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Efficient catalytic systems based on cobalt for oxidation of ethylbenzene, cyclohexene and oximes in the presence of N-hydroxyphthalimide

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ABSTRACT

The selective oxidation of ethylbenzene and cyclohexene to acetophenone and 2-cyclohexene-1-one using N-hydroxyphthalimide (NHPI) under oxygen atmosphere in the presence of an SiO_2/Al_2O_3-supported cobalt catalyst occurs with conversions of 83 and 75% and selectivities of 99%. The supported cobalt is also a suitable and efficient catalyst for the oxidative deprotection of oximes to the corresponding carbonyl compounds. The reaction conditions have been optimized considering the effect of various parameters such as reaction time, amount of catalyst, temperature and reusability of the catalyst after several runs. Moreover, some possible mechanisms for the oxidation of ethylbenzene, cyclohexene and oximes have been proposed.

1. Introduction

Oxidation reaction plays an important role in synthetic organic chemistry and in this field variety of oxidants and substrates have been developed. The oxidation of abundant and cheapness hydrocarbons to produce more valuable compounds such as aldehydes and ketones, needs the selective oxidation of C—H bonds. Therefore, selectivity control is a key issue in oxidation reactions. Recent research has indicated that the heterogeneous catalysts have also very efficient impact in enhancing selectivity. Aerobic oxidation of organic substrates such as ethylbenzene, cyclohexene and oximes to oxygenic compounds is an extremely consequential industrial manufacture for the production of main chemicals and monomer material [1,2]. The dominant position of oxygen for main part of chemical oxy-functionalization is due to the fact that is economically and eco-friendly, achievable oxidant and reasonable chemical strategy for industrial processing. Furthermore, the catalytic oxidation of ethylbenzene and cyclohexene are attracting much attention because theirs oxidation products are very useful synthetic intermediates. In fact, acetophenone, the valuable product of the selective oxidation of ethylbenzene, has many applications in industries such as the production of synthetic musk for perfumes and pharmaceuticals. Although, Friedel-Crafts acylation of aromatics by acyl halide or acid anhydride can produce acetophenone, but this manner leads to the formation of a large amounts of hazardous and corrosive wastes. However, the allylic oxidation of cyclohexene has been the subject of extensive investigations due to the potential use of 2-cyclohexen-1-one as one of the important products in organic synthesis, owing to the presence of a very reactive carbonyl group, which is used in chemical industries (e.g. cycloaddition reactions and pharmaceutical). Oximes are preferred in readily preparation of derivatives of carbonyl compounds, which also are used extensively for the protection, purification and characterization of carbonyl compounds. The production of carbonyl derivatives from them provides an alternative procedure for the preparation of aldehydes and ketones [3,4]. Therefore considerable attention has been given to developing methods for the regeneration of carbonyl compounds from ketoximes and aldoximes. The large number of methods is consisting of oxidative and reductive reactions, acid catalyzed and deoximation of exchange of oximes with other carbonyl compounds. These methods suffer some disadvantages such as requirements for refluxing temperature, strong mineral acids, generate equal amounts of toxic and hazardous transition metal oxidants, not readily available, tedious work up, the problems associated with waste disposal, long reaction times and formation of polymeric by products [3]. Furthermore, these reactions are usually carried out under acidic or basic conditions, which are not suitable for acid sensitive functional groups. However, oximes can also be prepared from noncarbonyl compounds

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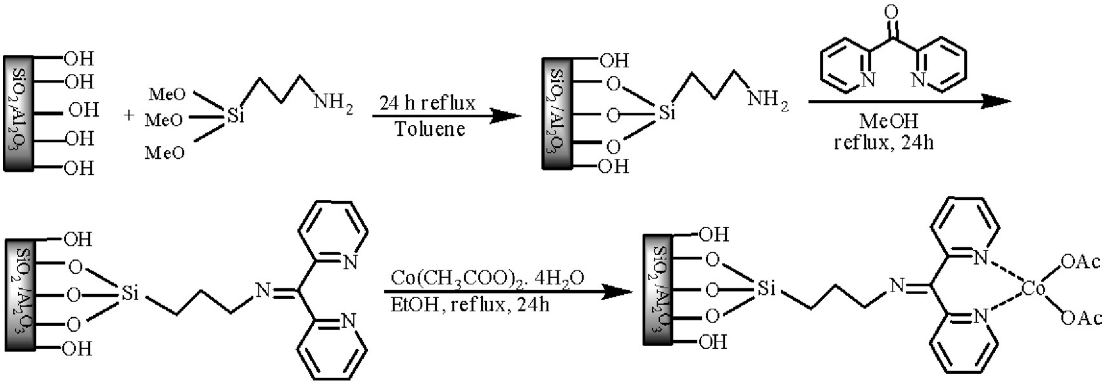


Scheme 1. Schematic representation of the preparation process for SiO_2/Al_2O_3-APTMS-BPK-Co.

as the starting materials. Therefore, aldoximes and ketoximes can be used in turn as synthetic precursors of the corresponding carbonyl compounds. For example, this precursor applied in the commercial synthesis of carvone, which is an essential oil used in fragrance industry [5]. Therefore, oxidation of organic compounds over heterogeneous catalysts using oxygen is an especially attractive goal but, O_2 show a relatively little tendency to react with the strong bond of C-H. To overcome this obstruction, several catalyst and co-catalyst have been applied for the catalytic oxidation of organic substrates [6–9]. Indeed, transition metals such as $Co(OAc)_2$ [10], CuCl [11], $Co(OAc)_3$ [12], and $Mn(OAc)_3$ [13], are added in the presence of nonmetallic compounds such as NHPI [10–13], alkyl hydroperoxide [14,15], -azobisisobutyronitril [16], aldehydes [17,18] and NO_2 [19,20], because they are known to catalyze the initiation reaction [9,10,21–28]. However, finding a catalytic system for aerobic oxidation of organic compound under mild conditions is still a challenging issue. To extend previous study on the aerobic oxidation reaction by using NHPI/Co, we synthesized new type of Co catalyst that immobilized onto the functionalized SiO_2-Al_2O_3 through a Schiff base ligand, and have been investigated the oxidation of ethylbenzene and cyclohexene in the presence of NHPI/Co as the catalytic system. We have also studied oxidation of oximes to show that cobalt-catalyst could serve as an efficient heterogeneous catalyst for the cleavage of the C=N bonds to the corresponding carbonyl compounds without any over oxidation.

2. Experimental

2.1. Materials and characterization techniques

All reagents were purchased from the Merck and Fluka chemical companies. Reagents were used without extra purification, but solvents were purified with standard methods. Inductively coupled plasma (ICP) measurements for cobalt content evaluation were performed using a Perkin-Elmer ICP/6500. Infrared was collected on KBr pellets using a JASCO FT/IR (680 plus) spectrometer. Diffuse reflectance spectra were registered on a JASCO-550 UV–vis spectrophotometer that was equipped with a Diffuse reflectance attachment in which $BaSO_4$ was as the reference. For elemental analysis a CHN-Rapid Heraeus elemental analyzer (Wellesley MA) was used. Before carrying out the nitrogen (99.999%) adsorption experiments, the sample was outgassed at 393 K for 14 h, then the experiment have been carried out at 77 K using a volumetric apparatus (Quantachrome NOVA automated gas sorption analyzer). The specific surface areas were calculated using the BET method. The images of scanning electron micrograph (SEM) and transmission electron microscopy (TEM) were taken using a Philips 501 microscope and a Tecnai F30TEM operating at 300 kV, respectively. In addition, energy dispersive X-ray analysis was conducted on each sample. Size distribution was measured in order to number of nanoparticles in reverse microemulsion by Zetasizer Nano-ZS-90 (ZEN 3600, MALVERN instruments).

