# Nickel Hydroxide/Cobalt−Ferrite Magnetic Nanocatalyst for Alcohol Oxidation

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S *Supporting Information*

ABSTRACT: A magnetically separable, active nickel hydroxide (Brønsted base) coated nanocobalt ferrite catalyst has been developed for oxidation of alcohols. High surface area was achieved by tuning the particle size with surfactant. The surface area of 120.94 m^2 g^{-1} has been achieved for the coated nanocobalt ferrite. Improved catalytic activity and selectivity were obtained by synergistic effect of transition metal hydroxide (basic hydroxide) on nanocobalt ferrite. The nanocatalyst oxidizes primary and secondary alcohols efficiently (87%) to corresponding carbonyls in good yields.

KEYWORDS: *nano cobalt ferrite, transition metal hydroxide, high surface area, alcohol oxidation*
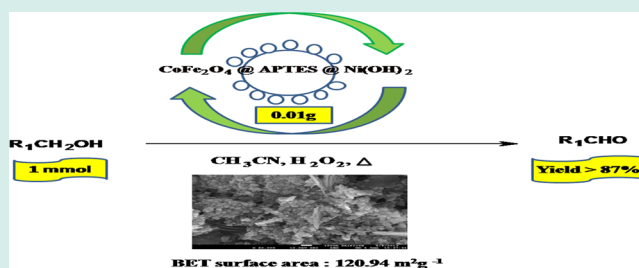
◼ INTRODUCTION

Heterogeneously catalyzed selective oxidation of alcohols to aldehydes presents a great challenge in the fine chemical industry. The facile recovery and reuse of the nanoparticles have received increasing attention in catalysis.[1] In recent years, nanostructured spinel ferrite have aroused as potential applicant for catalysis with combination of green oxidants.[2] Therefore, researchers have employed magnetic nanoparticles as recyclable support matrix with superior catalytic activity. Recent studies explore that high catalytic activity can be harnessed by tuning the particle size of the catalyst in heterogeneous selective aerobic oxidation of alcohols.[3]

Chemical modification of spinel ferrite with different transition metal ion leads to products with variable surface area.[4] Among the ferrites, cobalt substituted spinel ferrite are attractive candidates because of their strong anisotropy, high coercivity, moderate saturation magnetization, good mechanical and excellent chemical stabilities at higher temperature.[5,6] Rapid electron exchange between tetrahedral and octahedral sites of spinel containing transition metal ion enhances its catalytic activity.[7] The catalytic activity of cobalt ferrite has been reported for Knoevenagel condensation reaction and aerobic oxidation of cyclohexane to cyclohexanol.[8,9]Gawande et al. reported inexpensive magnetic Co−Fe$_2$O$_4$ nanocatalyst as viable alternative for oxidation of alcohols to carbonyl compounds with excellent yield using TBHP (tert-butyl hydroperoxide) as oxidant.[10]

In this study, we report the synthesis of nickel hydroxide coated cobalt ferrite nanocatalyst for the oxidation of alcohols under mild condition with H$_2$O$_2$ as terminal oxidant.

◼ RESULTS AND DISCUSSION

Characterization of the Catalyst. The amount of nickel in the catalyst was determined to be 3 w% by Atomic Absorption Spectroscopy (AAS). The FTIR spectrum of the catalyst exhibited intense band at 3400 and 570 cm^{-1} corresponding to −OH stretch and Fe−O stretch, respectively, as observed in Figure 1A. The band in the region of 1040 cm^{-1} assigned to Si−O stretching, evidently confirms the aminosilane functionalization of the catalyst.[11] The appearance of absorption peak at 340 nm in the UV−vis spectra of the catalyst further confirms silane adsorption as shown in Figure 1B.

The patterns of X-ray powder diffractograms of the catalyst (Figure 2) showed three major diffraction peaks (JCPDS 22-1086): 35.0, 57.2, and 62.0 indexed as (311), (511), and (440), respectively.

The crystallite size present in solids was calculated from the main diffraction lines of these phases using Scherer equation

$$D = 0.9\lambda / B \cos\theta \qquad (1)$$

where B is the full wave half width maximum (fwhm) of the diffraction peak at 2θ recorded using X-rays of wavelength $\lambda = 1.514$ Å.

