxygen, generating the cyclohexylperoxyl radical. The cyclohexylperoxyl

radical can then react with another cyclohexylperoxyl radical, forming molecular oxygen and the nonradical products, cyclohexanol, and cyclohexanone.[34,35]

CONCLUSIONS

In this article, formation of polymer-anchored cobalt complex by modification of polymer surface by NO_x and further functionalization by amination was investigated. The catalyst characterized by various techniques confirms the modification of the polymer surface and bond formation between functionalization surface and metal ion. The catalytic activity was determined for cyclohexane oxidation using O_2 oxidant. The maximum conversion of cyclohexane (18.4%) was obtained at 413 K and 1.2 MPa oxygen pressure. Maximum combined selectivity of 92.0% was observed for cyclohexanol and cyclohexanone at these reaction conditions. The catalyst was recycled three times with no appreciable change in catalytic activity and product selectivity was observed.

The result of this article was also compared with the reported literature. Table III presents a quantitative comparison of this article with published literature. It is clear from the table that in this article high conversion and selectivity (yield) is found compared to other reported work except the work presented by Wu et al.[16] They have reported slightly higher conversion and selectivity (yield) compared to this article.

Good recycling efficiency along with high selectivity of the desired products makes polymer-anchored catalysts useful for the synthesis of various fine chemicals under environment friendly conditions.

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