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A Recyclable Ferrite–Co Magnetic Nanocatalyst for the Oxidation of Alcohols to Carbonyl Compounds

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Oxidation of alcohols into carbonyl compounds is one of the most important and fascinating reactions in organic chemistry which stems from the fact of it being valuable raw material for the chemical and pharmaceutical industries. An enormous variety of oxidizing reagents and catalysts are available for the oxidation of alcohols.[1] Traditional reagents as those derived from Cr or Mn must be used in stoichiometric amounts and are often accompanied by the formation of toxic waste products, which can be deleterious during the work-up procedure, resulting in tricky product isolation, and rendering impossible the reusability of the catalyst. The use of hypervalent iodine reagents such as Dess–Martin periodinane (DMP) presents some problems, however, advances have been achieved with the development of various 2-iodoxybenzoic acid (IBX, a DMP precursor) derivatives which have improved solubility, are non-explosive, and/or are recyclable.[1e]

Homogeneous and heterogeneous catalysts combined with environmentally benign oxidants, such as molecular oxygen, organic peroxide, and hydrogen peroxide are major challenges in the oxidation of alcohols.[1d, 1g, 2] Molecular oxygen and hydrogen peroxide are considered to be green oxidants because they are inexpensive and minimize the chemical waste, having water as the sole by-product. In line with this, Beller and coworkers reported selective oxidation of alcohols to aldehydes and ketones using ruthenium-based catalysts and H_2O_2 as the oxidant.[2c]

Notably, the homogeneous catalyst systems show good catalytic activity compared to heterogeneous catalysts[3] but on an industrial scale the problems related to handling, recovery, and reuse of the catalyst represent limitations for these processes. Instead heterogeneous catalysts have been frequently used for the oxidation of alcohols owing to easy recovery, ease in handling, and safety of the catalyst. Recently, developmental work has been carried out on the catalytic aerobic oxidation of alcohols mediated by several heterogeneous catalyst systems based on Ru, Mo, Pt, or Pd.[3,4]

Other successful reported procedures involve the nitroxyl radical TEMPO (2,2,6,6-tetramethylpiperidin-1-yloxyl) employed as a recyclable oligomeric catalyst (PIPO, polymer immobilized TEMPO) using sodium hypochlorite as the oxidant and avoiding the use of halogenated hydrocarbon solvents.[5] The main drawback of this method is the use of a stoichiometric quantity of oxidant, NaOCl, which generates NaCl as waste. The conjugation of TEMPO with noble metals such as Ru or Pd could circumvent this problem replacing NaOCl with O_2 although a shortcoming is the lack of activity with some alcohols.[5]

Following the first cobalt-catalyzed aerobic oxidation of alcohols using cobalt–nitro complexes by Tovrog et al.[6] several systems for cobalt-catalyzed aerobic alcohol oxidations have emerged.[7] Although most secondary alcohols are converted into ketones, primary alcohols are often oxidized to the carboxylic acid. There are different strategies for the heterogenization of redox-active elements in solid matrices.[8] Functionalized magnetic nanoparticles (MNPs) are heterogeneous catalyst supports, which have emerged as viable alternatives to conventional materials because they are robust, inert, inexpensive, reusable, and recyclable using a simple magnet.[9] A variety of catalytic systems involving metal-supported MNPs have been devised and used in synthetic organic reactions such as nano ferrite-supported Pd,[10] hydroxyapatite-supported Pd,[11] alumina-supported Pd,[12] silver nanoparticles supported on hydrotalcites,[13] ruthenium-supported ferrite,[9p] Pd on mesoporous carbon,[14] gold-supported on metal oxides,[15] and Au–Pd–titania.[16] Among the numerous methods, free nano-Fe_2O_3,[9k] and recyclable SBA-15 TEMPO-supported catalysts are the most promising because they avoid the use of transition metals.[4b] With a few exception these protocols include the use of noble metals, expensive ligands, and involve multistep synthesis for the catalyst preparation. Therefore, there is an urgent need to developed inexpensive and benign protocols for oxidation reactions. In continuation of our research on the development of greener protocols,[17] new methods, and nanocatalysis[18] we have developed a new, simple, and efficient method for functionalization of ferrite MNPs with Co and its application for the oxidation of alcohols. Fe_3O_4–Co MNPs were prepared by the simple wet impregnation method followed by chemical reduction as reported in the literature[19a,b] (Scheme 1). Characterization of the nanocatalyst was achieved through X-ray diffraction (XRD), inductive coupled plasma atomic emission spectroscopy (ICP–AES), transmission electron microscopy (TEM), secondary ion mass spectrometry (SIMS), and X-ray photoelectron spec-

