



Ceria nanoparticles as an efficient catalyst for oxidation of benzylic C–H bonds

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ABSTRACT

Catalytic oxidation of benzylic C–H bonds with potassium bromate to carbonyl compounds was studied in the presence of ceria nanoparticles (NPs). Aldehydes and ketones in high yields were obtained when the oxidation was conducted in water/1,4-dioxane/acetic acid (AcOH) by ratio 5/1/1 (v/v/v). Benzyl esters were also yielded as the main products from the oxidation of benzylic C–H bonds with potassium bromate in the presence of ceria NPs in glacial acetic acid. In comparison with other methods reported in the literature, ceria NPs as an efficient catalyst in oxidation of benzylic C–H bonds have advantageous such as selectivity, recyclability, high reaction rate, and high yield of product because of their large specific surface area to volume ratio.

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1. Introduction

In synthetic organic chemistry, oxidation is an important methodology for the introduction and modification of functional groups [1–4]. During the last two decades, there has been a spectacular development in this field and a large number of novel and useful oxidation reagents and methods have been discovered. The oxidation of benzylic C–H bonds to their corresponding carbonyl compounds is of significant importance in organic chemistry both for fundamental research and industrial manufacturing [5–8]. The world-wide annual production of carbonyl compounds is over 1×10^7 tons and most of these compounds are produced from the oxidation of alkyl arenes and alcohols [8].

The use of cerium salts with stoichiometric amounts have been reported by several research groups [9,10]. Oxidations of organic compounds with cerium (IV) are potentially interesting since cerium (IV) is an unusually strong and one-electron oxidant. The unique reactions of cerium (IV) with organic compounds can be expected because of its specific coordination properties with various organic and inorganic ligands. However, using cerium (IV) in organic synthesis has been limited since the large quantities of the reagent are required. To overcome this drawback, Amer et al. [11–13] used the catalytic amounts of cerium ammonium nitrate (CAN) which is continuously regenerated by a less expensive oxidant such as KBrO_3 . In Amer's method, purification of products was very difficult because of formation of by-products. Ceria as a

cheaper catalyst than CAN in the presence of sodium bromate can oxidize benzylic C–H bonds to aldehydes or ketones [14]. Again, this method has some limitations such as long reaction times and low yields.

Nanomaterials are more effective than conventional catalysts because of their extremely small size and tremendous surface area-to-volume ratio. In continuation of our research program to develop more efficient synthetic methodologies and to remove the drawbacks of the previous methods, the present study suggests a novel and efficient nanocatalyst, ceria NPs, for oxidation of benzylic C–H bonds.

2. Experimental

2.1. General

The products were purified by column chromatography. The purity determinations of the products were accomplished by TLC on silica gel polygram STL G/UV 254 plates. The melting points of products were determined with an Electrothermal Type 9100 melting point apparatus. The FT-IR spectra were recorded on an Avatar 370 FT-IR Thermo Nicolet spectrometer. The NMR spectra were provided on Bruker Avance 100 and 400 MHz instruments in CDCl_3 . All products were known compounds and characterized by IR and ^1H NMR spectra and comparison of their melting points (or those of the derivatives) with known compounds.

The phases of ceria NPs were determined by means of a Bruker/D8 Advanced diffractometer in the 2θ range from 20° to 80° , by step of 0.04° , with graphite monochromatic $\text{Cu K}\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$). In order to obtain a TEM image of the ceria NPs, the NPs

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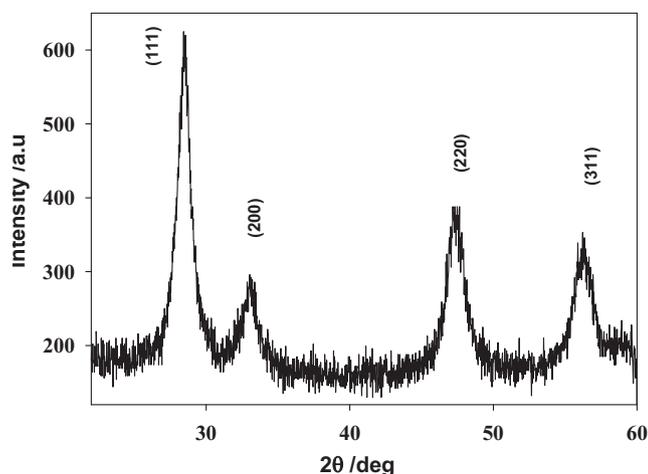


