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ARTICLE



Synthesis and characterization of a bifunctional nanomagnetic solid acid catalyst ($Fe_3O_4@CeO_2/SO_4^{2-}$) and investigation of its efficiency in the protection process of alcohols and phenols via hexamethyldisilazane under solvent-free conditions

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Hossein Ghafuri, Catalysts and Organic Synthesis Research Laboratory, Department of Chemistry, Iran University of Science and Technology, P.O. Box 16846-13114, Tehran, Iran. Email: ghafuri@iust.ac.ir In this research, $Fe_3O_4@CeO_2$ (FC) was synthesized using the coprecipitation method and functionalized by an ammonium sulfate solution to achieve a heterogeneous solid acid $Fe_3O_4@CeO_2/SO_4^{2-}$ (FCA) catalyst. The synthesized bifunctional catalyst was used in the protection process of alcohols and phenols using hexamethyldisilazane (HMDS) at ambient temperature under solvent-free conditions. Due to its excellent magnetic properties, FCA can easily be separated from the reaction mixture and reused several times without significant loss in its catalytic activity. Excellent yield and selectivity, simple separation, low cost, and high recyclability of the nanocatalyst are outstanding advantages of this procedure. The characterization was carried out using different techniques such as Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), energy dispersive Xray spectroscopy (EDX), X-ray diffraction (XRD), and vibrating sample magnetometry (VSM).

KEYWORDS

Fe₃O₄@CeO₂/SO₄²⁻, heterogeneous solid acid, HMDS, magnetic nanocatalyst

1 | INTRODUCTION

Today, improvement of the research in the catalyst sciences has a significant role in solving the environmental problems. Catalysts can be designed to give higher activity and better selectivity to the reactions.^[1–4] Functionalization of catalysts is considered as the main technique to devolop their activities. Recently, to increase the surface area and the efficiency of catalysts, sulfation and phosphatation treatments of catalysts are carried out.^[5,6] Some reports have shown that the sulfation and phosphatation treatments are used to produce solid superacid catalysts with high thermal stability (more than 600 °C).^[7] There are different reactions such as esterification and isomerization that are catalyzed by these functionalized catalysts.^[8] Solid acids can have Lewis or Brønsted

acid sites. Recently, both of Lewis and Brønsted acid cites have been assembled in one compound with interesting synergistic effects to improve the catalytic activity of catalysts.^[9] Sulfated zirconia ($ZrO_2.SO_4^{2-}$),^[7] sulfated titania (TiO_2.SO_4^{2-}),^[10] sulfated tungstate,^[11] and some other sulfated transition metal oxides are obtained from these bifunctional acids^[12] (Scheme 1). Also, the magnetization of these catalysts allows easy separation from the reaction mixture using an external magnet.^[15]

Among the transition metal oxides, CeO_2 has a high oxygen storage capacity and high oxygen ion conductivity. The high oxygen mobility of ceria causes changes in its oxidation state between Ce^{3+} and Ce^{4+} facilitating oxygen buffer calibration for catalytic redox reactions.^[16,17] Ceria has also shown catalytic activity in other reactions such as oxidation

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$$\frac{\text{Fe}_{3}O_{4}@\text{CeO}_{2}/\text{SO}_{4}^{2-}}{\text{Solvent free, RT}} \rightarrow \text{ROSiMe}_{3} + \text{NH}_{3}$$

SCHEME 2 The protection of alcohols and phenols in the presence of $Fe_3O_4@CeO_2/SO_4^{2-}$ as an effective magnetic nanocatalyst

and reforming reactions.^[18,19] In addition, the high thermal stability of ceria is appropriate for some reactions at high temperatures. Because of these interesting capabilities, ceria has been widely utilized as catalysts and in fuel cells.^[20–29]

Many methods were reported in recent years for protecting of alcohols. This reaction has been carried out using different reagents like alkylsilanes^[30–32] and bis (trimethylsilyl) amine (HMDS)^[33] in the presence of an appropriate catalyst.^[34] HMDS as a cheap reagent is a conventional compound for the protection of a hydroxyl functional group that can be used as an alternative silylating agent.^[35,36] However, low efficiency, moisture sensitivity, long reaction times, and hard workups are considered as the main disadvantages of the various protection methods using a HMDS reagent.^[37]. Recently, application of some effective catalysts such as ZnCl₄,^[38] LiClO₄,^[39] and MgBr₂ resulted in suitable improvements in these methods, but still they should be developed.

In this research, we introduced $Fe_3O_4@CeO_2/SO_4^{2-}$ as a new heterogeneous solid acid catalyst for the protection of

alcohols and phenols. The Lewis and Brønsted acidity of the synthesized nanocatalyst was measured and reported in the characterization section (Scheme 1). The reaction is carried out under solvent-free conditions with very simple recovery of the catalyst using an external magnet. High selectivity and environmentally friendly nature are remarkable advantages of this procedure.

2 | RESULTS AND DISCUSSION

Based on the results obtained, this nanocatalyst can be considered as an effective bifunctional acid catalyst with Brønsted and Lewis acid sites in its structure (Scheme 1). According to our measurement, the Brønsted acidity value of the catalyst is 1.51 and Lewis acid value is 1.21.