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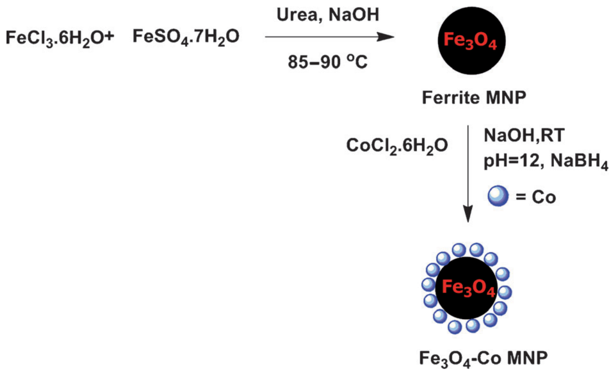


Scheme 1. Synthesis of Ferrite (Fe_3O_4) and Fe_3O_4–Co MNPs.

troscopy (XPS). The weight percentage of Co was determined to be 8.12 % by ICP–AES analysis (ESI).

Characterization of the catalyst by SIMS reveals the presence of Co over the surface of ferrite. The positive and negative mass spectra of intact and sputtered surfaces are shown in Figure 1. Distinct ions of ferrite are observed at m/z 56 $[Fe]^+$, 72 $[FeO]^+$, and 73 $[FeOH]^+$. The characteristic ions of cobalt oxide (CoO) were observed at m/z 59, 75, 76, and 77, corresponding to Co^+, CoO^+, $CoOH^+$, and $CoOH_2^+$, respectively. In negative ion mode the cobalt oxide ions, CoH^-, CoO^-, $CoOH^-$, $CoOH_2^-$, CoO_2^-, CoO_2H^-, $CoO_2H_2^-$, CoO_3^-, and CoO_3H^- were observed at their respective m/z as shown in Figure 1 b.

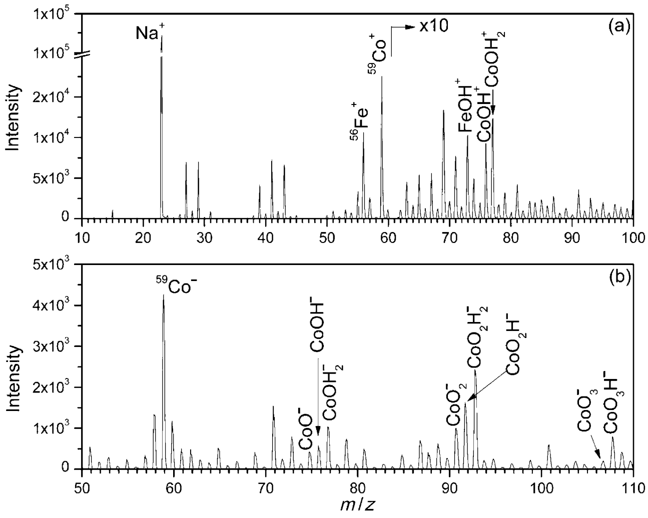


Figure 1. Positive (a) and negative (b) TOF-SIMS spectra from Fe_3O_4–Co analyzed with an upgraded VG Ionex, equipped with a Ga^+ liquid metal ion gun.

The TEM image of ferrite-Co, Figure 2, shows that magnetic nanoparticles are obtained in the nano size range with uniformly sized particles presenting a somewhat spherical morphology with an average diameter range from 10 to 30 nm.