Fig. 1. The XRD pattern of ceria NPs.

were dispersed in ethanol using a sonocating bath. The TEM analysis of the catalyst was performed on a LEO 912 AB transmission electron microscope and the electron beam accelerating voltage was 120 kV. The surface area was measured by an ASAP-2010 system from Micromeritics. The catalyst, ceria NPs was prepared and purified by the method described in the literature [15].

2.2. Characterization of the catalyst

Fig. 1 illustrates the XRD pattern of ceria NPs. All the diffraction peaks can be indexed to (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (3 3 1), and (4 2 0) reflections corresponding to the face-centered cubic phase with the lattice parameter of $a = b = c = 0.5410$ nm. No additional peak is seen in the XRD pattern of the catalyst which reveals the high purity of the prepared ceria NPs.

The average crystallite size, D , can be calculated by the well-known Scherrer's equation:

$$D_{hkl} = \frac{h \times l}{\beta_{hkl} \times \cos \theta_{hkl}} \quad (1)$$

where D_{hkl} is the crystallite size perpendicular to the normal line of (hkl) plane, k is a constant (0.9), β_{hkl} is the full width at half maximum of the (hkl) diffraction peak (FWHM), θ_{hkl} is the Bragg angle of (hkl) diffraction peak, and λ is the wavelength of X-ray. The average crystallite size of ceria NPs is about 10 nm.

The TEM image of ceria NPs was shown in Fig. 2. All the particles display the uniform cubic morphology with the average particle size of about 8 nm which is in a good agreement with the results deduced from the XRD. The BET specific surface area of NPs was $92 \text{ m}^2 \text{ g}^{-1}$.

2.3. The oxidation of ethyl benzene to acetophenone

To a solution of KBrO_3 (0.167 g, 1 mmol) in $\text{H}_2\text{O}/1,4$ -dioxane/glacial acetic acid (5/1/1, v/v/v 3 ml), ceria NPs (5×10^{-4} g, 0.003 mmol) were added at room temperature with continuous stirring. The reaction mixture was stirred for 5 min. Ethyl benzene (0.104 g, 1 mmol) was added with stirring for 1 h at 95°C . Then, the red brown mixture was filtered to remove the catalyst. The filtrate was extracted with CH_2Cl_2 (2×5 ml). The organic layer was dried with anhydrous Na_2SO_4 and passed through a short silica-gel column using n -hexane/ethylacetate (8/1) as an eluent. After removing the solvent under reduced pressure, acetophenone was obtained in 80% yield.

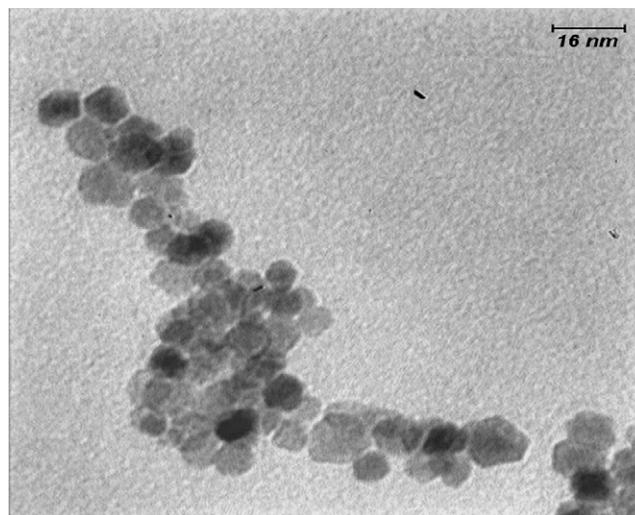


Fig. 2. TEM image of ceria NPs.