Based on the considerable acidity value and magnetic properties, it can be an interesting replacement for some toxic, homogenous, and expensive catalysts in the protection process of alcohols.

The trimethylsilylation of hydroxyl groups of alcohols was simply carried out under the solvent-free and room temperature conditions in the presence of $Fe_3O_4@CeO_2/SO_4^{2-}$ catalyst (Scheme 2).

The possible mechanism for the protection reaction is shown in Scheme 3.

According to our suggested mechanism, this catalyst can facilitate the reaction in two steps. First, the amine group of HMDS can be protonated by the Bronsted sites of the catalyst causing easy separation of ROSiMe₃. Next, the Lewis sites can interact with Ce facilitating the nucleophilic attack of alcohols on the complex. Finally, with separation of the NH₃ group and the catalyst, silylether is prepared.

To optimize the reaction condition, different conditions were tested and the results are summarized in Table 1. The reaction was done by mixing benzyl alcohol, HDMS, and



SCHEME 3 The proposed mechanism of protection of alcohols and phenols in the presence of $Fe_3O_4@CeO_2/SO_4^{2-}$

TABLE 1 Optimization of the reaction of benzyl alcohol (1 mmol) and HMDS (.7 mmol) in the presence of $Fe_3O_4@CeO_2/SO_4^{2-}$

Entry	Temp. (°C)	Solvent	Cat. (mg)	Yield (%)
1	25	—	3	89
2	25	—	5	91
3	25	—	7	95
4	25	—	10	95
5	65	CH ₃ CN	5	—
6	65	CH_2Cl_2	5	80
7	25	—	5	99
8	40	—	5	95
9	60	_	5	90

different amounts of catalysts. According to the results, the best results were achieved with 7 mg of the catalyst under solvent-free conditions at room temperature.

After optimization of the reaction conditions, to show the generality of the procedure, the reactions were carried out with various alcohols and the results are summarized in Table 2.

The achieved results show that electron-withdrawing groups can improve the reaction yield (entry: 1a, 1h). In addition, the results display that aliphatic alcohols have less yield than aromatic alcohols (entry: 11, 1r, 1s, and 1t). Thus according to Table 2, among the different alcohols some of them such as benzyl, primary, secondary, and phenolic show the best results on the yields and reaction time (entry: 1a, 1g, 1h, 1k). The reaction progress was monitored by TLC and FT-IR was used to demonstrate complete protection of hydroxyl groups. The results show that all reactions have well to high yields for all alcohols under the solvent-free conditions at room temperature. Also, it was determined that the catalyst has high selectivity for protection of hydroxyl groups in the presence of amine groups (entry: 1j and 1m).

2.1 | FT-IR analysis

FT-IR spectra of Fe₃O₄, CeO₂, and Fe₃O₄@CeO₂/SO₄²⁻ samples are shown in Figure 1. In the CeO₂ spectra, the presence of a sharp peak at 508 cm⁻¹ is related to the stretching mode of Ce-O bonds.^[40] Two well-defined bands appeared at 1,618 and 3,400 cm⁻¹ that are ascribed to the bending vibration of absorbed water and surface hydroxyl and OH stretching mode, respectively. In Fe₃O₄, there is a peak at 574 cm⁻¹ that shows the Fe-O bonding (peaks at 588 and 574 cm⁻¹ are assigned to the Fe³⁺ O Fe³⁺ and Fe²⁺ O Fe²⁺ symmetrical stretching vibrations, respectively).^[33] The peaks at 1,012, 1,124, and 1,260 cm⁻¹ in the Fe₃O₄@-CeO₂/SO₄²⁻ spectra are attributed to the O=S=O asymmetric groups, and S-O vibrations of the (SO₄) groups, respectively.

2.2 | XRD patterns of Fe₃O₄@CeO₂/SO₄²⁻

X-ray diffraction (XRD) patterns of Fe_3O_4 and $Fe_3O_4@$ - CeO_2/SO_4^{2-} are shown in Figure 2. The diffraction peak labeled "a" represents the Fe_3O_4 phase and the CeO_2 phase is denoted by "b". As shown in the XRD patterns of $Fe_3O_4@CeO_2$ and final catalyst $Fe_3O_4@CeO_2/SO_4^{2-}$ (C and D), there are similar peaks for Fe_3O_4 and $CeO_2^{[34]}$ obviously. Disappearance of some peaks demonstrates that this modification has a low effect on the Fe_3O_4 phase. In addition, the results have indicated that the crystalline structure of the Fe_3O_4 and CeO_2 compounds is maintained in the nanocatalyst structure.

2.3 | FE-SEM analysis

To gain information about external morphology and structure of synthesized nanocatalyst, scanning electron microscopy (SEM) was used. SEM images of $Fe_3O_4@CeO_2/SO_4^{2-}$ are illustrated in Figure 3. According to the size distribution chart, the distribution is narrow and the size of the majority of the particles of the synthesized catalyst is nearly 40–50 nm. However, the catalyst particle size is a suitable proof of successful synthesis of the catalyst.