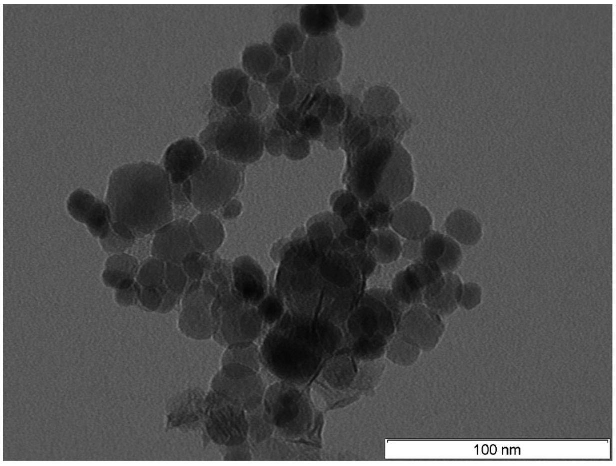


Figure 2. TEM of Fe_3O_4–Co MNPs at 100 nm.

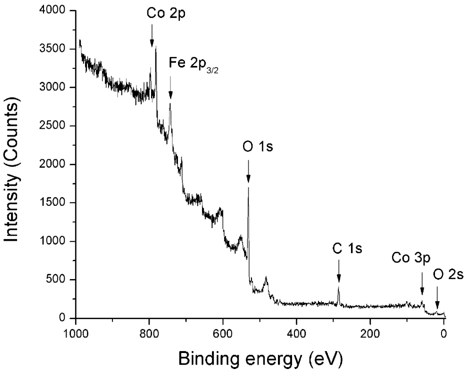


Figure 3. Survey spectrum of Co–Fe_3O_4 powder supported on In plate. The spectrum was taken in FAT 44 mode with energy step of 0.5 eV and acquisition time of 0.5 s.

The survey XPS spectrum of the sample taken in fixed analyzer transmission mode with the pass energy of 44 eV (FAT 44) is given in Figure 3. The most intensive XPS lines are marked by arrows. Besides the main O, Fe, and Co lines we also observe a C 1s line which is an expected impurity.

The surface composition of the powder was determined from the characteristic XPS peak intensities of Co, Fe, O, and C which are Co $2p_{3/2}$, Fe $2p_{3/2}$, O 1s, and C 1s, respectively. To improve the sensitivity, the lines were recorded with long acquisition times. As for the sensitivity factors, we use recommended values for the $Mg_{K\alpha}$ line.[19c] Oxygen appears to be the most abound element in the powder (49 %) followed by carbon (38 %), cobalt (8 %), and iron (5 %). The presence of carbon corresponds to surface contamination. The main contribution of the carbon peak, which should correspond to adventitious carbon, is at 285.5 eV instead of the more common value 285.0 eV, thus indicating some charging effects. The characteristic peaks of cobalt (Co 2p) and iron (Fe $2p_{3/2}$) are presented in the Figure 4 and Figure 5, respectively. The spectra were taken in fixed analyzer transmission mode with the pass energy of 22 eV, the energy step was 0.1 eV, and the acquisition time window was 12 s.

The main Co $2p_{3/2}$ and Co $2p_{1/2}$ peaks shown in Figure 4 are at 780.0 eV and 795.6 eV, respectively. In addition, both peaks are 'accompanied' by broad shake-up satellites meaning that

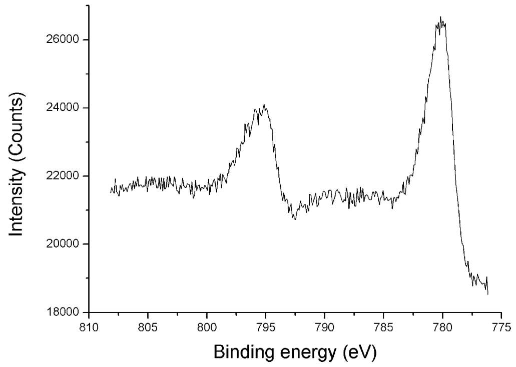


Figure 4. Co 2p XPS line taken with the energy step of 0.1 eV and acquisition time window of 12 seconds.