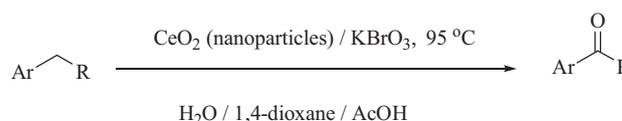
2.4. The oxidation of ethyl benzene to 1-phenylethyl acetate

To a solution of KBrO_3 (0.167 g, 1 mmol) in anhydrous acetic acid (3 ml), NaOAc (0.082 g, 1 mmol) and ceria NPs (5×10^{-4} g, 0.003 mmol) was added at room temperature with continuous stirring. Ethyl benzene (0.104 g, 1 mmol) was added with stirring for 1 h at 110°C . Then, the red brown suspension was filtered to remove the catalyst. The filtrate was extracted with cold $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$ (3×10 ml). The organic layer was dried with anhydrous Na_2SO_4 and passed through a short silica-gel column using n -hexane/ethyl acetate (8/1) as an eluent. After removing the solvent under reduced pressure, 1-phenylethyl acetate was obtained in 95% yield.

3. Results and discussion

Herein, we report a novel and efficient method for oxidation of benzylic C–H bonds to the corresponding aldehydes and ketones (Scheme 1).

The optimum reaction parameters, shown in Scheme 1, were chosen after examining a variety of reaction factors. The oxidation of ethyl benzene was initially performed in the presence of a catalytic amount of ceria NPs (5×10^{-4} g, 0.003 mmol) and a variety of oxidants, different molar ratios of substrate/oxidant, and various solvents (Table 1). As Table 1 (entries 6–14) shows the use of ceria NPs/potassium bromate is the most efficient mixed reagent system for the oxidation of ethylbenzene to acetophenone. The high surface area-to-volume ratio of ceria NPs is mainly responsible for their high catalytic activity. Replacing KBrO_3 with H_5IO_6 , NaClO_3 , H_2O_2 , and NaIO_3 do not produce any acetophenone (Table 1, entries 1–4) since these oxidants cannot reproduce Ce (IV). Another mixed reagent system, ceria NPs/ KMnO_4 , produces acetophenone in only 20% yield (entry 5). The effect of different molar ratios of PhCH_2CH_3 /oxidant (entries 6–8), various temperatures (entries 9–11), and different ratios of (v/v/v) $\text{H}_2\text{O}/1,4$ -dioxane/ AcOH (entries 11–15) were also examined. By diluting the reaction media by distilled water, the reaction rate



Scheme 1.

Table 1

The oxidation of ethylbenzene with various oxidants, different molar ratios of substrate/oxidant, different ratios of (v/v/v) H₂O/1,4-dioxane/AcOH, and various temperatures in the presence of catalytic amount of ceria NPs.

Entry	Oxidant	Substrate/oxidant	H ₂ O/1,4-dioxane/AcOH	Temperature (°C)	Time (h)	Conversion (%)
1	H ₅ IO ₆	1:1	5:1:1	95	12	0
2	NaClO ₃	1:1	5:1:1	95	12	0
3	H ₂ O ₂	1:1	5:1:1	95	12	0
4	NaIO ₃	1:1	5:1:1	95	12	0
5	KMnO ₄	1:1	5:1:1	95	12	20
6	KBrO ₃	1:2	5:1:1	95	1	100
7	KBrO ₃	1:1	5:1:1	95	1	100
8	KBrO ₃	1:0.5	5:1:1	95	12	50
9	KBrO ₃	1:1	5:1:1	70	10	100
10	KBrO ₃	1:1	5:1:1	50	12	30
11	KBrO ₃	1:1	10:1:1	95	75 min	100
12	KBrO ₃	1:1	15:1:1	95	1.5	100
13	KBrO ₃	1:1	20:1:1	95	2	100
14	KBrO ₃	1:1	5:1:0	95	2.5	100
15	KBrO ₃	1:1	H ₂ O	95	12	0

Table 2

The oxidation of diphenylmethane to benzophenone under different molar ratios of diphenylmethane/ceria NPs.