Average crystallite size of 20 nm was observed. The compositional analysis show the respective elements present in the catalyst as observed in Figure 3.
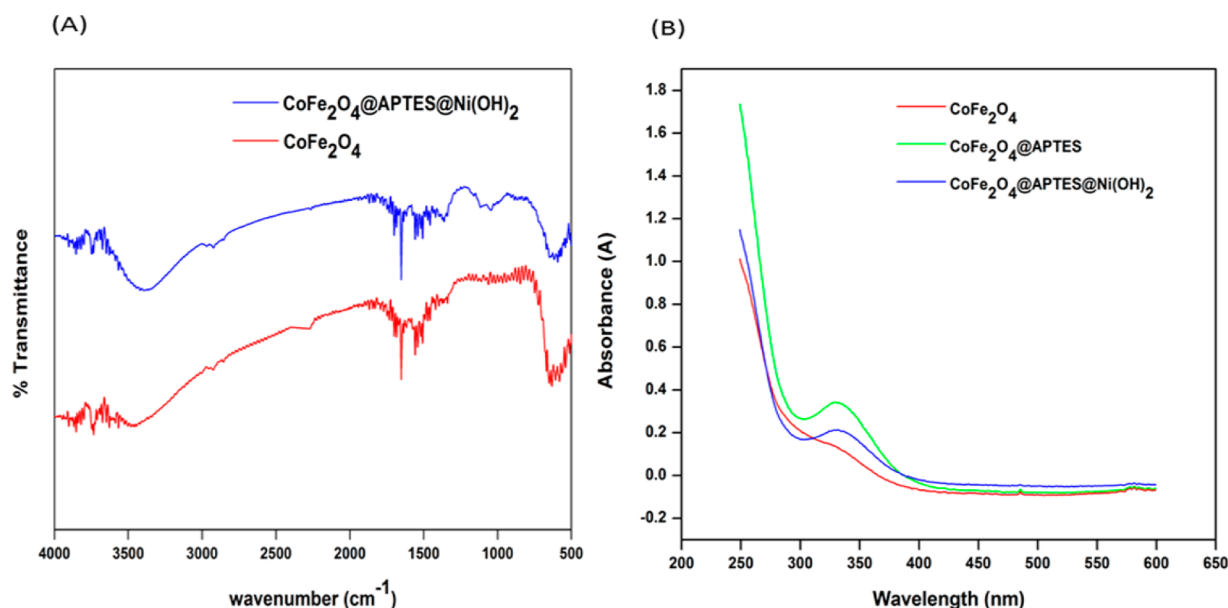
(A)

(B)

Figure 1. (A) FTIR spectra and (B) UV−vis spectra of the catalyst.
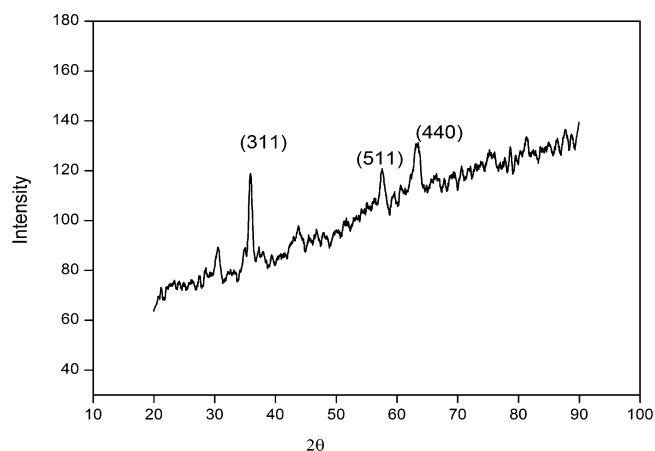
Figure 2. XRD pattern of cobalt ferrite.

The surface morphology of the catalyst shows that magnetic nanoparticles were formed having dimensions less than 100 nm (Figure 4). Uniform sized nanoparticles with different morphology were obtained by using 3-aminopropyltriethoxysilane (APTES) as a surfactant. TEM micrographs exhibited dispersion of nickel hydroxide on the spherical and flake shaped ferrites with a smoothened surface. The hydroxide coating on the nanocobalt ferrite is indicated by yellow circle (Figure 5). The surfactant added forms an envelope on the magnetic nanoparticles and prevents it from further agglomeration. Hydroxide coating is observed as a thin dispersed layer on the surface of the nanoparticles. Average crystallite size observed in FESEM is comparable with the obtained TEM results. The corresponding selected area electron diffraction (SAED) pattern shows the well-defined rings and spots, characteristic of the cubic structure of nanocrystalline $CoFe_2O_4$ in nickel hydroxide-coated $CoFe_2O_4$ catalyst.