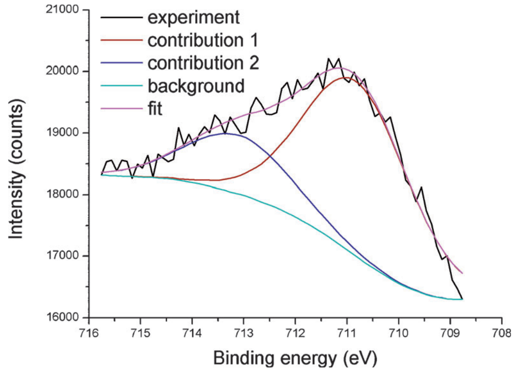


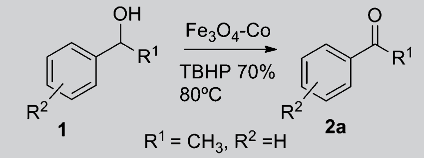
Figure 5. Fe $2p_{3/2}$ XPS line taken with the energy step of 0.1 eV and acquisition time window of 12 seconds.

cobalt is in the paramagnetic state. The position of the Co 2p multiplet, low intensity of the satellites, and their shift with respect to the main peaks of about 8.5 eV clearly indicate that cobalt is present in the sample as Co_3O_4. Indeed, Co_3O_4 spinel surface is characterized by sharp Co 2p peaks at 779.8 eV and 795.7 eV with the weak and broad satellite structure located about 9 eV higher in binding energy with respect to the main peaks.[19d–f] The satellite structure is usually used to differentiate between CoO and Co_3O_4 oxide phases, because the former have satellite peaks having about 26 % of the main peak intensity.[19g,h] Therefore, the CoO phase was not registered. Because of the same reason we may also exclude the presence of $Co(OH)_2$ for which the satellite peak intensity should be about 33 % of that of the main peak.[19h,i] However, one should have in mind that Co_3O_4 spinel has a unit cell consisting of 56 atoms: 32 O^{2-} anions, 16 Co^{3+} cations occupying octahedral sites and 8 Co^{2+} cations occupying tetrahedral sites.[19j] According to the study of Chuang et al.[19d] the Co 2p structure in the photoelectron spectrum can be separated into two contributions attributed to Co^{2+} and Co^{3+}. The contributions of Co^{+2} cations are shifted towards higher binding energies with respect to the latter. Besides, satellites are present only for the ionization state +2. Because the crystalline structure should not be formed on our sample, the shape of the Co 2p peak most probably corresponds to the mixture of oxides in which cobalt is present as both Co^{2+} and Co^{3+}. The spectrum presented in Figure 4 is very similar to that of Co_3O_4 (110) surface,[19g,j] suggesting that the ratio between the amounts of Co^{2+} and Co^{3+} is about 1:2. However, being aware of the charging problems owing to which the peaks are slightly shifted towards higher binding energies, the relative amount of Co^{3+} is probably overestimated.

The characteristic photoelectron peak of iron Fe $2p_{3/2}$ is presented in Figure 5. By using the pseudo-Voigt GL (30) as the peak model and the constraint that the width of each contribution is constant, the peak can be fitted to two contributions. The main one at 710.8 eV and relative intensity of about 75 % perfectly matches Fe_3O_4,[19k,l] The second contribution at 713.1 eV and relative intensity of 25 % is most probably due to the sample charging.

The synthesized and well characterized Fe_3O_4–Co MNPs were explored for the oxidation of alcohols. The oxidation of 1-phenylethanol (**1**) to acetophenone (**2a**) was used as a model reaction and the results are collected in Table 1. Under catalyst-free and oxidant-free conditions no reaction was observed (Table 1, entries 1 and 5). Using H_2O_2 (30 %) as the oxidant the reaction proceeds sluggish and only 20 % yield was obtained (Table 1, entry 2). Using TBHP (*tert*-butyl hydroperoxide; 70 %) as the oxidant an excellent yield of **2a** was obtained (92 %) in short reaction time (Table 1, entry 3). However, cobalt-free Fe_3O_4 gave only a trace amount of **2a** (Table 1, entry 4).

