

RESEARCH PAPER

Aqueous-Phase Oxidation of Alcohols with Green Oxidants (Oxone and Hydrogen Peroxide) in the Presence of MgFe_2O_4 Magnetic Nanoparticles as an Efficient and Reusable Catalyst

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ABSTRACT

Nanomagnetic MgFe_2O_4 is an active, stable, and reusable catalyst for the oxidation of alcohols. The oxidation of various primary and secondary alcohols has been examined and related corresponding products were obtained in good yields. The reactions were carried out in the presence of water as solvent and oxone (at room temperature) or H_2O_2 (at 60 °C) as an oxidant. The catalyst was investigated by X-ray powder diffraction, scanning electron microscope, inductively coupled plasma and infrared techniques. Furthermore, the catalyst could be easily recovered and reused up to 7 runs without loss of activity.

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INTRODUCTION

Oxidation is one of the most fundamental reactions in synthetic organic chemistry and a variety of oxidants have been developed. Advances in the development of novel oxidation reagents and methodologies and their utilizations in both target- and diversity-oriented synthesis have been regularly probed, and constituted one of the most widely and actively investigated areas of present organic synthesis. The oxidation of alcohols into their corresponding carbonyl compounds shows a basically important functional group transformation and possesses a chief position

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in new synthetic organic chemistry. They have normally been oxidized in noncatalytic ways with stoichiometric oxidants such as chromium and manganese compounds in the attendandance of strong mineral acids, which produce enormous amounts of toxic metal salts as waste [1,2]. Although a variety of different catalytic systems for catalytic oxidation of alcohols has been developed, there is a growing interest in the search for new efficient metal catalysts for this concern. Therefore, cleanliness, non-toxic and safe oxidation methods are needed [3-6]. Water can be counted as the most agreeable reaction

medium for alcohol oxidation [7]. In recent years, the oxidation processes using hydrogen peroxide (H_2O_2) as reagent in combination of a catalyst have received considerable attention, because H_2O_2 is very mild in nature, relatively cheap and produce only water as product [8,9]. In organic synthesis, oxone is a convenient, easy of handling because its solid state, readily available, relatively stable at room temperature and inexpensive [10-14].

Therefore, in comparison with chromium (VI) reagents, permanganates, or N-chlorosuccinimide (NCS) the use of hydrogen peroxide or oxone has great benefits from both the economic and green chemistry view points.

Recently, nanostructures of magnetic materials have received growing attention due to their new material qualities that are significantly different from those of their bulk counterparts [15-18]. To solve environmental Problems, the application of magnetic particle technology has received increasing attention. By the application of an external magnetic field, the magnetic nanoparticles can easily be separated from the solution [19,20]. These materials have a wide variety of distinctive physico-chemical properties which have relevance to and potential for applications in catalysis [21-24]. Magnesium ferrite ($MgFe_2O_4$) is one of the most fundamental ferrites. It has a cubic structure of normal spinel-type and is a soft magnetic n-type semiconducting material, which finds a variety of utilizations in heterogeneous catalysis, adsorption, sensors, and in magnetic technologies [25,26].

Herein, Magnesium ferrite nanoparticles were synthesized via the auto-combustion assisted sol-gel method [27]. These magnetic nanoparticles were employed as high active and reusable catalyst through magnetic separation for the oxidation of alcohols in the presence of an oxidant oxone (at room temperature) or H_2O_2 (at 60 °C) in water (Fig. 1).

MATERIALS AND METHODS

All the reagents used in the experiments were analytically pure and were purchased from Merck Chemicals Company and Fluka and were used without further purification. The FT-IR transmission spectra were taken with a Jasco 6300 FT-IR spectrometer (KBr disks). The IR spectra were determined from 4000 to 400 cm^{-1} . X-ray diffraction (XRD) patterns of the synthesized