Entry	Molar ratio of diphenylmethane/ceria NPs	Time (min)	Conversion (%)
1	100	30	100
2	200	30	100
3	300	30	100
4	350	30	93
5	400	30	82
6	500	30	45
7	600	30	20

was decreased (entries 11–15). Employing the 1/1 molar ratio of PhCH₂CH₃/oxidant at 95 °C in 5/1/1 (v/v/v) H₂O/1,4-dioxane/AcOH gave the best results and produced acetophenone after 1 h in a quantitative yield (entry 7). Whereas, Shi et al. [14] obtained acetophenone from ethylbenzene in 85% yield after 24 h by using bulk ceria and applying our similar conditions.

The oxidation of benzylic C–H bonds with KBrO₃ in the presence of catalytic amounts of ceria NPs exhibited high efficiency. In a set of experiments, we studied the oxidation of diphenylmethane to benzophenone with different molar ratios of diphenylmethane/ceria NPs. The results of this study were shown in Table 2.

On the basis of the data in Table 2, the best molar ratio for oxidation of diphenylmethane to benzophenone is 300. Using the results of Table 2, it is possible to calculate turnover number for this transformation (Scheme 2) [16]:

Various structurally arenes were rapidly oxidized to the corresponding carbonyl compounds (aldehydes and ketones) with excellent conversions in a short reaction time (Table 3). Oxidation of toluene leads to formation of benzaldehyde as the chief product (entry 1). 1-Ethyl-4-methyl-benzene, as a dialkyl benzene, was oxidized selectively to 1-*p*-tolyl-ethanone in high yield (entry 3). Also, 2-phenyl propane-2-ol and acetophenone by 78/17 molar ratio were obtained from the oxidation of *iso*-propyl benzene (entry 8). 3,4-Dihydro-10H-antracene-9-one and 2-benzyl pyridine were oxidized to the corresponding ketones in excellent yields (entries 7 and 9).

We observed that in anhydrous acetic acid as solvent and in the presence of sodium acetate and ceria NPs/KBrO₃ system, arenes can be converted to benzyl acetates. The yields of the

$$\text{turn over number} = \frac{\text{mole of product}}{\text{mole of catalyst}} = 300$$

Scheme 2.

benzyl acetates obtained from the oxidation of various arenes were shown in Table 4. In most cases, excellent yields were obtained.

The results of Tables 3 and 4 suggest that the oxidation reaction proceeds via the formation of a benzylic carbocation which reacts with water and acetic acid to give the corresponding hydroxyl or ester derivatives, respectively. The oxidation of benzylic C–H bonds to carbonyl compounds in aqueous acetic acid probably proceeds through the alcohol since the alcohol is present in small amounts at the end of the reaction. The alcohols were oxidized to the corresponding carbonyl groups rapidly by Ce (IV) [33]. The Ce (IV) and bromate salts act as efficient oxidants. The bromate salt oxidizes Ce (III) ion. It is now generally accepted that the side-chain oxidation of arenes by Ce (IV) occurs via an electron-transfer mechanism leading to the formation of carbocations as the reaction intermediates [34–37]. The suggested mechanism was given in by the following reactions [35] (Scheme 3).

As it was mentioned before, subsequent reaction of the carbocation with water and acetate ion leads to formation of alcohol and acetate ester, respectively. The presence of alcohol in the proposed mechanism was investigated by performing the oxidation reaction on 1-phenylethanol in aqueous and anhydrous conditions. By employing 1/1 molar ratio of substrate/oxidant at 95 °C in 5/1/1 (v/v/v) H₂O/1,4-dioxane/AcOH, the alcohol was oxidized to acetophenone completely after 30 min whereas ethylbenzene after 60 min produced acetophenone at the same reaction conditions.