Table 1. Optimization of reaction conditions.[a]



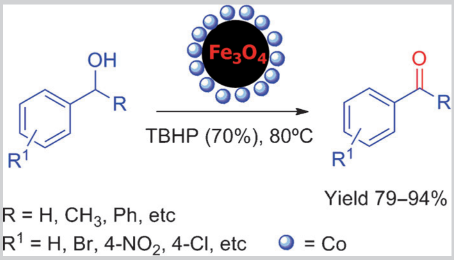
Entry	Catalysts	Oxidant	Time [h]	Yield [%][b]
1	Fe_3O_4–Co	–	48	NR
2	Fe_3O_4–Co	H_2O_2 (30 %)	24	20
3	Fe_3O_4–Co	TBHP (70 %)	6	92
4	Fe_3O_4	TBHP (70 %)	6	trace
5	–	TBHP (70 %)	24	NR

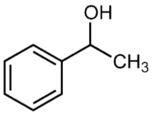
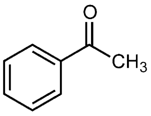
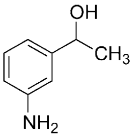
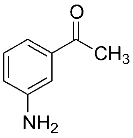
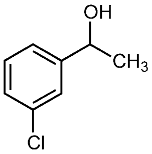
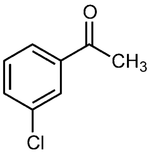
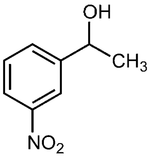
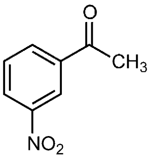
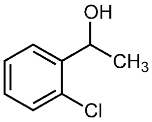
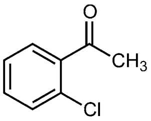
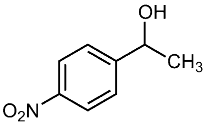
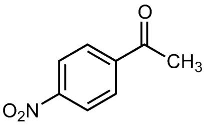
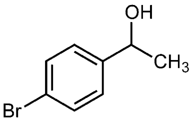
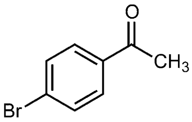
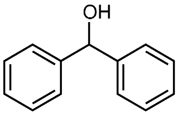
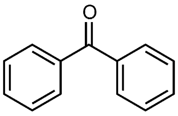
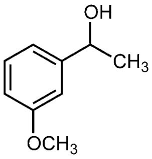
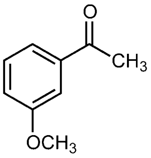
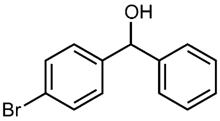
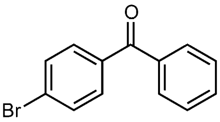
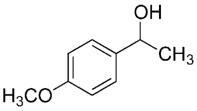
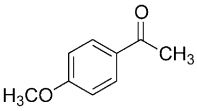
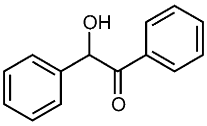
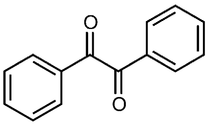
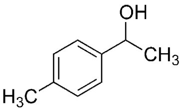
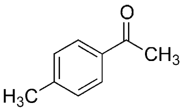
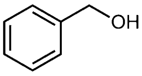
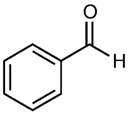
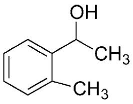
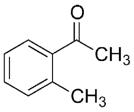
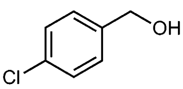
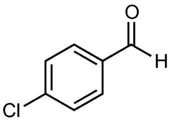
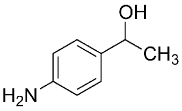
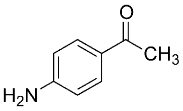
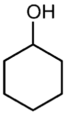
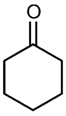
[a] Reaction conditions: 1-phenylethanol (1 mmol), oxidant (1.2 mmol), catalyst (100 mg; 13.7 mmol % of Co), 80 °C. [b] Yield of isolated product. NR = no reaction.