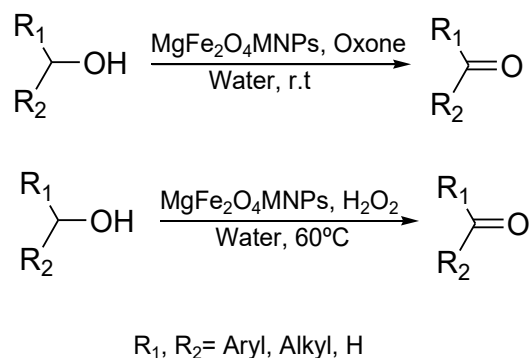
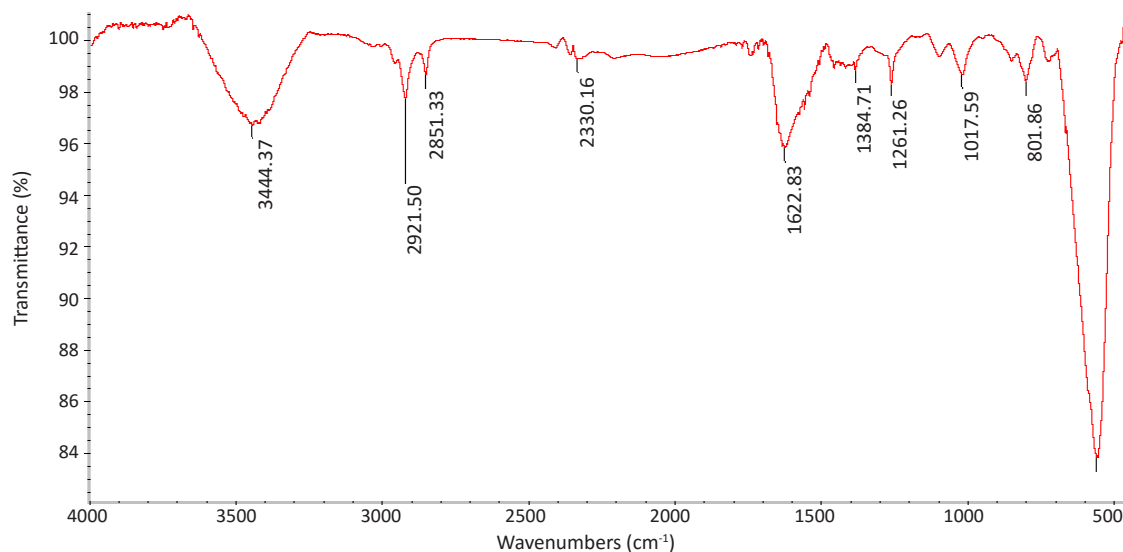


Fig. 1. Alcohols oxidation in the presence of magnetic nanocatalyst.

nanoparticles were taken with a X'Pert-PRO advanced diffractometer using Cu ($K\alpha$) radiation (wavelength: 1.5406 Å), operated at 40 kV and 40 mA at room temperature in the range of 2θ from 10 to 80°. The particle size and morphological characterizations of the of sample were analyzed by a scanning electron microscopy (LEO Co., England, Model : 1455VP). The disc was coated with gold in an ionization chamber. Elemental analysis was performed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Model: VISTA-PRO). TLC and GC were used to follow the reactions. The aliphatic products detected by GC-FID (VARIAN C-P-3800 with FID detector, column CP-Sil 5 CB30m \times 0.32mm).

Catalyst preparation

Magnesium ferrite nanoparticles ($MgFe_2O_4$ MNPs) were synthesized via the auto-combustion assisted sol-gel method of Mg^{2+} and Fe^{3+} ions (molar ratio 1:2) in ammonia solution [27]. Briefly, $Fe(NO_3)_3 \cdot 9H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$ and chelating agent were dissolved in distilled water. The molar ratio of metal nitrate to citric acid was 1:1. The pH value was adjusted in 7 by dropwise adding ammonia solution (28%) to the reaction mixture under constant stirring. Then, the solution was evaporated on a water bath (60 °C) to form a sticky gel. The temperature was increased to 80 °C in order to obtain a thick gel. The gel was kept on a hot plate for auto-combustion and the temperature was increased to ca. 200 °C. A large amount of gases (CO_2 , H_2O , and N_2) released and auto-combustion occurred giving rise to a dark brown ferrite powder. The powder washed with distilled water and acetone several times and isolated in a magnetic field. The final product was dried.

Fig. 2. FT-IR spectrum of $MgFe_2O_4$ MNPs.