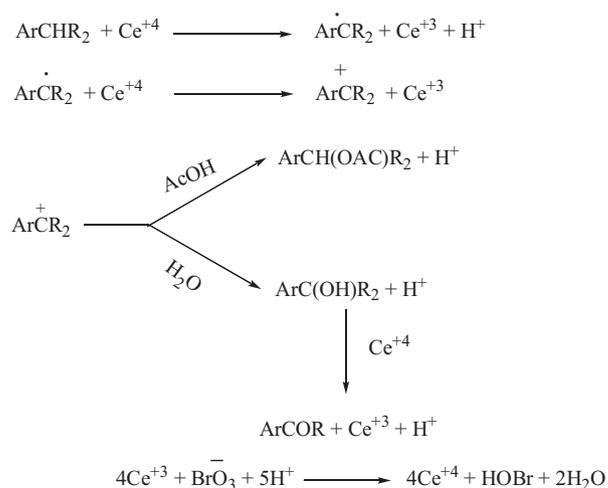
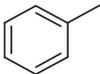
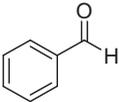
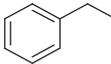
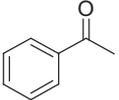
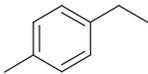
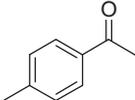
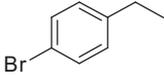
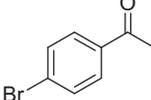
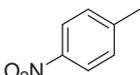
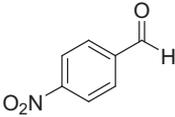
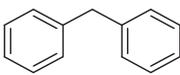
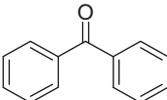
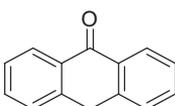
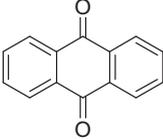
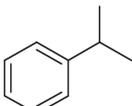
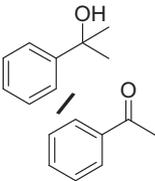
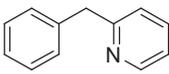
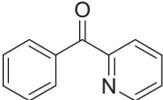
**Scheme 3.**

Table 3
The oxidation of benzylic C—H bond catalyzed with ceria NPs/KBrO₃.

Entry	Substrate	Product ^a	Time (min)	Isolated yield (%)	m.p. °C (lit [Ref.])
1			2 (h)	90	Oil [17]
2			60	80	Oil [18]
3			60	85	Oil [19]
4			15	90	51–52(50–53 [18])
5			5 (h)	75	105–107(106–108 [20])
6			45	95	Oil [21]
7			30	95	285–287(285–288 [22])
8			120	78/17	Oil [23,18]
9			4 (h)	95	Oil [24]

^a The products was identified by the comparison of its physical constants, IR and NMR spectral data with those of an authentic sample.

According to the results, it is plausible to conclude that formation of carbonyl compounds from the oxidation of arenes in aqueous conditions passes through the formation and then oxidation of alcohol.

When the oxidation of 1-phenylethanol was performed in anhydrous conditions, acetic acid 1-phenylethyl ester and acetophenone were produced in 50% and 20% yield, respectively after 60 min. The oxidation reaction was not completed even after prolonged reaction time (3–4 h) and 30% of 1-phenylethanol was remained intact. Acetic acid 1-phenylethyl ester may be obtained from dehydration of 1-phenylethanol and the subsequent reaction of the corresponding carbocation with acetate ion or via from the esterification reaction of 1-phenylethanol with acetic acid. Also, acetophenone was obtained from oxidation of 1-phenylethanol in acidic and anhydrous media (Scheme 4).

On the basis of this study, in anhydrous media, formation of acetate esters only proceeds through the reaction of carbocation with acetate ion and not through the formation of alcohol.