2.2. Preparation of organometallic-SiO_2/Al_2O_3

SiO_2/Al_2O_3 was used as the support prepared by the sol-gel method. First, some defined value of tetraethyl orthosilicate (98%) and aluminum butyrate in n-butanol were dissolved. The obtain solution was heated up to 70 °C and the components were entirely mixed. Then it was coold down to the room temperature. 2,4-Pentandione (H-acac) as the complacing agent was added to it. In this way, the apparent solution was obtained. After that by adding deionized water (12.0 mol H_2O/mol alkoxide) to the obtained solution, the solution was hydrolyzed and the apparent gel was produced. Then for removing the solvent and water from the gel, it was dehydrated up to 100 °C. Also for eliminating of organic compounds, it was calcined at 550 °C for 5 h. So, the synthesized solid SiO_2/Al_2O_3 was being used as the support in synthesis of the catalyst [29]. At first, 3.5 g of SiO_2/Al_2O_3 was activated at 500 °C for 5 h under air and then was refluxed with 4.3 cm^3 of trimethoxysilylpropylamine (APTMS) in dry toluene (50 cm^3) for 24 h. The solid achieved during this process was filtered and washed off with dry methanol at 100 °C under vacuum for 5 h. Then, bipyridylketone (BPK) was added to a suspended solution of SiO_2/Al_2O_3-APTMS in dry methanol. To synthesize of SiO_2/Al_2O_3-APTMS-BPK-Co (Scheme 1), 2.0 g SiO_2/Al_2O_3-APTMS-BPK was suspended in 50 cm^3 of ethanol in a round bottom flask followed by adding of 3.0 mmol $Co(OAc)_2{\cdot}4H_2O$. The mixture was refluxed during 24 h under magnetically stirring.

2.3. General procedure for oxidation of ethylbenzene and cyclohexene

A suspension of the heterogeneous catalyst (0.1 g), solvent (5 cm^3 of acetic acid), 2 mmol substrate and N-hydroxyphthalimide (2-hydroxy-1H-isoindole-1,3-dione, NHPI) (15 mol %) were mixed in a three necked round bottom flask which was fitted with a equipped water condenser through a balloon filled with O_2. The liquid phase oxidation reactions were carried out at desired temperature with vigorous stirring. After filtration and washing with solvent, the type and quantity of the resulting products from oxidation were determined using a HP 6890/5973 GC/MS instrument. Besides, a comparative experiments with various conditions was carried out.

Table 1
Chemical composition and physicochemical properties of the immobilized Co-catalyst on the SiO_2/Al_2O_3 mixed oxide.

Sample	Elemental analysis (wt.%)[b]			Organic functional group (mmol/g mixed oxide)[c]	Immobilized Co-Schiff base-complex (mmol/g mixed oxide)[d]	% Coordinated Schiff base groups to Co ions	Structural parameters[e]		
	C	N	Co				Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (Å)
SiO_2/Al_2O_3[a]	–	–	–	–	–	–	498	0.045	36
SiO_2/Al_2O_3 -APTMS	8.13	3.75	–	2.67	–	–	378	0.031	25
SiO_2/Al_2O_3 -APTMS-BPK	10.9	4.92	–	3.51	–	–	320	0.026	20
SiO_2/Al_2O_3 -APTMS-BPK-Co	7.459	1.38	1.14	0.98	0.193	**58.7**	281	0.021	18

[a] Molar ratio of SiO_2/Al_2O_3 was 60:40, determined from EDX analysis.
[b] Nitrogen was estimated from the elemental analyses. Co content determined from EDX analysis.
[c] Determined from the N-contents.
[d] Determined from the Co-content, assume that cobalt ions coordinated with Schiff base ligands.
[e] From N_2 adsorption experiments.

2.4. General procedure for oxidation of oximes

In this procedure, a suspension of the heterogeneous catalyst (0.15 g), solvent (5 cm^3 of toluene), oxime (2 mmol) and benzaldehyde (10 mol) were mixed in a three necked round bottom flask which was fitted with a equipped water condenser with a balloon filled of O_2. The liquid phase oxidation reactions were carried out at desired temperature with vigorous stirring. After completing the reaction, the catalyst has been separated through filtering and the products and the amounts of them have been quantified by GC–MS and GC. Finally, a suitable reaction condition has been optimized

3. Results and discussion

3.1. Synthesis of cobalt-supported catalyst

Using BPK and $Co(OAc)_2{\cdot}4H_2O$ through the covalently immobilization, the heterogeneous cobalt catalyst was synthesized onto the SiO_2/Al_2O_3 mixed oxides, as illustrated in Scheme 1. The loading of cobalt in the heterogeneous cobalt catalyst was characterized by elemental analyses. The final metal content was 0.193 mmol/g, indicating that 58.7% of the immobilized ligands were complexed with cobalt ions (see Table 1).

The FT-IR spectra of SiO_2/Al_2O_3-APTMS, SiO_2/Al_2O_3-APTMS-BPK, and SiO_2/Al_2O_3-APTMS-BPK-Co are shown in Fig. 1. The strong absorption bands related to Si-O-Si stretching vibrations are observed in the spectrum of SiO_2/Al_2O_3 at 798 and 1010–1290 cm^{-1}. The FT-IR spectrum of SiO_2/Al_2O_3-APTMS shows several signals originating from amino propyl groups, which are related to C—H stretching modes of the propyl, appeared in the area of 1450–1560 cm^{-1} and 2860–2935 cm^{-1}. By observing the FTIR results it could be concluded that the SiO_2/Al_2O_3 was successfully modified by amine spacer groups. The N—H deformation peak at 1540–1560 cm^{-1} confirms the successful functionalization of the Si/Al mixed oxide with 3-APTMS. The C=N imine vibration signal was observed at 1630 cm^{-1}, which shows the condensation reaction between BPK with organo-functionalized SiO_2/Al_2O_3 (see Fig. 1B). The peaks in the 3020–3066 cm^{-1} ranges and the peaks at 1434–1437 cm^{-1} are attributed to the C—H stretching vibrations of pyridine groups and C=C stretching vibration of pyridine groups. Furthermore, after complexing of cobalt with immobilized BPK over modified SiO_2/Al_2O_3, the weak absorption peak at 466 cm^{-1} was appeared that is attributed to the Co—N bands.

The UV–vis spectrum of the SiO_2/Al_2O_3 had a side-band adsorption near 249 nm. In the SiO_2/Al_2O_3-APTMS-BPK transitions π→π* and n→π* of the ligands caused strong adsorption in the 255–320 nm (see Fig. 2). After the reaction of

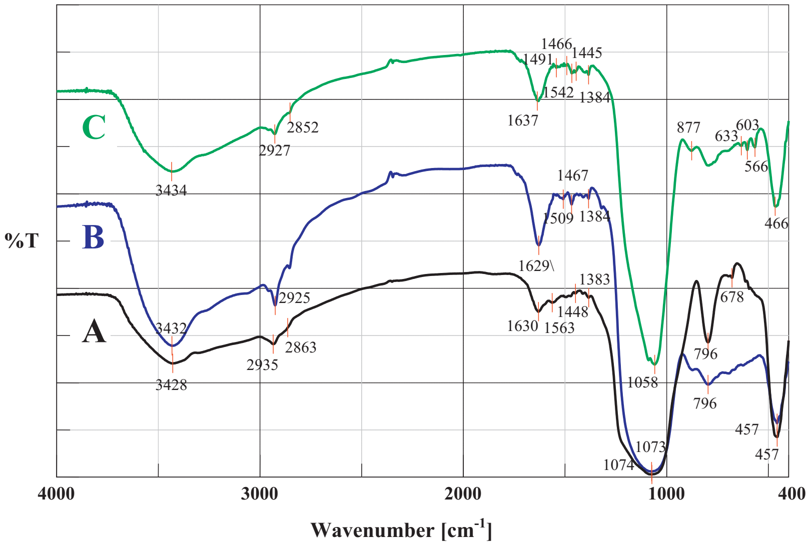


Fig. 1. FTIR spectra of: (A) SiO_2/Al_2O_3-APTMS; (B) SiO_2/Al_2O_3-APTMS-BPK; (C) SiO_2/Al_2O_3-APTMS-BPK-Co.