The BET specific surface area of the catalyst was determined over the relative pressure ranging from 0.05 to 0.3. The
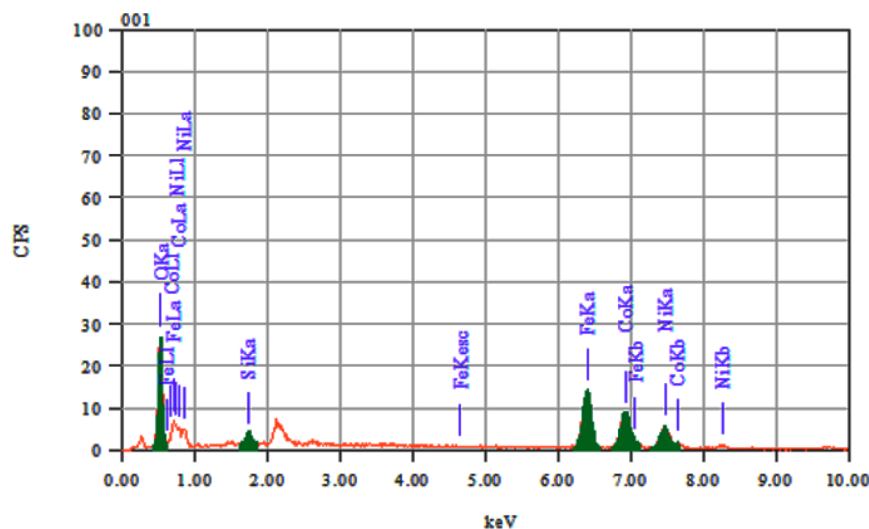
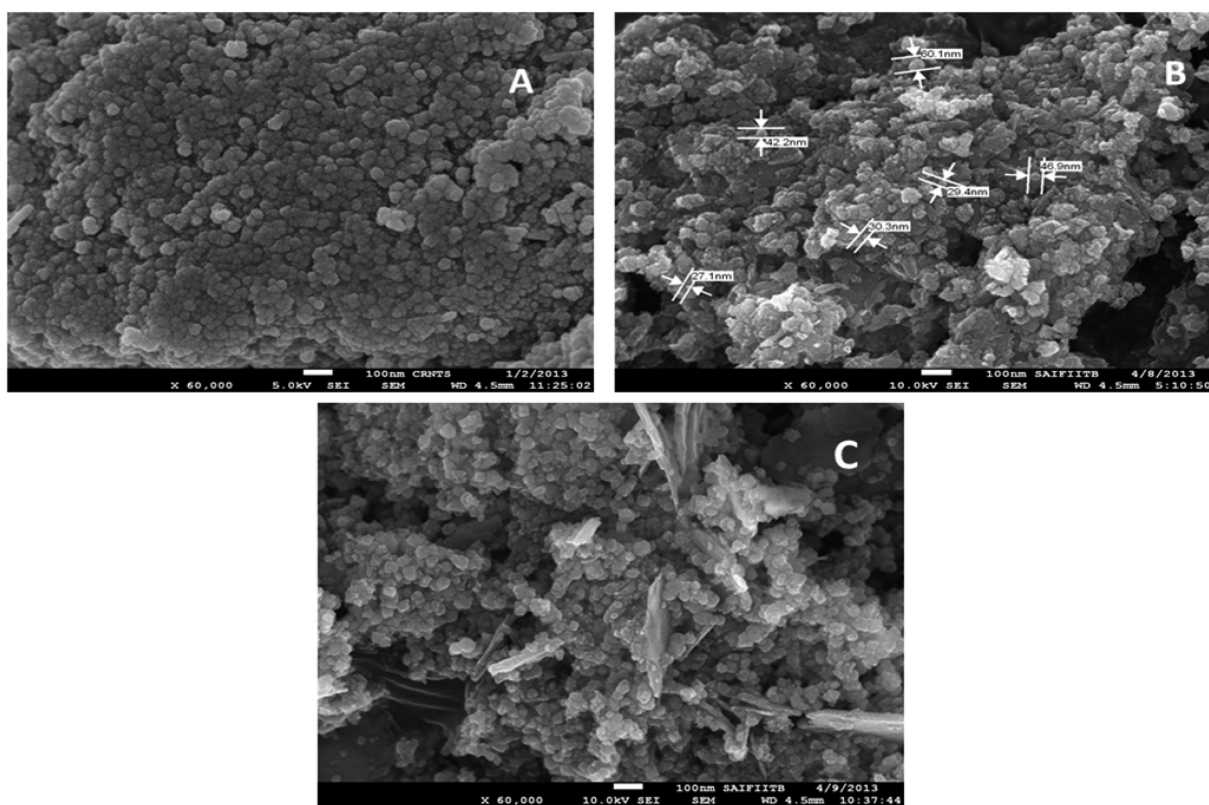**Figure 3.** Energy dispersive X-ray (EDX) analysis of the catalyst.