Oxidation of *iso*-propyl benzene leads to formation of 2-phenylpropan-2-ol as a tertiary alcohol and acetophenone (Table 3, entry

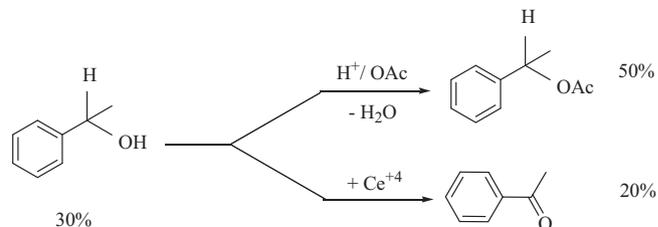
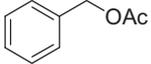
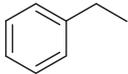
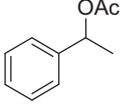
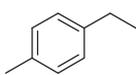
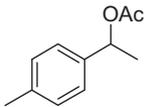
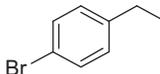
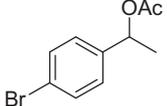
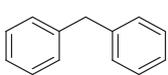
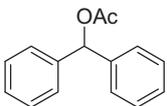
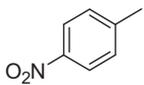
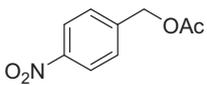
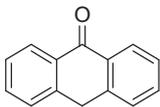
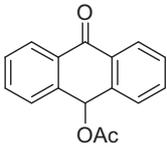
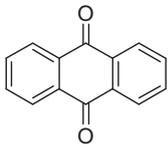
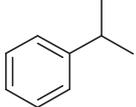
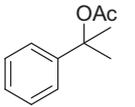
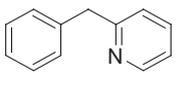
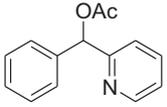
**Scheme 4.**

Table 4
The oxidation of benzylic C–H bonds catalyzed with ceria NPs/KBrO₃ in anhydrous acetic acid.

Entry	Substrate	Product ^a	Time (min)	Conversion (%)	Isolated yield%	m.p. °C (lit [Ref.])
1			120	100	92	Oil [25]
2			60	100	95	Oil [26]
3			60	100	80	Oil [27]
4			45	100	81	Oil [28]
5			30	100	80	Oil [29]
6			300	100	55	78–79 (78 [30])
7 ^b		 	30	100	5/90	105 (107–109 [31])/287(285–288 [22])
8			120	100	85	Oil [32]
9			60	100	92	Oil [33]

^a The products were identified by the comparison of its physical constants, the IR and NMR spectral data with those of an authentic sample.

^b The reaction was performed at 65 °C.

8). According to the proposed mechanism in Scheme 3, formation of tertiary carbocation and subsequent reaction with water produces 2-phenyl propane-2-ol as the major product of the oxidation reaction. Also, the tertiary-formed radical can abstract methyl radical from *iso*-propyl benzene which produced *iso*-propyl benzyl radical and *t*-butyl benzene. The oxidation of *iso*-propyl benzyl radical and its subsequent reaction with water leads to formation of 1-phenylethanol which then produced acetophenone as minor product after oxidation with ceria NPs/KBrO₃ [14,34] (Scheme 5).

The oxidation of 10H-anthracen-9-one (Table 4, entry 7) produces acetic acid 10-oxo-9, 10-dihydro-anthracen-9-yl ester with 5% and anthraquinone with 90% isolated yield. The oxidation reaction produces only one product which is an acetate ester. The obtained acetate ester converts to anthraquinone during the aqueous work up process (Scheme 6) [38].