General procedure for the oxidation of alcohol

In a round-bottomed flask Alcohol (1 mmol), water (2 mL) and 5 mol% of nanomagnetic- $MgFe_2O_4$ (10 mg) were placed. The reaction mixture was vigorously stirred for two minutes. Then, oxone (0.5 mmol at r.t) or H_2O_2 (1.3 mmol at 60 °) was added in three portions due 15 minutes. The reaction mixtures were placed at the mentioned conditions. The progress of the reaction was monitored by TLC (EtOAc-cyclohexane, 2:10) in comparison with the standard samples of corresponding alcohols and carbonyl compounds. After the oxidation was completed, the product was extracted with dichloromethane. The solvent was evaporated under reduced pressure to give the corresponding pure aromatic products. Purification of the residue using flash column chromatography (silica gel) provided the pure carbonyl compounds. The aliphatic products in dichloromethane were dried by using anhydrous $MgSO_4$ and detected by GC-FID in comparison with the standard samples of corresponding alcohols and carbonyl compounds. The GC yields of the aliphatic products products were calculated based on their gas chromatogram.

RESULTS AND DISCUSSION

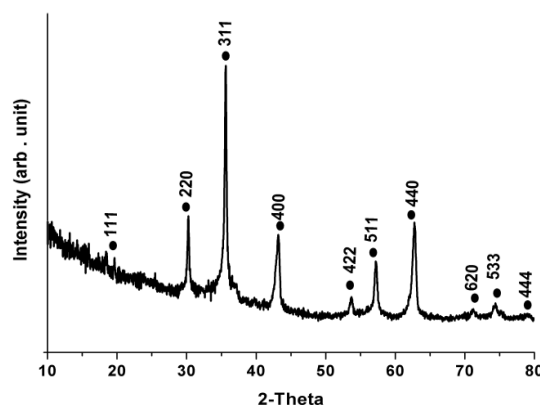
Characterization of the catalyst

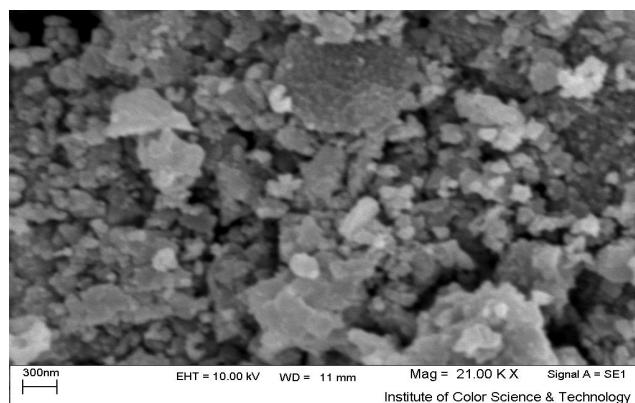
The FT-IR spectrum of $MgFe_2O_4$ MNPs (Fig. 2) shows two ranges of the absorption bands: 4000–1000 and 1000–400 cm^{-1} . The strong band of OH (3431 cm^{-1}) indicates that a large number of OH groups are presented on the surface of the MNPs.

In the range of 1000–400 cm^{-1} , a typical metal–oxygen absorption band for the spinel structure of the ferrite at ~ 580 cm^{-1} was observed. This band strongly suggests the intrinsic stretching vibrations of the metal ($Fe \leftrightarrow O$) at the tetrahedral site [28].

Fig. 3 shows the XRD pattern of the synthesized $MgFe_2O_4$ MNPs that shows reference XRD pattern of JCPDS card No. 98-011-0971. Comparison of these figures revealed that the synthesized sample entirely consisted with cubic spinel structure of magnesium diiron (III) oxide [27,29-31]. The particle size of the $MgFe_2O_4$ determined by the Debye-Scherrer equation via XRD data ($D = 0.94 \lambda / B \cos \theta$) was 33.9 nm.

From the ICP result, the atomic ratio of Mg-Fe is 0.22, which is close to that of $MgFe_2O_4$ and 12% of weight is magnesium. The SEM analysis suggests that the $MgFe_2O_4$ MNPs are nanocrystalline and

Fig. 3. XRD pattern of $MgFe_2O_4$ MNPs.

Fig. 4. SEM image of the obtained $MgFe_2O_4$ MNPs.

most of the $MgFe_2O_4$ particles are also irregular spherical (Fig. 4). These results are in good harmony with the XRD analyses.