Figure 4. FESEM image of (A) naked $CoFe_2O_4$, (B) $CoFe_2O_4$: APTES (1:1), (C) $CoFe_2O_4$: APTES (1:0.5).
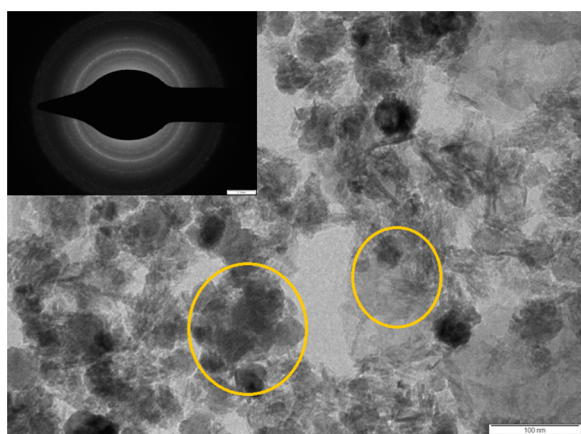

Figure 5. TEM image of the catalyst showing nanoflakes and nanoparticles enveloped by a hydroxide layer (circled). Inset shows SAED image of the catalyst.

obtained belong to type IV according to IUPAC classification[12] and exhibited hysteresis loop with BET surface area 120.94 m^2 g^{-1} (Figure 6A). These hysteresis loops are characteristic of mesoporous solid. BJH approach was used to calculate pore size distribution for all the samples. The mean pore radius of the investigated cobalt ferrite samples was in the range of 3−5 nm which confirms the nature of the prepared system as mesoporous solid. Figure 6B evidently showed narrow pore size distribution.

The magnetization measurements determined by a vibrating sample magnetometer (VSM) showed ferromagnetism and hysterisis loop with coercivity (H_c) of 515.51G.

Catalytic Oxidation of Alcohols. Oxidation of alcohols can be accelerated with base as a cocatalyst due to its high coordinating ability.[13,14] Product selective liquid phase oxidation of alcohols by different bases has been carried out with synthesized catalyst as shown in Figure 7. The oxidation of benzyl alcohol to benzaldehyde was used as a model reaction. It is clear that bases, such as KOH, pyridine are prone to form acids, while maximum conversion to aldehyde is observed by the synthesized transition metal hydroxide constituted $CoFe_2O_4$@ APTES@ $Ni(OH)_2$ catalyst.

In this study, optimization of the reaction conditions of alcohol conversion by the synthesized catalyst was carried out under the influence of solvent, temperature, alcohol/oxidant molar ratio, and length of the reaction time. Among the various solvents, acetone, acetonitrile, dichloromethane, and methanol, the activity of nano catalyst with H_2O_2 gave a good yield in acetonitrile medium. Product analysis was done at regular intervals of time under similar reaction conditions to study the effect of time on the activity (Figure 8). It was observed that the gas chromatography (GC) yield remained constant after a reaction time of 7 h. The effect of the concentration of catalyst in oxidation of alcohols with respect to model substrate showed significant conversion for 0.01 g of catalyst which revealed the catalytic role of transition metal hydroxide coated nanocobalt ferrite.