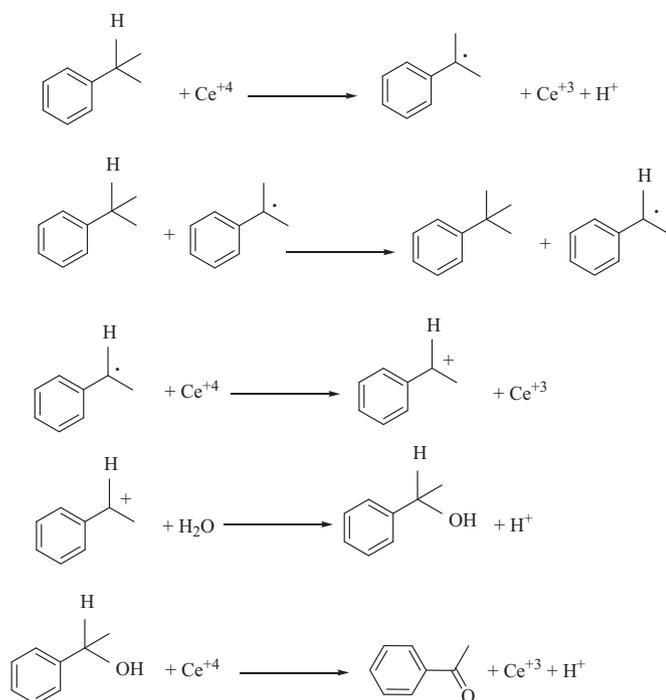
One of the advantages of the ceria NPs as the catalyst is its ability to function as a recyclable reaction medium. We were able to separate ceria NPs from the reaction medium easily by filtering the reaction mixture, washing the residue with dichloromethane and

water, and drying it under vacuum. The recovered ceria NPs can be used again for subsequent reactions. In a set of experiments, we investigated the recyclability of the catalyst (Table 5).

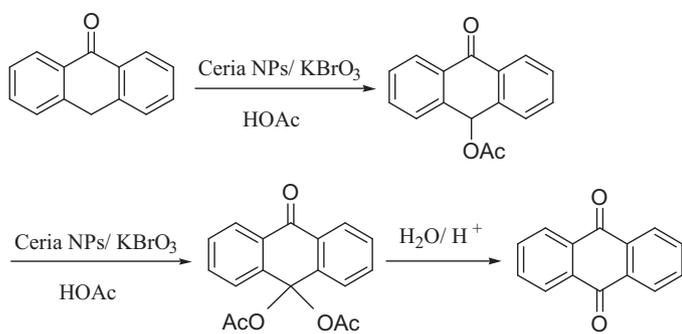
The complete conversion of diphenylmethane to benzophenone was obtained in the presence of ceria NPs which recovered for several times. For all time, the recycled catalyst gave 100% conversion. In this study, ceria NPs as an interesting catalyst provide a novel method for oxidation of benzylic C–H bonds. This catalyst shows the excellent selectivity and high reusable capacity which is

Table 5
The oxidation of diphenylmethane to benzophenone in the presence of reused ceria NPs.

Entry	Time (min)	Temperature (°C)	Conversion%	Isolated yield%
1	30	95	100	92
2	30	95	100	89
3	30	95	100	95
4	30	95	100	93
5	30	95	100	96
6	30	95	100	95



Scheme 5.



Scheme 6.

easily separated from the reaction mixture. Availability, safety, ease in handling of the reagents, high yields, and mildness of the reaction conditions make this method novel for oxidation of benzylic C–H bonds to the corresponding carbonyl compounds and esters. This method is expected to be widely applicable to organic synthesis due to the low cost of the reagents. We believe this protocol will be a useful method in modern synthetic organic chemistry.

4. Conclusions

We developed an efficient and simple procedure for the selective oxidation of benzylic C–H bonds using ceria NPs and KBrO₃ as oxidant. Most importantly, the ceria NPs could also be recycled and reused in subsequent reactions without any significant loss of activity. This method possesses increased compatibility with different functional groups in mild conditions.

Unlike previously reported methods, ceria NPs requires short reaction time to obtain high yields of the products. In summary, the catalyst introduced in the present study gives high yields and it has the operational simplicity and easy recyclability. Further applications of this reagent combination are under investigation in our laboratory.

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