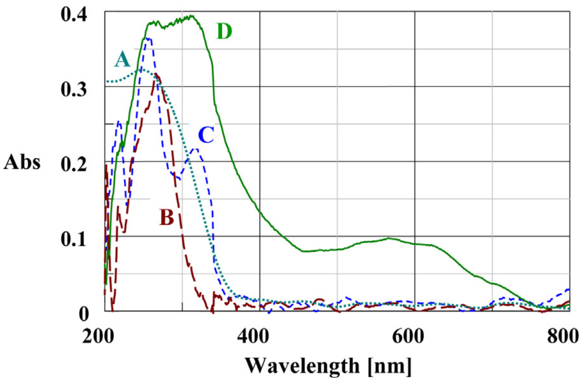


Fig. 2. UV–vis spectra of: (A) SiO_2/Al_2O_3; (B) SiO_2/Al_2O_3-APTMS; (C) SiO_2/Al_2O_3-APTMS-BPK; (D) SiO_2/Al_2O_3 -APTMS-BPK-Co.

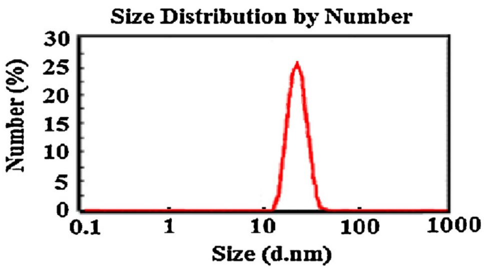


Fig. 4. Particle size distribution on the SiO_2/Al_2O_3-APTMS-BPK-Co.

SiO_2/Al_2O_3-APTMS-BPK with $Co(OAc)_2{\cdot}4H_2O$, the color of the reaction mixture was changed from yellow to deep brown. Consequently, UV–visible spectra of the immobilized Co(II) species indicated the appearance of several new metal d–d migration bands around 570 nm upon complexation.

A selected image of scanning electron microscope (SEM) and transmission electron microscope (TEM) of catalyst is shown in Fig. 3, from which it can be seen that the nanoparticles appearance and size of them were similar, demonstrating that the particles of SiO_2-Al_2O_3 have good mechanical stability and they have not been destroyed during the whole modification. However, the average particle size in reverse micro emulsion solution of the catalyst was around 28 nm (see Fig. 4). According to the small nanoparticle size and ligand capping as an obstacle in agglomeration, the Co-catalyst could be used as a suitable catalyst for oxidation of several substrates such as ethylbenzene, and cyclohexene. The energy dispersive spectrum (EDS) of Co-catalyst was shown in Fig. 5. In the EDS spectrum of the cobalt catalyst, signals related to Si, Al, O and Co were observed. The existence of Co signal in the spectrum resulted from the Co complexation with active sites of the organic functional groups ($-\mathrm{C{=}N}$) that increased the catalytic activity of the synthesized catalyst in comparison with the unmodified support.

Thermal stability of the synthesize materials were studied with TGA (thermo gravimetric analysis) and DTG (derivative thermogravimetric) in Ar atmospheres in the range of 25–1200 °C with a rate of heating of 10 °C/min (see Fig. 6). Thermal analysis of nanoscale SiO_2/Al_2O_3 showed two stages of weight loss, stage I (25–115 °C) corresponds to the desorption of physically held water (2.6 wt.%), on the surface of SiO_2/Al_2O_3, and Stage II (120–1200 °C) is due to the condensation of Al-OH and Si-OH (13.4 wt.%), present in the structure of support (for example; $2\mathrm{Si{-}OH} \rightarrow \mathrm{Si{-}O{-}Si} + H_2O$). However, Co catalyst showed four distinct steps: at 25–94, 94–295, 295–549 and 549–1200 °C (see Fig. 6). Stages II and III (94–549 °C) are due to desorption of water molecules from the pores of SiO_2/Al_2O_3 and also decomposition of the immobilized organic functional groups (-*pr*-NH_2). The additional weight losses in stage IV could be observed due to the several phenomena; the calcination of coke, the loss of the new generated Al—OH and Si—OH groups and decomposition of the immobilized Co complex groups. From

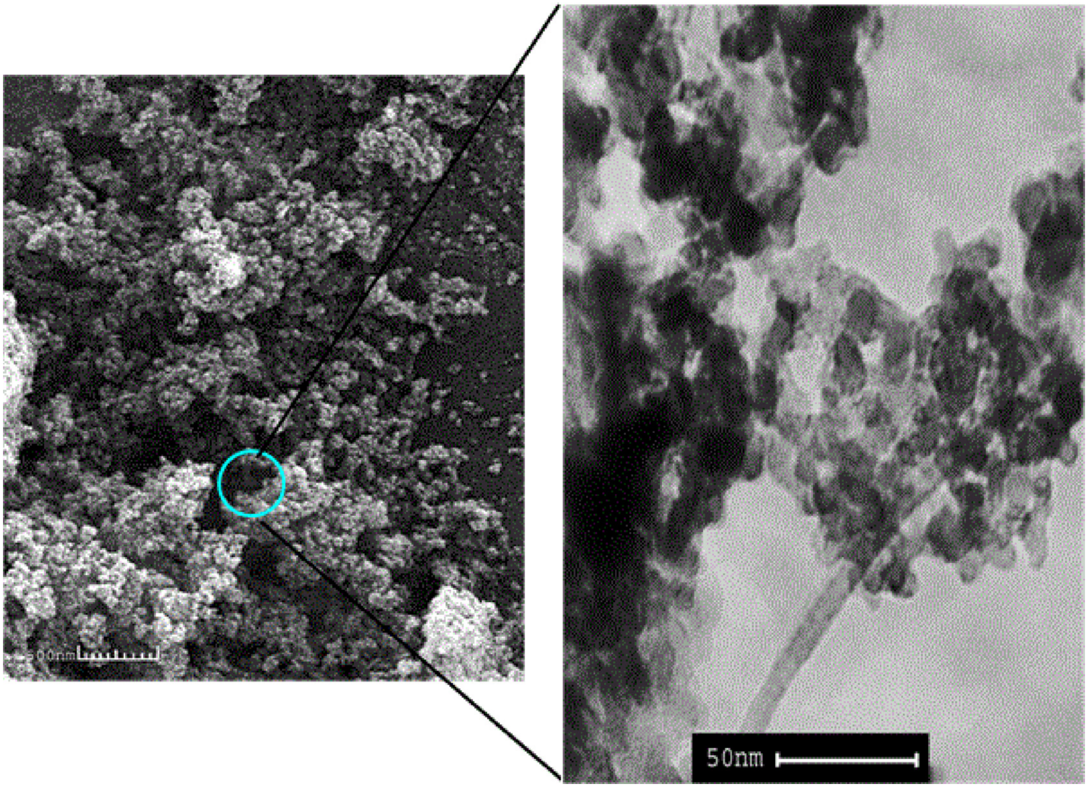


Fig. 3. SEM and TEM images corresponding to SiO_2/Al_2O_3-APTMS-BPK-Co sample.

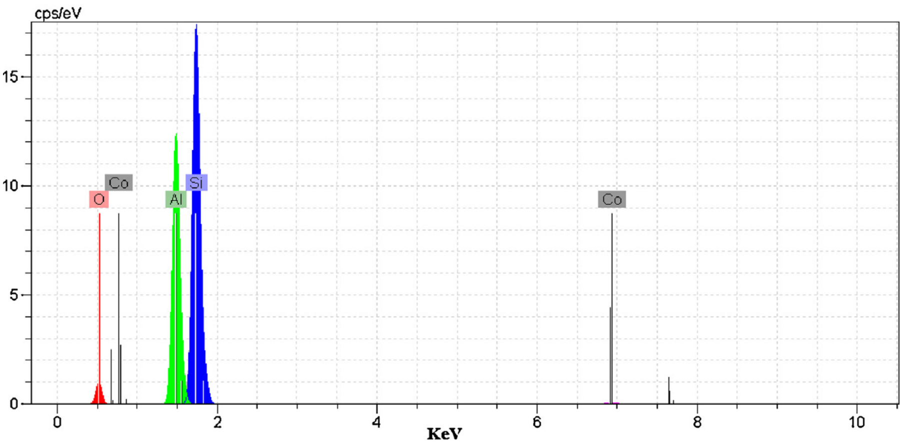


Fig. 5. EDS spectrum of SiO_2/Al_2O_3-APTMS-BPK-Co.

thermogram analysis of samples, it could be concluded that thermal stability of SiO_2/Al_2O_3 in Co catalyst improved rather than unmodified SiO_2/Al_2O_3 and the weight losses of the modified SiO_2/Al_2O_3 with Co complex groups in the temperature range of dehydration are less than that for unmodified SiO_2/Al_2O_3.