Reduction in dimension of the catalyst offers higher surface area with higher number of coordination sites and surface vacancies which are responsible for the higher catalyst activity. GC conversion of 87% on model substrate was observed for the synthesized catalyst. Oxidation reaction was extended to a variety of alcohols using the optimized reaction conditions. The results for the oxidation of a variety of alcohols are summarized in Table 1. Aromatic substituent was found to be more reactive than aliphatic alcohols which can be attributed to its delocalization. Similarly electron donating groups were found
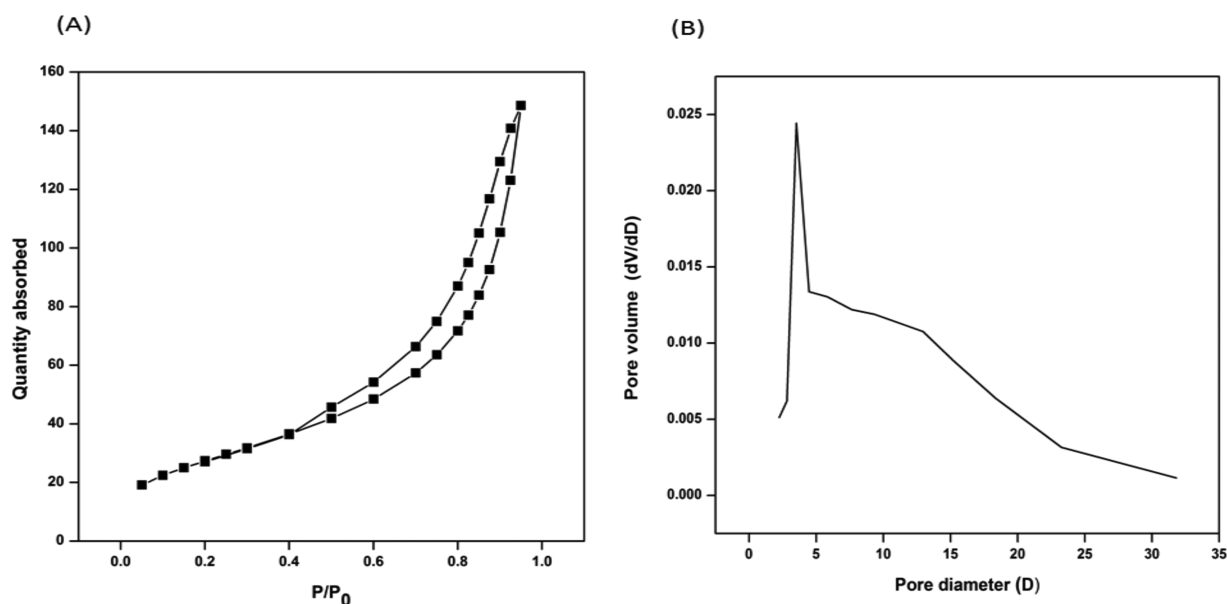
(A)

(B)

Figure 6. (A) Nitrogen sorption isotherm and (B) BJH pore size distribution of the catalyst.

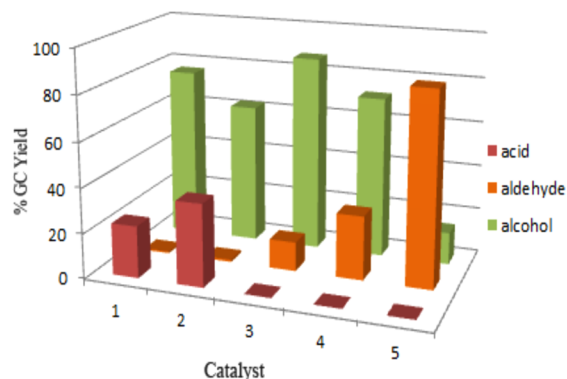**Figure 7.** Product selectivity of the catalyst $CoFe_2O_4@APTES$ treated with [1] KOH (0.25 mmol), [2] pyridine (0.25 mmol), and [3] $Cs(CO_3)_2$ (0.25 mmol) and [4] without base and [5] synthesized catalyst.
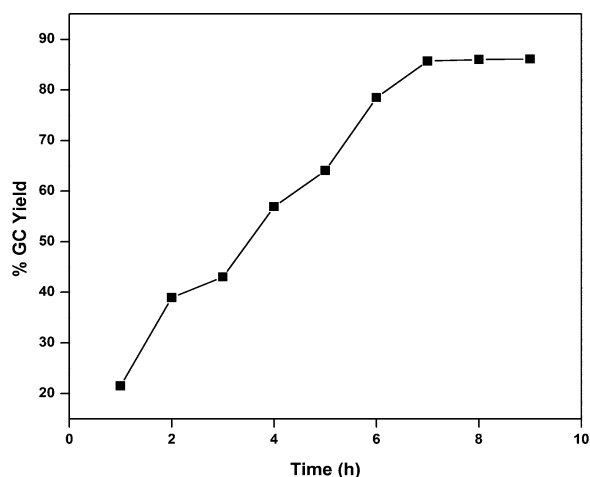
Figure 8. Effect of time on the catalyst.