Other alcohol substrates were subject to the oxidation reaction with the well characterized Fe_3O_4–Co MNPs (Table 2) with excellent results. The reaction under solvent-free conditions proved to be of large applicability to a wide variety of structurally and electronically diverse primary and secondary alcohols. The reaction was also successfully carried out for benzyl alcohols containing electron-releasing or electron-withdrawing groups and the corresponding ketones **2** were obtained in high yields (Table 2).

This oxidation protocol tolerates a variety of functional groups such as methoxy, chloro, bromo, methyl, amino, and nitro groups. Aliphatic secondary alcohol such as cyclohexanol reacted well under these conditions and cyclohexanone was

Table 2. Ferrite-Co catalyzed oxidation of aldehydes and ketones.[a]



Entry	Alcohol	Product	Time [h]	Yield [%][b]	Entry	Alcohol	Product	Time [h]	Yield [%][b]
1		**2a** 	5	92	10		**2j** 	5	83
2		**2b** 	6	89	11		**2k** 	5	82
3		**2c** 	6	85	12		**2l** 	5	84
4		**2d** 	6	88	13		**2m** 	5	93
5		**2e** 	5	92	14		**2n** 	5	88
6		**2f** 	5	94	15		**2o** 	5	94
7		**2g** 	5	91	16		**2p** 	5	82
8		**2h** 	5	90	17		**2q** 	5	79
9		**2i** 	5	86	18		**2r** 	6	85

[a] Reaction conditions: alcohol (1 mmol), oxidant (1.2 mmol), catalyst (100 mg; 13.7 mmol% of Co), 80 °C. [b] Yield of isolated product.

obtained in 85% yield. The functional group at the *ortho* or *para* positions of the benzyl alcohol did not have much influence on the reaction. The present protocol offers a good catalytic system for the oxidation of benzoin, with no cleavage of carbon–carbon bonds, which is generally observed with other conventional methods (Table 2, entry 15).[20]

To understand the efficiency of our protocol with respect to others for the oxidation of diphenylmethanol to benzophe-

Table 3. Comparison of reported procedures for the oxidation of diphenylmethanol to benzophenone (**2 m**).

Entry	Reaction conditions	Yield [%][a]	E Factor	Mass intensity
1	resin-dispersion of Pd; K_2CO_3, H_2O, Reflux, O_2, 20 h[8e]	85	35.10	40.76
2	SBA-15 Pd NPs, K_2CO_3,toluene, 80 °C, O_2/air, 20 h[21]	99	32.61	34.77
3	IBX, Bu_4NHSO_4, water, oxone, nitromethane, 70 °C, 8 h[23]	88	31.77	33.27
4	NAP–Mg–Pd(0), K_2CO_3, toluene, RT, 10 h[22]	99	19.96	21.11
5	Fe_3O_4–Co, TBHP (70 %), 80 °C, 5 h (this study)	93	0.98	2.40

[a] Yield of isolated product.

none, the results compared in Table 3 clearly indicate that the present conditions are the most efficient, clean, and comparatively more sustainable (Table 3, entry 5). However, other protocols have their own advantages. The protocol reported by Karimi et al.[21] and Kantam and co-workers[22] (Table 3, entry 2 and 4, respectively) presents comparable yields, but not the related E Factor (cost and environmental impact of the process) and mass intensity. Also, the main drawbacks of these protocols are the use of toluene as solvent and Pd metal, which is quite expensive. For specific reaction conditions see the corresponding literature and the Supporting Information for calculations.

To prove that the reaction is heterogeneous, a standard leaching experiment was conducted by the hot filtration method. The model reaction of oxidation of 1-phenylethanol proceeded for 20 minutes in the presence of the Fe_3O_4–Co at 80 °C. The hot filtered reaction mixture was then stirred without catalyst for 12 hours. Notably, no formation of the corresponding product was observed, even after 12 hours, indicating that no homogeneous catalyst was involved.