The XP spectroscopic analysis of the heterogeneous catalyst was used to study for the characterization of oxidation state of the active sites of immobilized cobalt complexes on the surface of SiO_2/Al_2O_3. This technique has previously been shown to provide valuable information regarding the chemical state of the catalytically active sites in various catalysts [30–33]. The XPS spectrum of Co catalyst produced a Co $2p_{3/2}$ peak at 781.61 eV, and is depicted in Fig. 7. However, there is a satellite peak at 786.70 eV beside the main peak of Co $2p_{3/2}$ in the catalyst. These results indicated that most of the Co ions on the surface of the heterogeneous catalyst were in +2 oxidation state (due to the binding energy (BE) 781.61 eV which are attributed to Co(II) state of cobalt), and they are in accordance with earlier literature data [34,35].

3.2. Oxidation of ethylbenzene

The oxidation of ethylbenzene with oxygen by the new catalytic system using a heterogeneous transition metal in the presence of NHPI was investigated. The effects of various operating

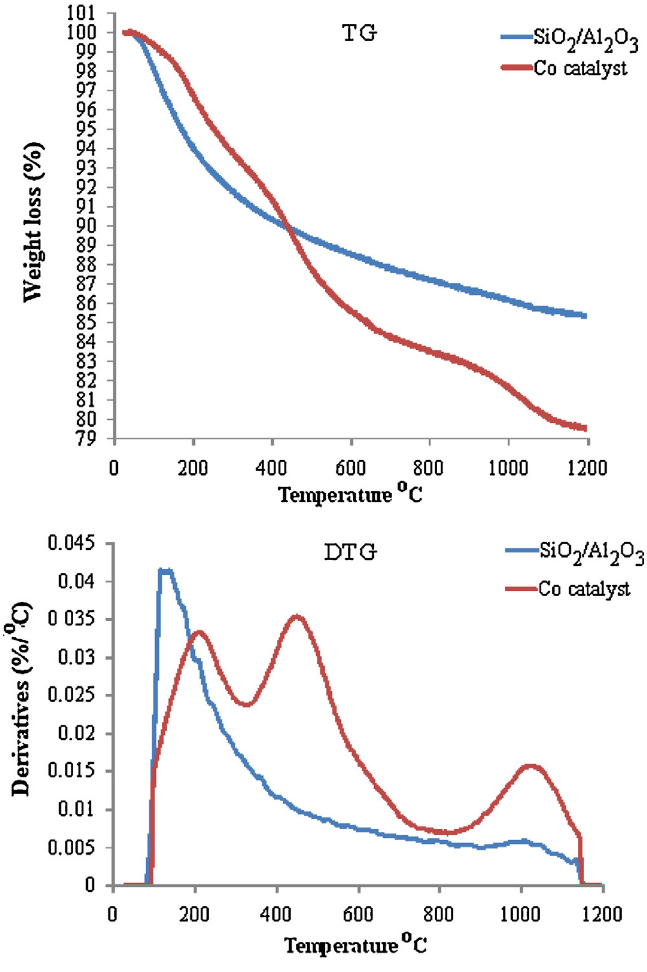


Fig. 6. TGA and DTG curves of the SiO_2/Al_2O_3 and Co-catalyst.

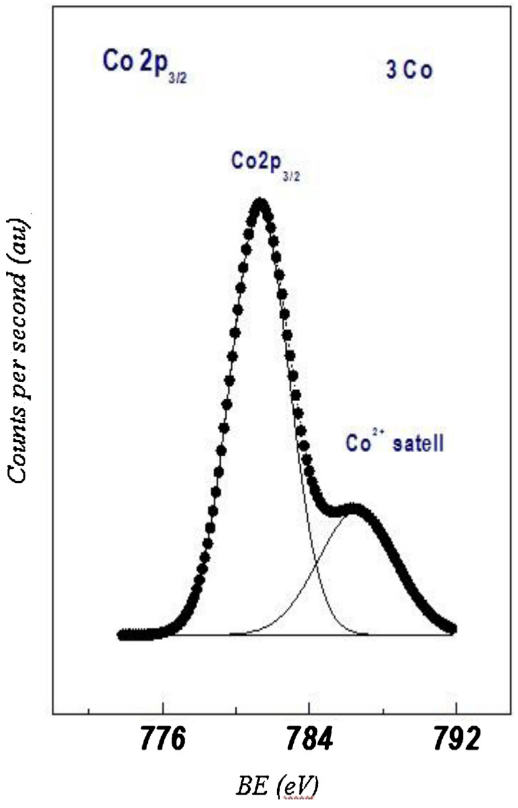
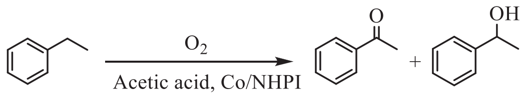


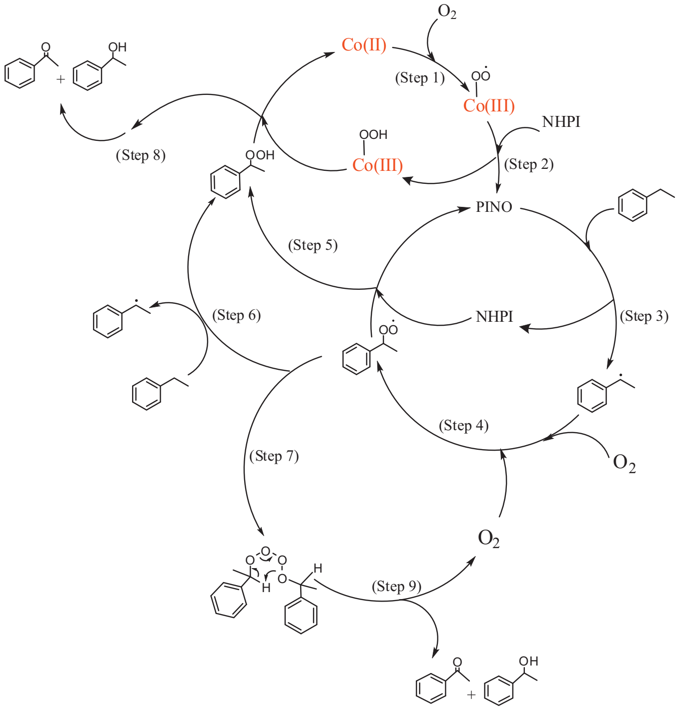
Fig. 7. XPS image of the SiO_2/Al_2O_3-APTMS-BPK-Co.



Scheme 2. Possible products of the oxidation of ethylbenzene.

parameters, such as the amount of the catalyst to NHPI, the temperature, and the reaction time, on the performance of the heterogeneous cobalt-catalyst was investigated in the oxidation of ethylbenzene by O_2 in the presence of the acetic acid as solvent. In fact, due to its polar nature, NHPI has a low solubility in ethylbenzene at the mild temperature employed in our protocol. Thus, the use of acetic acid is mandatory in order to dissolve the quantities of NHPI necessary for observing a good catalytic activity. Acetophenone and α-phenyl ethanol (Scheme 2) were the major reaction products obtained. The GC analysis did not show any oxidation products of the aromatic ring in effluents.

Among the several solvents, acetic acid was found to be the optimum solvent [45–48]. In order to assess the effect of catalyst to oxidant molar ratio on the catalytic activity and selectivity in acetic acid under oxygen, the reactions were studied at various amount of catalyst:NHPI (see Table 2). It was observed that catalytic activity and selectivity is strongly affected by increasing amount of catalyst to NHPI. The most promising observation is that acetophenone was found to be the major product in most of the catalytic reactions. In all EB oxidation reaction conditions, conversion and selectivity to acetophenone increased with reaction time.