to slow down the oxidation reaction, whereas electron withdrawing groups were found to accelerate the oxidation

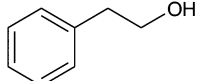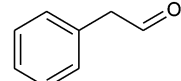reaction. Among the various alcohols studied here, phenylethanol showed maximum conversion with GC yield of 99.5%.
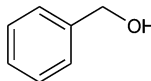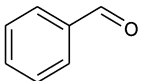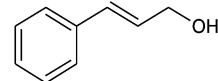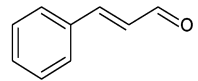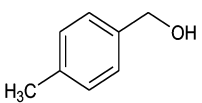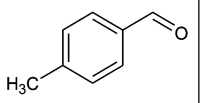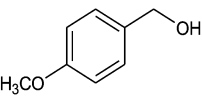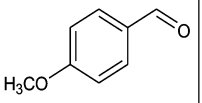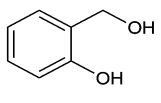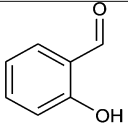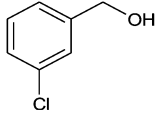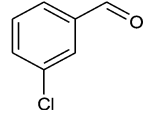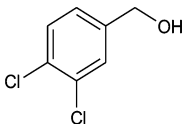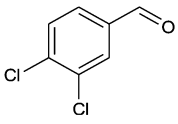
Heterogeneous Catalysis and Reusability. Magnetic catalysts can be easily recovered after the reaction and can be reused (Figure 9) without the significant loss of the catalytic activity and selectivity. After the reaction, catalyst was removed from the reaction mixture by magnet, dried at 80 °C and reused. Atomic absorption spectroscopy was carried out on the synthesized $CoFe_2O_4@$ APTES@ $Ni(OH)_2$ catalyst to verify whether the observed oxidation of alcohols was caused by the synthesized catalyst or because of the leached nickel species. Catalyst media was separated by magnet around 50% conversion and the oxidation reaction was continued with the filtrate in the same condition. The separated catalyst media was subjected to AAS. Clearly, the filtrate obtained after the reaction had nickel concentration 0.2 w% compared to 3 w% of $CoFe_2O_4@APTES@Ni(OH)_2$ catalyst. This confirmed that the catalyst is heterogeneous in nature. Furthur heterogeneity of the catalyst was confirmed by mercury drop test.[15]

In conclusion, high surface area of cobalt ferrite with variable catalytic activity can be achieved with lower amount of surfactant. The high surface area of 120.94 m^2 g^{-1} has 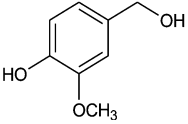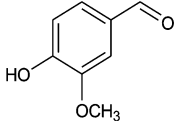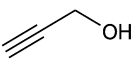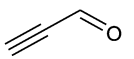been achieved for nickel hydroxide coated nanocobalt ferrite. Coordinatively unsaturated metal centers (Lewis acid) with transition metal hydroxide sites (Brønsted base) can provide outstanding catalytic performance in oxidation of alcohols. The synthesized magnetic nanocatalyst provides efficient and environment friendly method for oxidation of aromatic alcohols to corresponding carbonyls with high yield. Hence, this catalyst is a viable alternative for oxidation of alcohols.

■ EXPERIMENTAL PROCEDURES

The FTIR spectra was measured on JASCO FTIR-4200 (KBr technique). The flame atomic absorption spectroscopy (FAAS) measurements was recorded on GBC 932-PLUS. The UV–vis spectra were recorded in Analytikjena SPECORD S600. Powder X-ray Diffraction (XRD) measurements were performed on JEOL JDX 8P diffractometer. Surface morphology and composition was studied by Field Emission Gun Scanning Electron Microscopy (FEG-SEM) JSM-7600F, Transmission

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Table 1. Catalytic Activity for Alcohol Oxidation Catalyzed by CoFe$_2$O$_4$@APTES@Ni(OH)$_2$

Entry	Substrate	Conversion* (%)	Product	Selectivity* (%)
1		87.01		>99
2		99.54		>99
3		97.38		>97
4		69.88		>99
5		67.79		>99
6		61.90		>98
7		73.38		>98
8		78.51		>99
9		70.65		>98
10		42.32		>97
11	(CH$_3$)$_2$CH$_2$OH	34.30	(CH$_3$)$_2$CH$_2$CHO	>98

*Substrate (1.0 mmol); catalyst (Ni: 3 w%); oxidant (H$_2$O$_2$, 30%, 10 mmol) acetonitrile (3.0 mL). Conversion and selectivity were determined by GC. Average of GC 3 trials.