Optimization of alcohol oxidation conditions

In a trial reaction, we tried to convert 2-chlorobenzyl alcohol (1 mmol) to 2-chlorobenzaldehyde, as a model reaction in the presence of $MgFe_2O_4$ as a nanomagnetic catalyst (5mg, 2.5 mol%) and oxone(1 mmol was added in three stages) in various solvents at room temperature and the results are given in Table 1. In the all conditions, 2-chlorobenzaldehyde was formed

as the major product but the highest yield for 2-chlorobenzaldehyde was achieved in the water (Table 1, Entry 3).

We also studied the oxidation of 2-chlorobenzyl alcohol to 2-chloro benzaldehyde with other oxidants such as O_2 or H_2O_2 in the presence of nanomagnetic $MgFe_2O_4$ catalyst in water at room temperature. These results showed that the higher yield was achieved with oxone as an oxidant. We observed that in the absence of oxidant (under nitrogen atmosphere), 2-chlorobenzyl alcohol did not oxidize with this system, even in long reaction time (Entry9).

Table 1. Oxidation of 2-chlorobenzyl alcohol (1mmol) in the presence of $MgFe_2O_4$ MNPs catalyst at room temperature.

Entry	Catalyst (mol%)	Oxidizing agent (mmol)	Solvente	Yield ^a (%)	Time(min)
1	2.5	Oxone(1)	Cyclohexane	trace	60
2	2.5	Oxone(1)	Acetonitrile	20	60
3	2.5	Oxone(1)	Water	55	60
4	2.5	Oxone(1)	Ethanol	trace	60
5	2.5	Oxone(1)	Dry toluene	trace	60
6	2.5	Oxone(1)	Ethyl acetate	10	60
7	2.5	H_2O_2 (1)	Water	22	60
8	2.5	O_2 atmosphere	Water	10	60
9	2.5	-	Water	0	60
10	10	Oxone(1)	Water	87	60
11	5	Oxone(1)	Water	88	60
12	4	Oxone(1)	Water	70	60
13	0	Oxone(1)	Water	23	60
14	5	Oxone(0.7)	Water	86	60
15	5	Oxone(0.5)	Water	88	60
16	5	Oxone(0.3)	Water	50	60
17	5	Oxone(0.1)	Water	20	60

^a Yields refer to isolated products.

Table 2. Oxidation of 2-chlorobenzyl alcohol (1 mmol) to 2-chlorobenzaldehyde with H₂O₂ (1mmol) at different temperatures in the presence of MgFe₂O₄ MNPs catalyst (5 mol%) in water (2mL).

Entry	Temperature(°C)	Yield(%)	Time(min)
1	80	Mixture of aldehyde and acid	60
2	60	74	60
3	40	50	60
4	r.t	25	60

Table 3. Oxidation of 2-chlorobenzyl alcohol (1mmol) to 2-chlorobenzaldehyde with different amounts of H₂O₂ in the presence of MgFe₂O₄ magnetic nanocatalyst (5 mol%) at 60 °C in water.

Entry	H ₂ O ₂ (mmol)	Yield(%)	Time(min)
1	1.4	85	60
2	1.3	85	60
3	1.2	83	60
4	1.1	81	60
5	1	74	60
6	0.8	58	60

The amount of the catalyst and oxidant were also optimized. The results show that 5 mol% of catalyst (10 mg) and 0.5 mmol of the oxidant is the optimum amount for 1 mmol alcohol (Entries 11 and 15). The suitable temperature for the oxidation in the presence of oxone was room temperature and at high temperatures (>40 °C), the reaction produces corresponding carboxylic acid as a byproduct.

We also carried out the reaction with H₂O₂ in the presence of MgFe₂O₄ magnetic nanocatalyst (5 mol%). The results show that 1.3 mmol of H₂O₂ at

60 °C is the optimum amount for the oxidation of 1 mmol alcohol to the corresponding aldehyde (Table 2 and Table 3).