Scheme 3. Proposed mechanism for the oxidation of ethylbenzene with the Co-catalyst/NHPI system.

NHPI has been demonstrated to be a free radical oxidation catalyst [36,37]. In contrast to transition metals, NHPI does not accelerate the hydroperoxide decomposition reaction; therefore, the catalytic activity of NHPI results from phthalimide-Noxyl radical (PINO) formation in the propagation step of the oxidation process. In fact, transition metals, such as Co(II)/(III) and Mn(II)/(III), are typically used as catalysts in these oxidation processes, that is, their catalytic effect lowers the activation energy of the decomposition reaction of the hydroperoxide. As it shown in the proposed mechanism (see Scheme 3), at first step, by the complexation of Co(II) with oxygen molecule a labile dioxygen complex such as superoxocobalt(III) or peroxocobalt(III) complexes could be formed [10,38]. However, it is observed that the oxidation of ethylbenzene by the combined system of NHPI and $Co(acac)_3$ did not take place, since a cobalt-oxygen complex cannot be generated from $Co(acac)_3$ and dioxygen under ambient conditions (data not published), while in the presence of a small amount of benzaldehyde the oxidation reaction was carried out, ethylbenzene was oxidized to acetophenone (27%), because Co(III) species is reduced by benzaldehyde to Co(II) ion. Therefore, it is reasonable to assume that such cobalt species assist in the generation of the PINO radical from NHPI under these conditions [10,38,39]. Furthermore, for demonstrating the role of the nano Co-catalyst pyridine molecule was added into the system which resulted in decreasing the catalytic activity of cobalt complex quickly, in fact, the nitrogen of pyridine molecule easily occupies the active sites of the nano catalyst [45]. In the second step, NHPI in situ could be converted to PINO by the reaction of NHPI with the catalyst-oxygen complex that would be the most important step in the present oxidation [10]. The BDE (Bond Dissociation Energy) value of the O-H bond for NHPI is >86 kcal/mol by means of ESR spectroscopy [40,41]. The BDE of the benzylic C—H bond in ethylbenzene is estimated to be about 87 kcal/mol. This suggests that PINO could abstract the benzylic hydrogen atom of ethylbenzene, therefore, at third step, PINO abstracts benzylic hydrogen of ethylbenzene and eventually formed ethylbenzyl radical. However capturing the obtaining ethylbenzyl radicals by dioxygen molecules provides alkylperoxy radicals, which are eventually converted into oxygenated products through ethylbenzylhydroperoxides (step 4). This intermediate can produce acetophenone and 1-phenylethanol in two paths (steps 5 and 7), at step 5, alkylproxy radical can abstract hydrogen from NHPI and at step 7, two alkylproxy radicals combine to form a tetroxide intermediate, which further decomposes through a 6-membered ring transition state rearrange to a molecule of oxygen, an alcohol, an acethophenone and

Table 2
Effect of temperature and amount of catalyst on the conversion and selectivity of the catalytic oxidation of ethylbenzene by Co-supported catalyst.

Entry	Catalyst (g)	Time (h)	*T* (°C)	Conversion[a] (mol %)	TON[b]	Selectivity (mol%)	
						Acetophenone	α-pheniletanol
1	–	10	25	8	–	31	69
2	0.02	10	25	12	63.15	40	60
3	0.03	10	25	13.4	47.01	46	54
4	0.05	10	25	17.5	36.84	62	38
5	0.05	8	100	64	134.7	82	18
6	0.1	2	25	10.4	10.94	58	42
7	0.1	10	25	23	24.21	64	36
8	0.15	10	25	29	20.35	69	31
9	0.1	8	100	81	85.26	98	2

[a] Reaction condition: ethylbenzene; 2 mmol, solvent; 5 cm^3 acetic acid, 15 mol% NHPI.
[b] TON, turn over number, moles of substrate converted per mole of metal.

phenylalcohol; well-known as Russell termination. It is expected from this mechanism that the ratio of these products are 1.0. During the first 2 h of the reaction, ketone and alcohol formation takes place only via Russell termination but at higher conversions it is clear that other mechanisms play an important role [36,37,10]. In the next step, the ethylbenzylhydroperoxides was catalytically decomposed by the Co(III) complex, so, the selectivity of ethylbenzylhydroperoxides decreases after the increase of reaction time. However, in the presence of acetic acid, the rate of this reaction increased and the selectivity of ethylbenzylhydroperoxides decreased, that is, the proton of solvent can prompt decomposition of ethylbenzylhydroperoxides, and eventually this step becomes more rapid [10,38]. The ethylbenzylhydroperoxides in the next steps further converts to acetophenone and 1-phenylethanol (steps 8 and 9).

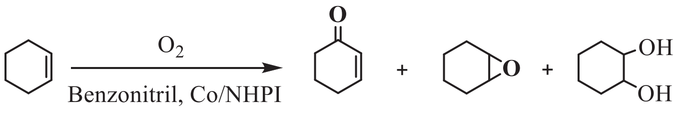
The high selectivity to acetophenone and the absence of 2-phenylacetaldehyde can be rationalized from the following discussion. The methyl group carries more number of hydrogen than the methylene group that was not oxidized. However, the methyl group might be rotating more rapidly than the methylene group and hence its hydrogen was not abstracted by activated oxygen as shown in Scheme 3. The existence of a barrier to rotation about $C_{sp2}—C_{sp3}$ was already reported [42]. Therefore, the hydrogen of methylene group was more readily available for oxidation than that of methyl group. The distant chemisorbed oxygen abstracts the hydrogen from the methylene group of ethylbenzene and fashions phenyl ethyl radical and metal hydroperoxide. The free radical rapidly reacts with metal hydroperoxide to form 1-phenylethanol. The local magnetic field of active sites of heterogeneous catalyst (cobalt ions) could be thought to retain the paramagnetic phenyl ethyl radical until it is hydroxylated [43]. The obtaining 1-phenylethanol is rapidly acted upon by the chemisorbed oxygen on the metal active site or PINO to form the product radical as shown in the reaction (Scheme 3). Furthermore, the oxidation of 1-phenylethanol might be more rapid than ethylbenzene, as the rotation of -CHOH group is slower than the $—CH_2—$ group. Consequently, the hydrogen atom which reacted with active sites of Co-supported catalyst was ejected by radical in order to form water and acetophenone.

Besides coordination to a Schiff base ligand, the cobalt ions may also interact with the surface Si—OH and Al—OH groups of the SiO_2/Al_2O_3. Thus, the materials of blank SiO_2/Al_2O_3 that adsorbed cobalt acetate (0.1 g) were also used for oxidation experiment. It turned out that the conversion of ethylbenzene was almost 9.2% with TON of 39.14 (similar to the result of blank experiments, Table 2, entry 1). Therefore, in the oxidation of ethylbenzene with NHPI and oxygen under acetic acid, the cobalt ions absorbed on the surface of the support did not contribute in the oxidation reaction. The above observations suggest that the oxidation occurs due to the catalytic nature of the chemically immobilized of Co catalysts onto the Schiff base ligands.

To assess the reusability, the catalyst was separated by filtration after the first run, washed with ether and dried at 100 °C under vacuum and then used for the next runs under the same conditions (see Fig. 8). No significant loss of activity and selectivity was observed, confirming that the Co-supported catalyst has high stability during the oxidation process. To further proof that the reaction was catalyzed by the cobalt sample, we added extra ethylbenzene to the filtrate after the removal of the catalyst and found that no more products were produced under the same conditions.

3.3. Oxidation of cyclohexene

To extend the present method, the oxidation catalytic activity of the cobalt catalyst has been examined using NHPI and oxygen under benzonitrile as solvent at several temperatures.



Scheme 4. Reaction products of catalytic oxidation of cyclohexene with SiO_2/Al_2O_3-APTMS-BPK-Co.

After the reaction, the products were identified and quantified by GC–MS. The products of the reaction were cyclohexene (CH) oxide, 2-cyclohexene-1-one and 2-cyclohexene-1-ol (see Scheme 4).