Electron Microscope (TEM) Philips CM200. Surface area and pore size distribution were studied by Gemini V2.00 surface analyzer. All magnetic properties were determined by Lakeshore VSM 7410 Vibrating Sample Magnetometer at room temperature. The reaction product analysis was carried out using Gas Chromatography (GC) (Shimadzu 2014, Japan), siloxane Restek capillary column (30 m length and 0.25 mm diameter) and Flame Ionization Detector. Column temperature was increased at the rate of 10 °C/min and nitrogen was used as the carrier gas.
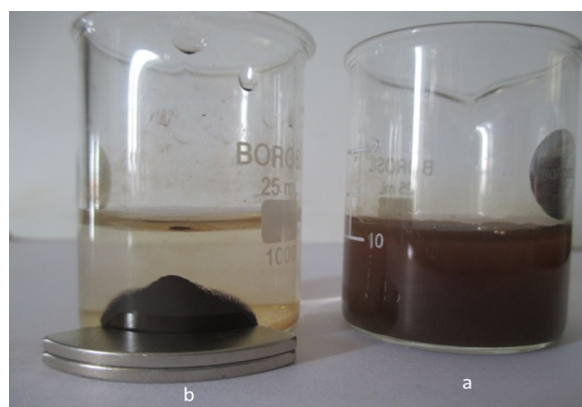
Figure 9. Magnetically separable catalyst: (a) before magnetization and (b) after magnetization.

Synthesis of CoFe$_2$O$_4$@APTES. Magnetic CoFe$_2$O$_4$ were prepared by coprecipitation technique. The detailed synthesis and optimization were reported elsewhere.[16,17] Purified CoFe$_2$O$_4$ were modified with 3-aminopropyltriethoxysilane (APTES). One gram of CoFe$_2$O$_4$ nanoparticles were treated with 0.5 g of APTES in the presence of toluene at 80 °C for 6 h in argon atmosphere. After 1 h of aging, the resultant were centrifuged and dried at 80 °C.

Synthesis of CoFe$_2$O$_4$@APTES@Ni (OH)$_2$. The synthesized CoFe$_2$O$_4$ were vigorously stirred with aqueous solution of NiCl$_2$.7H$_2$O for 24h at room temperature with pH >13.2. The nickel hydroxide functionalized CoFe$_2$O$_4$ was washed with deionized water, ethanol, and dried at 80 °C.

Oxidation Reaction. All reactions were carried out on a glass reactor (∼50 mL) in which benzyl alcohol (1 mmol), nanocatalyst (0.01 g), and acetonitrile (3 mL) were added, respectively. H$_2$O$_2$ (30 wt % in water, 10.0 mmol) was added as oxidant and the reaction mixture was vigorously stirred at 80 °C. The aliquots of the reaction mixture were used for product analysis at regular interval by gas chromatography technique. The retention times for various compounds were determined by injecting pure compounds under identical GC conditions.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed information about optimization of the catalyst and its magnetic reusability is attached, so as to facilitate the understanding of magnetically retrievable catalyst. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

REFERENCES

(1) Gill, C. S.; Price, B. A.; Jones, C. W. Sulfonic acid-functionalized silica-coated magnetic nanoparticle catalysts. *J. Catal.* **2007**, *251*, 145−152.

(2) Shi, F.; Tse, M. K.; Pohl, M. M.; Bruckner, A.; Zhang, S.; Beller, M. Tuning catalytic activity between homogeneous and heterogeneous catalysis: Improved activity and selectivity of free nano-Fe$_2$O$_3$ in selective oxidations. *Angew. Chem.* **2007**, *119*, 9022−9024.

(3) Shi, F.; Tse, M. K.; Pohl, M. M.; Radnik, J.; Bruckner, A.; Zhang, S.; Beller, M. Nano-iron oxide-catalyzed selective oxidations of alcohols and olefins with hydrogen peroxide. *J. Mol. Catal. A: Chem.* **2008**, *292*, 28−35.