Application scope

The optimized condition was used for various alcohols to screen the generality of the work. As indicated in Table 4, MgFe₂O₄ MNPs catalyst showed high efficiency for the oxidation of a wide range of alcohols. The competing reaction such as over oxidation of aldehydes to the corresponding carboxylic acids was not observed in any of the

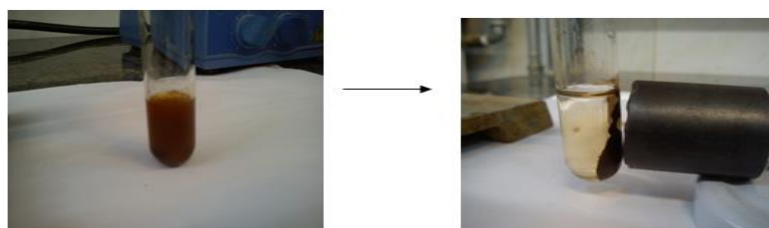


Fig. 5. Separation of nanomagnetic catalyst from the reaction mixture by exposure of the reaction vessel to an external magnet.

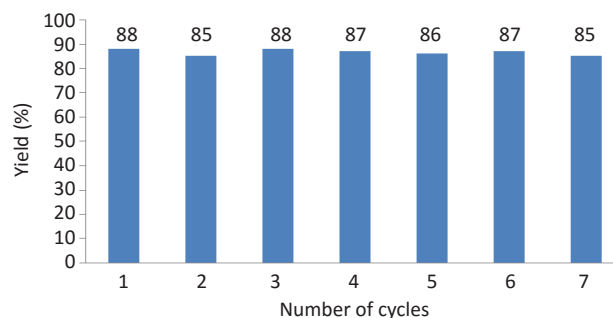
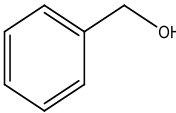
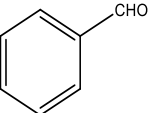
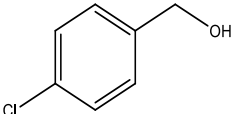
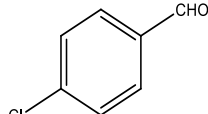
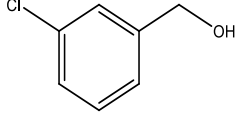
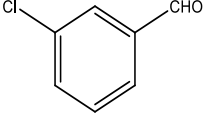
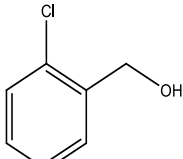
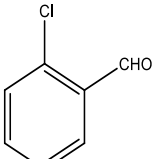
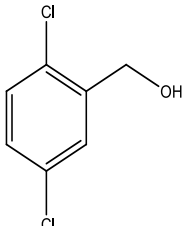
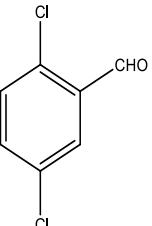
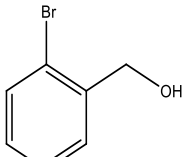
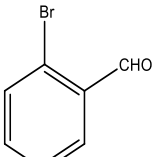
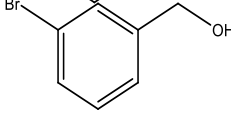
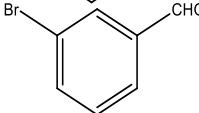
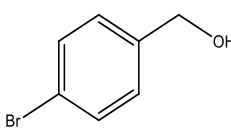
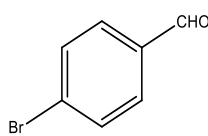
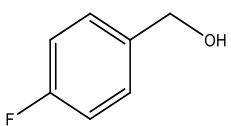
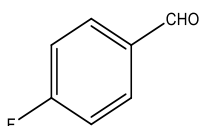
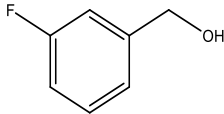
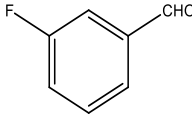
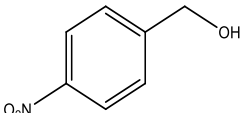
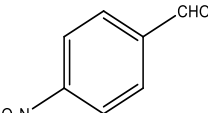
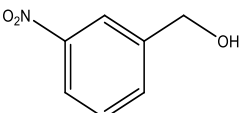
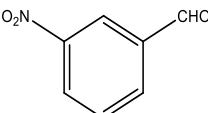
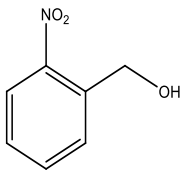
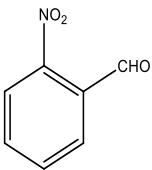
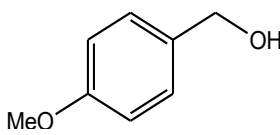
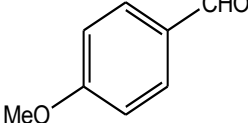
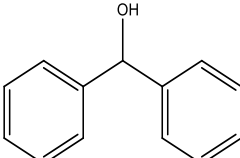
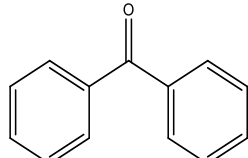
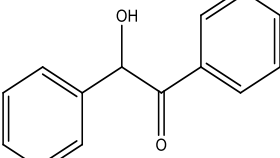
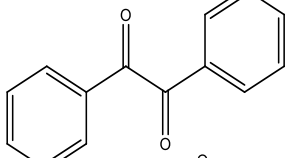
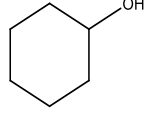
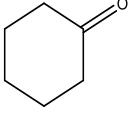
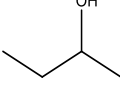
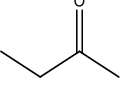
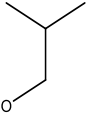