Several results of the cyclohexene conversion and the selectivity of the products are summarized in Table 3. The oxidation of CH using NHPI proceeded even at 25 °C to give 2-cyclohexene-1-one in higher selectivity after 24 h (81.7%). As the reaction time were raised from 2 to 24 h, the CH conversion and the selectivity to 2-cyclohexene-1-one increased from 44.0 to 84.2 and 88.4 to 99.9%, respectively, while the selectivity to cyclohexene oxide and 2-cyclohexene-1-ol were decreased at 80 °C. In the oxidation of cyclohexene, all the reaction conditions showed excellent selectivity for the ketone with only trace amounts (in total <1.0%) of by-products after 8 h at 100 °C.

The oxidation of CH in the absence of catalyst gives low conversion and selectivity to 2-cyclohexene-1-one at 25 °C (entry 1). Furthermore, no reaction was observed in the absence of NHPI because no radical formations from Co centers occur under the conditions selected in this work [37,38]. Reaction carried out to some extent in the absence of the catalyst, but the activity is lower (4%) than when this compound is present. NHPI oxidizes CH slowly, and selectivity to 2-cyclohexene-1-one was not high after 24 h (58.9%). This result is in accord to the previously reported reaction mechanisms [37,38], where NHPIs are responsible for radical formation and the heterogeneous Co is the co-catalyst that enhance the activity of the NHPI. Therefore, these could be demonstrated again from the results that under the mentioned reaction conditions, the allylic hydrogen is more reactive than the C═C double bond. However, the abstraction of hydrogen from the allylic carbon leads to allylic radical, which requires lower activation energy than the reaction at double bond [44].

Reusability of the immobilized Co catalyst onto the SiO_2/Al_2O_3 was confirmed by performing a series of consecutive experiments in which the used catalyst was filtered, washed with fresh solvent, and employed without any further treatment in another run. The results shown in Fig. 9 clearly prove that a slight decline of activity and selectivity occurs after seventh run. Consequently, the results clearly suggest that the cobalt catalyst efficiently catalyze conversion of cyclohexene (75%) with ca. 99% selectivity to 2-cyclohexene-1-one under NHPI and oxygen in benzonitrile as solvent.

3.4. Oxidation of oximes

In this protocol, a novel useful procedure for the facile deoximation system by reusable Co supported catalyst and molecular oxygen as oxidant were studied (see Scheme 5). The experiments were designed with acetophenone oxime as a model substrate. For optimizing the conditions in oxidation of oximes, several factors have been investigated such as the amount of catalyst, the effect of temperature, the amount of benzaldehyde and the effect of solvent. In this reaction, the main product for oximes with electron-donating groups is carbonyl compounds. In order to examine the effect of catalyst on deoximation reaction; the reaction was carried out in the presence of various amounts of catalyst. The observations indicated that in the case of absence of catalyst, the reaction is carried out slowly while in the presence of the optimum amounts of the catalyst, the reaction is performed considerably. The maximum

Table 3
Effect of the temperature and the reaction time on the conversion and selectivity of the catalytic oxidation of cyclohexene by Co-supported catalyst.

Entry	Time (h)	*T* (°C)	Conversion (mol%)	TON[a]	Selectivity (mol%)		
					Alcohol	Ketone	Epoxide
1	24	25	4	–	23.6	58.9	17.5
2	2	25	15.4		54.9	44.6	0.5
3	6	25	21		40.6	53.9	5.5
4	8	25	26		33	57	10
5	10	25	30		24.5	62	13.5
6	12	25	32.4		17.4	68.4	14.2
7	16	25	37.9		13.1	73	13.9
8	18	25	41.8		10.5	77.5	12
9	24	25	47	49.47	8.6	81.7	9.7
10	2	60	32		25	70.7	4.3
11	6	60	49		17	80.4	2.6
12	8	60	54.6		14	83.6	2.4
13	10	60	59.4		8	88	4
14	12	60	61.5		5	91	4
15	16	60	64.8		4	95.6	0.4
16	18	60	67.9		2	97	1
17	24	60	71.4	75.15	0.7	98.5	0.8
18	2	80	44		10	88.4	1.6
19	6	80	62		3.5	95	1.5
20	8	80	66		1	96	3
21	10	80	70		0.8	98	1.2
22	12	80	75		0.4	99	0.6
23	16	80	78.7		–	99.9	0.1
24	18	80	79.5		–	99.9	trace
25	24	80	84.2	88.63	–	99.9	trace
26	2	100	53.5		6.8	92.6	trace
27	6	100	66.9		1	98.8	0.2
28	8	100	71		0.6	99	0.4
29	10	100	74.7		–	99.9	0.1
30	12	100	78		–	99.9	0.1
31	16	100	79.5		–	99.9	trace
32	18	100	82		–	99.9	trace
33	24	100	93	97.89	–	99.9	trace

[a] TON, turn over number, moles of substrate converted per mole of metal.

selectivity of carbonyl compound was obtained with 0.15 g of catalyst. The conversion of the acetophenone from 6% in the absence of the catalyst, to higher than 99% in the presence of the catalyst indicates that the catalyst has an efficient and effective role in this reaction.

For examining the role and effect of the solvent in the reaction, various solvents which are suitable for radical reactions have been used [45]. Therefore, acetonitrile, benzene, toluene, and cyclohexane solvents and water have been used (Table 4). The results showed that in various solvents the selectivity was 100% and the conversion decreased in the following order: toluene (99.9) > acetonitrile (87.0) > benzene (81.0) > cyclohexane (19.0) > and water (0.0). The reaction at the presence of coordinating solvents such as water made no reaction. It seems that the donor electrons of this solvent had more ability to occupy the vacant space around the metal in the catalyst, so this prevents coordinating from oxygen molecules [46]. In this work, toluene provided the highest

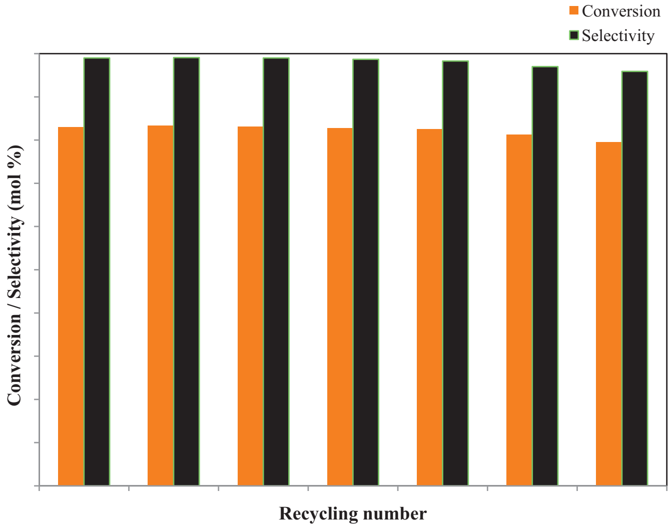


Fig. 8. Reusability of the cobalt-supported catalyst on the oxidation of ethylbenzene and selectivity to acetophenone. *Conditions*: ethylbenzene: 2 mmol; amount of catalyst: 0.1 g; NHPI, 15%; acetic acid, 5 cm^3; $T = 100\,^\circ\mathrm{C}$.

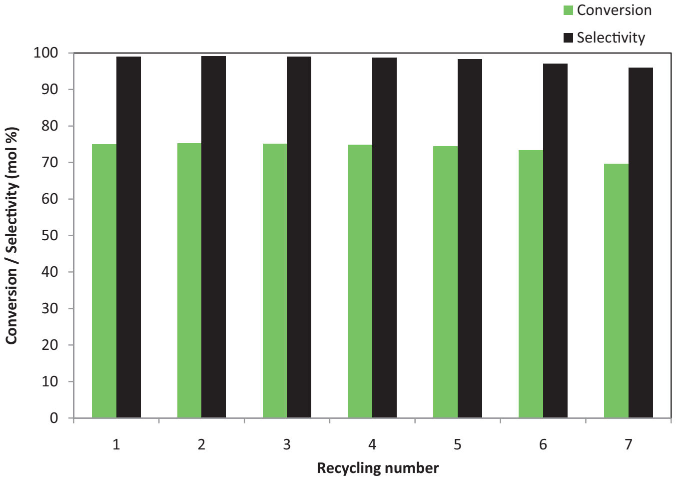
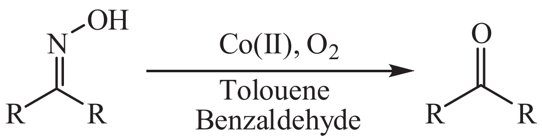


Fig. 9. Reusability of the cobalt-supported catalyst on the oxidation of cyclohexene and selectivity to 2-cyclohexene-1-one. *Conditions*: cyclohexene, 2 mmol; amount of catalyst, 0.1 g; NHPI, 15%; benzonitrile, 5 cm^3; $T = 80\,^\circ\mathrm{C}$.