(4) Khan, A.; Smirniotis, P. G. Relationship between temperature-programmed reduction profile and activity of modified ferrite-based catalysts for WGS reaction. *J. Mol. Catal. A: Chem.* **2008**, *280*, 43−51.

(5) Pang, X.; Fu, W.; Yang, H.; Zhu, H.; Xu, J.; Li, X.; Zou, G. Preparation and characterization of hollow glass microspheres coated by CoFe$_2$O$_4$ nanoparticles using urea as precipitator via coprecipitation method. *Mater. Res. Bull.* **2009**, *44*, 360−363.

(6) Soler, M. A. G.; Lima, E. C. D.; Silva, S. W.; Melo, T. F. O.; Pimenta, A. C. M.; Sinnecker, J. P.; Azevedo, R. B.; Garg, V. K.; Oliveira, A. C.; Novak, M. A.; Morais, P. C. Aging investigation of cobalt ferrite nanoparticles in low pH magnetic fluid. *Langmuir.* **2007**, *23*, 9611−9617.

(7) Mohapatra, S.; Rout, S. R.; Panda, A. B. One-pot synthesis of uniform and spherically assembled functionalized MFe$_2$O$_4$ (M = Co, Mn, Ni) nanoparticles. *Colloids Surf., A* **2011**, *384*, 453−460.

(8) Senapati, K. K.; Roy, K. S.; Borgohain, C.; Phukan, P. Palladium nanoparticle supported on cobalt ferrite: An efficient magnetically separable catalyst for ligand free Suzuki coupling. *J. Mol. Catal. A: Chem.* **2012**, *352*, 128−134.

(9) Tong, J.; Bo, L.; Li, Z.; Lei, Z.; Xia, C. Magnetic CoFe$_2$O$_4$ nanocrystal: A novel and efficient heterogeneous catalyst for aerobic oxidation of cyclohexane. *J. Mol. Catal. A: Chem.* **2009**, *307*, 58−63.

(10) Gawande, M. B.; Rathi, A.; Nogueria, I. D.; Ghumman, C. A. A.; Bundaleski, N.; Teodoro, O. M. N. D.; Branco, P. S. A Recyclable Ferrite−Co Magnetic Nanocatalyst for the Oxidation of Alcohols to Carbonyl Compounds. *ChemPlusChem.* **2012**, *77*, 1−7.

(11) Phan, N. T. S.; Jones, C. W. Highly accessible catalytic sites on recyclable organosilane-functionalized magnetic nanoparticles:An alternative to functionalized porous silica catalysts. *J. Mol. Catal. A: Chem.* **2006**, *253*, 123−131.

(12) Sing, K. S. W.; Everett, D. H.; Haul, R. A. W.; Moscou, L.; Pierotti, R. A.; Rouquerol, J.; Siemieniewska, T. *Pure Appl. Chem.* **1985**, *57*, 603−619.

(13) Zhu, J.; Figueiredo, J. L.; Faria, J. L. Au/activated-carbon catalysts for selective oxidation of alcohols with molecular oxygen under atmospheric pressure: Role of basicity. *Catal. Commun.* **2008**, *9*, 2395−2397.

(14) Yamaguchi, K.; Kim, J. W.; He, J.; Mizuno, N. Aerobic alcohol oxidation catalyzed by supported ruthenium hydroxides. *J. Catal.* **2009**, *268*, 343−349.

(15) Sheldon, R. A.; Wallau, M.; Arends, I. W. C. E.; Schuchardt, U. Heterogeneous catalysts for liquid-phase oxidations: Philosophers' stones or Trojan horses? *Acc. Chem. Res.* **1998**, *31*, 485−493.

(16) Shobaky, G. A.; Turky, A.; Mostafa, N. Y.; Mohamed, S. K. Effect of preparation conditions on physicochemical, surface and catalytic properties of cobalt ferrite prepared by coprecipitation. *J. Alloys Compd.* **2010**, *493*, 415−422.

(17) Qu, Y.; Yang, H.; Yang, N.; Fan, Y.; Zhu, H.; Zou, G. The effect of reaction temperature on the particle size, structure and magnetic properties of coprecipitated CoFe$_2$O$_4$ nanoparticles. *Mater. Lett.* **2006**, *60*, 3548−3552.