Fig. 6. Recycling of the catalyst for oxidation of the 2-chlorobenzyl alcohol.

A. Ramazani / MgFe₂O₄ Magnetic Nanoparticles as an Efficient and Reusable CatalystTable 4. Oxidation of various alcohols using MgFe₂O₄ MNPs as catalyst (5 mol%) in the presence of oxone (r.t) or H₂O₂ (60 °C) in water

Entry	Substrate	Product	Yield ^a (%) (Oxone)	Yield ^a (%) (H ₂ O ₂)	Time (min)
1			90	88	55
2			88	86	60
3			89	87	65
4			88	85	60
5			85	85	80
6			86	87	65
7			88	86	65
8			85	84	60
9			88	88	70

10			86	88	70
11			83	81	120
12			84	85	120
13			83	86	120
14			91	92	50
15			85	87	70
16			70	72	100
17 ^b			99.84	99.94	120
18 ^b			99.50	93.51	120
19 ^b			99.16	99.78	120

^aIsolated. ^bThe yields refer to GC analysis.

cases under above conditions. In most cases, the aldehyde selectivity was quite high (>99%). The oxidation of various benzylic alcohols gave the carbonyl compounds in high yields and short reaction times. The electron withdrawing groups reduced the reaction rate dramatically (Entry 11) and the electron donating groups accelerates the reaction rate (Entry 14). The oxidation times for aliphatic alcohols were fairly long (Entry17-19). In comparison with the other catalysts, for example nano Fe_2O_3 [32], we concluded that oxidation in the presence of nanomagnetic $MgFe_2O_4$ was accomplished at low temperatures and short reaction times. In comparison with nanomagnetic Fe_3O_4 [33], nanomagnetic $MgFe_2O_4$ is a more stable catalyst because this catalyst could be reused up to 7 runs without loss of activity.

Catalyst recycling

The catalyst was easily recovered from the reaction mixtures by exposure of the reaction vessel to an external magnet and decantation of the reaction solution (Fig. 5). The solid catalyst was washed with acetone and water to remove residual product and dried. The catalyst could be subsequently reused in 7 further iterative cycles. The recovered catalyst is found to exhibit almost the same catalytic activity for oxidation of 2-chlorobenzyl alcohol by the oxone (Fig. 6).

CONCLUSION

In conclusion, nanomagnetic- $MgFe_2O_4$ shows very good catalytic activity/selectivity in the oxidation of primary and secondary alcohols to aldehydes and ketones by oxone or H_2O_2 in water condition. In both cases, the catalyst can be easily removed from the reaction mixture and reused several times without a significant loss of its catalytic activity. Both the oxidation protocols are green/ environmentally friendly. The use of nontoxic and inexpensive materials, stability of the oxidation system, simple method, short reaction times, good yields of the products and mild reaction circumstances are the merits of this method. The extension of the application of this nanocatalyst to various oxidation reactions is currently under investigation in our laboratory.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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