Scheme 5. Reaction products of the catalytic oxidation of oximes with SiO_2/Al_2O_3-APTMS-BPK-Co.

conversion and selectivity to acetophenone. Therefore, toluene as a solvent plays an effective role in oxidation of oximes, because toluene was reluctant to undergo free radical addition [45,47].

In oxidation of oximes, the presence of several amounts of benzaldehyde can also have a determining role. Observations indicated that in the absence of benzaldehyde, the reaction has a little progress even in a long time period, but in the presence of benzaldehyde a great conversion was observed. This observation indicated that benzaldehyde was used as the oxygen transfer agent in this oxidation reaction. In addition, when isobutyraldehyde was used as the only oxygen transfer agent, great conversion was not observed.

To estimate the reusability of the cobalt supported catalyst, after the first performance the catalyst was filtrated and washed with ether and dried at 120 °C under vacuum and then used for the next performances under the same conditions. No apparent loss of activity and selectivity was observed after 8th runs, confirming that the cobalt catalyst has high stability during the process. To further proofs that the reaction was catalyzed by the heterogeneous Co-catalyst, we added extra acetophenone oxime to the filtrate after the removal of the catalyst and found that no more products were produced under the same conditions. In addition, the Co ions absorbed on the surface of the support did not contribute in the deoximation reaction. This observation indicated that this reaction occurs due to the catalytic nature of the chemically immobilized of Co catalysts onto the Schiff base ligands. To further explore the utility of this catalytic system, oxidation of several oximes (aldoximes and ketoximes) were also studied (see Table 5). Aldehydes were obtained with excellent yields and the overoxidation to carboxylic acid and Beckmann rearrangement were not observed, which was another advantage of the proposed system. Furthermore, steric structure almost has no effect on conversion and selectivity of oxime (entry 14). The hydroxyl group in the ortho position of oximes (entry 12 and 13) exerts only an partly inductive effect, but hydrogen bonding between the OH and the nitrogen atom in imine will decrease the electron density of the carbon atom in the C=N. This factor probably influences the reactivity of oxime. Consequently, the yield of this oxime against with other oximes is slightly decreased, and the reaction time is longer [48].

In order to verify the kind of mechanism, 2,6-di-tert-butyl-4-methylphenol (BHT), as a scavenger of chemical radical was used. The reaction appeared to be radical processes since it was totally inhibited in the presences of radical trap (5 mol%). It seems that oximes with different groups (electron-donating and electron-drawing) go in various paths in the oxidation reaction with oxygen over the catalyst (paths An and B). To further elucidate the reaction mechanism, series of experiments were conducted, when the oxidation of acetophenone oxime was conducted in the presence of dioxygen and benzaldehyde, in the absence of Co catalyst, the conversion of acetophenone could only reach 6%. However, the conversion was remarkably increased by adding 0.15 g of cobalt catalyst to the mixture (Table 1, 99%, entry 1). The results indicate that cobalt catalyst is crucial for the deoximation reaction. According to the proposed mechanism, at the first Co(II) ions and benzaldehyde generate an acyl radical (ph-CO·) [49], so the radical formed is quickly trapped by dioxygen to give an acylperoxy radical (ph-COO·). The acylperoxy radical acts as a carrier in a chain mechanism by reaction with another benzaldehyde molecule to give the peroxybenzoic acid, and generating another acyl radical as well (Eq. (1)) [49–55]. The peroxybenzoic acid is assumed to play important roles, where peroxybenzoic reacts with another Co(II) catalyst molecule to generate high-valent cobalt intermediate (Eq. (2)). The color of the reaction mixture changed to green which also indicated valence change of cobalt (Co(II) to Co(III)) [55,56]. Then, the intermediate attacks to the imine group of oxime through a nucleophilic attack [55], thereby, the reaction of an oxo-catalyst radical and oximes, which is proposed to generate a nitroso oxy radical species eventually loses NO to generate an aldehyde and ketone. Via this process, oxime will be converted to its

Table 4
Effect of solvent on the aerobic oxidation of acetophenoneoxime.[a]

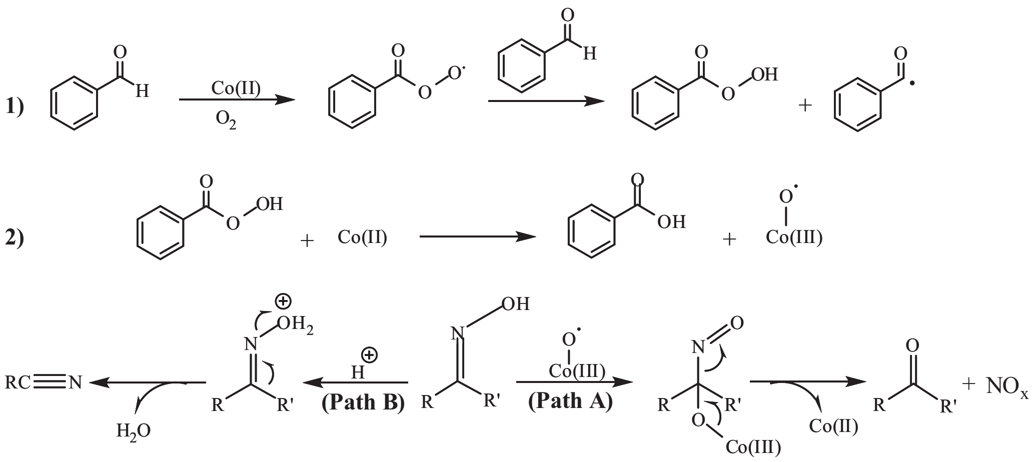
Entry	Solvent	Conversion (%)	Selectivity (%)
1	Toluene	99.9	100
2	Acetonitrile	87.0	100
3	Benzene	81.0	100
4	Cyclohexane	19.0	100
5	Water	0.0	–

[a] Reaction condition: Catalyst; 0.15 g, acetophenoneoxime; 2 mmol, benzaldehyde; 10 mmol, solvent; 5 cm^3, O_2 bubbling, Temperature; 50 °C.

Table 5
Several examples of aerobic oxidations of oximes by using Co-supported catalyst.