Inductively coupled plasma atomic emission spectra (ICP–AES) analysis of the filtrate (hot) revealed the absence of Fe and Co species in the filtrate. The stability of Fe_3O_4–Co was tested for the oxidation of **1 a** to **2 a** by recycling and reuse of the catalyst seven times without any significant loss of the catalytic activity. After completion of the reaction, and between each cycle the nanocatalyst was easily separated by simple decantation using an external magnet, washed with ethyl acetate, dried under vacuum, and subjected to the next cycle. Notably, after the 7th cycle negligible loss in the yield was observed (Figure 6). The Co content Fe_3O_4–Co catalyst was observed to be 8.12 % before the reaction and 8.03 % after the reaction and so indicated negligible Co leaching.

In summary, we have designed a robust magnetically separable and inexpensive nanocatalyst for oxidation of alcohols to corresponding ketones that renders the present protocol highly cost effective and environment friendly. This magnetic nanocatalyst can be easily prepared by the impregnation method. In addition, the nanocatalyst can be efficiently recovered from the reaction medium by decantation of the reactions mixture by simply exposing the mixture to a magnet and used for up to seven reaction cycles. We believe that this magnetic nanocatalyst is a viable alternative for existing protocols.

Experimental Section

All commercial reagents were used as received unless otherwise mentioned. For analytical and preparative thin-layer chromatography, Merck, 0.2 mm and 0.5 mm Kieselgel GF 254 percoated were used, respectively. The spots were visualized using UV light. ^1H NMR spectra were recorded on a Bruker 400 spectrometer, 5 mm at 400 Hz. ^1H shifts are reported relative to internal tetramethylsilane.

Preparation of Ferrites/Fe_3O_4

The $FeCl_3.6H_2O$ (5.4 g) and urea (3.6 g) were dissolved in distilled water (200 mL) at 85 to 90 °C for 2 h. The solution turned to brown. To the resultant reaction mixture was cooled to RT before

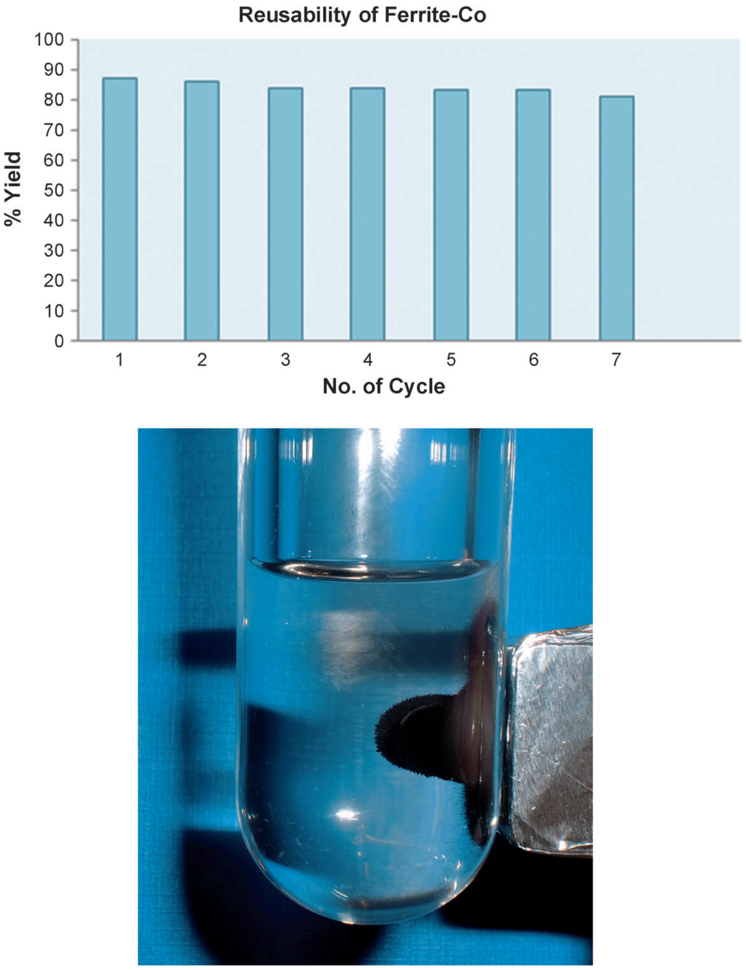


Figure 6. Reusability of Fe_3O_4–Co MNPs (Inset catalyst separated by magnet); Reaction conditions: 1-phenylethanol (1 mmol), oxidant (1.2 mmol), catalyst (100 mg), 80 °C (for details please see the Supporting Information).

$FeSO_4.7H_2O$ (2.8 g) was added and then 0.1 м NaOH until the pH value reached 10. The molar ratio Fe^{III} to Fe^{II} in the above system was nearly 2.00. The obtained hydroxides were treated by ultrasound in the sealed flask at 30 to 35 °C for 30 min. After ageing for 5 h the obtained black powder of Fe_3O_4 was washed, and dried under vacuum.

Preparation of Fe_3O_4–Co MNPs

Ferrite magnetic nanoparticles Fe_3O_4 (2 g) and $CoCl_2.6H_2O$ (10 wt% of cobalt on ferrite) were stirred at RT in water (50 mL) for 1 h. After impregnation, the suspension was adjusted to pH 12 by adding sodium hydroxide (0.5 м) and stirred for 10 to 12 h. The solid was washed with distilled water (5×10 mL). The obtained metal precursors were reduced by adding 0.2 м aqueous $NaBH_4$ drop wise under gentle stirring in an ice-water bath for 30 min until no bubbles were observed in the solution. The resulting Fe_3O_4–Co MNPs were subject to ultrasonication for 10 min and then washed with distilled water and subsequently with ethanol and dried under vacuum at 60 °C for 24 h.

General procedure for the oxidation reaction

A mixture of alcohol (1 mmol), 70% aqueous *tert*-butyl hydroperoxide solution (TBHP) (1.2 mmol), and 100 mg of Fe_3O_4–Co MNPs (13.7 mmol% Co), was stirred at 80 °C, for an appropriate time. After completion of the reaction, ethyl acetate (5 mL) was added and the catalyst removed by simple decantation. The organic solvent was evaporated under vacuum and the crude product purified by column chromatography on silica gel using *n*-hexane and ethyl acetate as eluent (90:10).

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Keywords: heterogeneous catalysis · magnetic nanoparticles · oxidation reactions · recyclable · sustainable protocol

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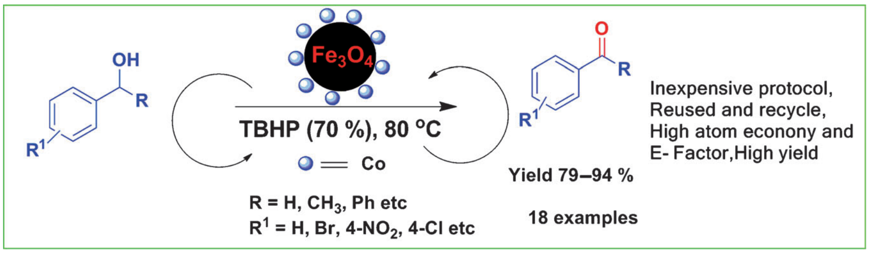
■■–■■

A Recyclable Ferrite–Co Magnetic Nanocatalyst for the Oxidation of Alcohols to Carbonyl Compounds



Magnetic cleansing: A magnetic Fe_3O_4–Co catalyst was prepared using inexpensive precursors and its catalytic activity was tested for the oxidation of alcohols using *tert*-butyl hydroperoxide (TBHP) as the oxidant. The corresponding carbonyl compounds were obtained in good to excellent yields (see scheme); furthermore, this magnetic catalyst could be separated by magnetic decantation without significant loss in activity.