Entry	Substrate	Product (selectivity %)	t (min)	Con. (%)	TON[a]	TOF (min^{-1})[b]
1	Acetophenoneoxime	Acetophenone (100)	90	>99	68.39	0.759
2	4-Bromobenzaldehyde oxime	4-Bromobenzaldehyde (100)	85	94	64.93	0.763
3	3-Bromobenzaldehyde oxime	3-Bromo benzaldehyde (100)	105	98	67.70	0.690
4	3-Methylbenzaldehyde oxime	3-Methyl benzaldehyde (100)	100	>99	68.39	0.683
5	4-Methylbenzaldehyde oxime	4-Methylbenzaldehyde (100)	110	97	67.01	0.609
6	4-Methylacethophenon oxime	4-Methyacetophenone (100)	90	95	65.63	0.729
7	4-Cholorobenzaldehyde oxime	4-Cholorobenzaldehyde (100)	80	93	64.24	0.803
8	2, 4-Dicholorobenzaldehyde oxime	2, 4-Dicholorobenzaldehyde (100)	105	92	63.55	0.605
9	2,6-Dicholorobenzaldehyde oxime	2,6-Dicholorobenzaldehyde	130	95	65.63	0.504
10	3,4-Dimethoxybenzaldehyde oxime	3,4-Dimethoxy benzaldehyde (100)	135	95	65.63	0.486
11	3,4,5-Trimethoxybenzaldehyd oxime	3,4,5-Trimethoxybenzaldehyde (100)	170	97	67.02	0.394
12	2-Hydroxy benzaldehydeoxime	2-Hydroxy benzaldehyde (100)	200	93	64.24	0.321
13	2-Hydroxynaphthaldehyde oxime	2-Hydroxynaphthaldehyde (100)	265	>99	68.39	0.258
14	Benzophenoneoxime	Benzophenone (100)	200	97	67.01	0.335
15	4-Cholorobenzophenone oxime	4-Cholorobenzophenone (100)	190	>99	68.39	0.359
16	Cyclohexanoneoxime	Cyclohexanone (100)	160	97	67.01	0.418
17	Cinnamaldehydeoxime	Cinnamaldehyde (100)	240	94	64.93	0.270
18	2-Nitrobenzaldehyde oxime	2-Nitrobenzonitrile (62)	150	42	29.01	0.193
19	4-Nitrobenzaldehyde oxime	4-Nitrobenzonitrile (78)	120	53	36.61	0.305

[a] TON, turn over number, moles of substrate converted per mole of metal.
[b] TOF, turn over frequencies.



Scheme 6. Proposed mechanism for the oxidation of oximes in the presence of molecular oxygen.

Table 6
Screening data (oxidations of ethylbenzene, cyclohexene and oximes).

Selectivity (%)	Conversion (%)	Product	Condition reaction[a]	Catalytic System	Substrate
85	26	Acethophenone	0.05 g Co-MCM-41(100), TBHP, solvent-free, 80 °C, 24 h	Bhoware et al. [62]	Ethylbenzene
75	64		3 μmol Mn (μ- NO_2 TDCPP)Cl, H_2O_2, 25 °C, 5.5 h	Caveleiro et al. [63]	
99	47		2.45 g NiAl-hydrotalcite, O_2, solvent free, 135 °C, 9 h	Jana et al. [64]	
98	24		0.09 g CoTPP-P(4VP-co-st)/SiO, O_2, solvent -free, 95 °C, 0.2 h	Baojiao et al. [65]	
69	45		0.1 g CNCr-2, TBHP, CH_3CN, 70 °C, 8 h	George et al. [66]	
99	83		0.1 g Si/Al-ATMPS-BPK-Co/NHPI,O_2,acetic acid, 100 °C, 8 h	This work	
80.3	73.6	2-Cyclohexen-1-one	5 mg (Ru/Co/Ce) (THNO), TBHP, CH_2Cl_2	Ghiaci et al. [67]	Cyclohexene
100	50		(0.01 mol) t-BuCo/MCM- 41, H_2O_2,CH_3CN, 60 °C, 5 h	Mapolie et al. [68]	
10.2	34.8		100 mg Co (III) SBA-15, H_2O_2, CH_3CN, 40 °C, 12 h	Park et al. [69]	
55.6	43.6		1.02×10^{-5} mol [Co($H_4C_6N_6$ S_2)], TBHP, CH_2Cl_2, 25 °C, 8 h	Salavati [70]	
60.8	92		(1.7 mg/ml) CoPc, TBHP, DMF/dichloromethane, 25 °C, 8 h	Nykong et al. [71]	
99	75		0.1 g Si/Al-ATMPS-BPK-Co/NHPI, O_2, benzonitrile, 80 °C, 8 h	This work	
100	99	Acetophenone	(10^{-3} mmol)MnTPPCl,O_2,toluene,benzaldehyde, 50 °C,2 h	Zhou et al. [72]	Acethophenon oxime
100	82		(0.01 g) Metallophthalocyanine, (0.30 g) [bmim]Br, 50 °C, 1.3 h	Shaabani et al. [73]	
100	92		(100 mg) CeO_2–ZrO_2,THBP, solvent-free, 80 °C, 5 h	Jayaram et al. [74]	
100	99		0.15 g Si/Al-ATMPS-BPK-Co, O_2, toluene,benzaldehyde, 50 °C, 1.5 h	This work	
100	93	Cyclohexanone	(10^{-3} mmol) MnTPPCl, O_2,toluene, benzaldehyde, 50 °C, 5 h	Zhou et al. [72]	Cyclohexanone oxime
100	30		(100 mg) CeO_2-ZrO_2,THBP, solvent-free, 80 °C, 12 h	Jayaram et al. [74]	
100	93		2 mmol $(HCHO)_n$, 0.25 mmol SiO_2-OSO_3H, SDS, H_2O, 50 °C under ultrasound irradiation, 1.5 h	Li et al. [75]	
100	97		0.15 g Si/Al-ATMPS-BPK-Co, O_2, toluene,benzaldehyde,50 °C, 2.6 h	This work	
100	93	4-Methyl benzaldehyde	PVCBSA, CCl4, reflux, 3 h	Khazaei et al. [76]	4-Methyl Benzaldehyde oxime
100	90		$Al(NO_3)_3{\cdot}9H_2O$, NaBr, CH_2Cl_2, 25 °C, 3.5 h	Ghorbani et al. [77]	
100	89		(0.01 g) Metallophthalocyanine, (0.30 g) [bmim]Br, 50 °C, 0.5 h	Shaabani et al. [73]	
100	97		0.15 g Si/Al-ATMPS-BPK-Co, O_2, toluene, benzaldehyde, 50 °C, 1.8 h	This work	

[a] Co TPP- P (4VP- co- st)/SiO_2: Co tetraphenylporphrins on P (4VP- co- st)/SiO_2, CNCr-2: $Cu_{1-x}Ni_xCr_2O_4$($x = 0.5$), THNO: Trimetallic hybrid nanomixed oxide (Ru/Co/Ce), $H_6C_6N_6S_2$: 1,2,5,6,8,11-hexazacylodoca- 7, 12- dithione-2, 4,8,10- tetraene, MnTPPCl: Manganese meso-tetraphenylporphyrin chloride, PVCBSA: Poly[4-vinyl-N,N-dichlorobenzenesulfonamide].

corresponding carbonyl compound. Although, the oxidation efficiency was not affected by electron denoting group of substrate, the presence of electron-drawing groups in oxime (like nitro group; entry 15 and 16) will change the path of reaction so as the speed of protonation of hydroxyl group in oxime will be more than the speed of oxo-catalyst attack to imine bond, consequently, it produces nitrile by the elimination of water, the same result was observed in the literature [57–63] (see Scheme 6).

To demonstrate the efficiency and effectiveness of the catalytic system, the results were compared with other catalytic systems in order to evaluate the benefits and disadvantages of this system. The gathering results from the literature (see Table 6) demonstrated that the catalytic system presented in this paper has advantages in terms of solid nature of catalyst, inexpensive and stability of catalyst, short reaction time, high conversion and selectively, use of dioxygen as a clean oxidant and widely used in catalytic oxidation reactions (ethylbenzene, cyclohexene and various oximes as substrates). Therefore, this protocol could be introduced for practical organic synthesis.

4. Conclusions

A catalyst was developed based on the immobilization of cobalt on SiO_2/Al_2O_3 to efficiently promote the aerobic oxidation of ethylbenzene, cyclohexene and oximes to acetophenone, 2-cyclohexene-1-one and carbonyl compounds, under oxygen atmosphere Oxidation of alkyl aromatic and allylic site was resulted with the oxidant of NHPI and O_2 without the use of any reductant.

The catalytic performance was remarkably high in the oxidation reaction. The effect of the catalyst amount, reaction time, reaction temperature and effect of various solvents on the oxidation of ethylbenzene and cyclohexene were investigated. The results indicated that catalyst/NHPI facilitated the generation of the active species phtalimide-N-oxyl (PINO) radical which further catalyzed the oxidation of ethylbenzene and cyclohexene. Furthermore, we have reported a new and efficient methodology for the regeneration of aldehydes and ketones from oximes. The extension of the method to other catalysts is currently under investigation.

Acknowledgments

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