2.4 | EDS patterns of Fe₃O₄@CeO₂ and Fe₃O₄@CeO₂/ SO₄²⁻

The EDS spectrum of Fe₃O₄@CeO₂ (Figure 4a) displays the peaks of iron, cerium, and oxygen. In the spectrum of Fe₃O₄@CeO₂/SO₄²⁻ (Figure 4b), in addition to these three elements, the peaks of sulfur and carbon were observed. The content of sulfur was shown to be 15.4 wt%. Also, the reduction of iron peak intensity demonstrates that Fe₃O₄@-CeO₂ was coated by sulfate, which confirms the successful synthesis of Fe₃O₄@CeO₂/SO₄^{2-.}

2.5 | Back titration in aqueous media catalyst (Fe₃O₄@CeO₂/SO₄²⁻)

Back titration method was used to determine the Bronsted acidity $[H^+]$ of the synthesized catalyst. First, 0.5 g of the catalyst, 0.5 g of NaCl, and 10 mL of NaOH (0.1 M) were added to 20 mL distilled water and stirred for 24 hr. Next, drops of phenolphthalein indicator were added, which results in the change of the solution color to bright brown. Then, the mixture was titrated with solution of HCl (0.1 M) until reaching the end point (colorless solution). The pH value of the catalyst was calculated to be 1.51.

2.6 | Surface acidity studies

This synthesized catalyst as a bifunctional solid acid catalyst has two acid groups whose Bronsted acidity value was measured with back titration, and in this section, the measurement of Lewis acidity value is reported.

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TABLE 2	HMDS protection of alcohols and pheno	Is in the presence of $Fe_3O_4@CeO_2/SO_4^{2-a}$		
Entry	Substrate	Product	Time (min)	Yield (%)
1	ОН	OSiMe ₃ 1a	15	93
2	НзСО	H ₃ CO OSiMe ₃	15	91
3	ме	Me OSiMe ₃	15	91
4	O ₂ N OH	O ₂ N OSiMe ₃	25	91
5	OH NO ₂	NO ₂ 1e	30	89
6	НО	HO OSiMe ₃	25	91
7	OH	OSIMe ₃ 1g	35	95
8	CI	CI-OSiMe ₃ 1h	45	95
9	Me ₃ SiO Ph	Me ₃ SiO Ph Ph 1i	50	90
10	CI-OH NH2	CI-OSiMe ₃ NH ₂ 1j	60	90
11	ІОН	$I \longrightarrow OSiMe_3$ 1k	30	95
12	ОН	OSiMe ₃	35	85
13	OH NH ₂	OSIMe ₃ NH ₂ 1m	35	90
14	ОН	OSiMe ₃	40	89
15	OH		30	90
16	OH	OSiMe ₃	20	80
17	OH	OSiMe ₃ 1q	25	80
18	ОН	OSiMe ₃ 1r	50	80
19	H ₃ C CH ₃	H ₃ C ^{OSiMe₃} H ₃ C ^{CH₃} 1s	30	80
20		H OSiMe ₃ 1	lt 25	85

^a Reaction conditions: alcohol (1 mmol), catalyst (10 mg), and HMDS (0.7 mmol) at room temperature.

The acidity strength of an acid in organic solvents can be determined using the Hammett acidity function (H_0) .^[41,42] It can be calculated using the equation: $H_0 = pK[I]_{aq} + \log ([I]_s/[IH^+]_s)$. In this equation, "I" represents the indicator base, [IH⁺] is the molar concentrations of the protonated forms of the indicator, and [I]_s is the molar concentrations of the unprotonated forms of the indicator. The pK(I)aq values

are previously determined and can be obtained from the literature (for example the $pK(I)_{aq}$ value of 4-nitroaniline is 0.99). According to the Lambert–Beer's Law, the value of $[I]_{s}/[IH^+]_{s}$ can be calculated using the UV–visible spectrum. In this test, 4-nitroaniline was used as the basic indicator and CCl_4 was selected as the solvent. The maximal absorbance of the unprotonated form of 4-nitroaniline was monitored at



FIGURE 1 FT-IR spectra of (a) CeO₂, (b) Fe₃O₄, (c) Fe₃O₄@CeO₂, and (d) Fe₃O₄@CeO₂/SO₄²⁻



FIGURE 2 XRD patterns of bare Fe_3O_4 (a), CeO_2 (B), $Fe_3O_4@CeO_2$ (C), and $Fe_3O_4@CeO_2/SO_4^{2-}$ (D)

329 nm in CCl₄. According to these results, the indicator was [IH⁺] (the absorbance of the unprotonated form of the indicator in Fe₃O₄@CeO₂/SO₄²⁻ was weak as compared to the sample of the indicator in CCl₄). The results of acidity strength of Fe₃O₄@CeO₂/SO₄²⁻ are summarized in Table 3 and the absorption spectra of 4-nitroaniline and Fe₃O₄@-CeO₂/SO₄²⁻ are shown in Figure 5.

2.7 | Magnetic properties of Fe₃O₄@CeO₂/SO₄²⁻

The vibrating sample magnetometry (VSM) measurement was used to study the magnetic properties of the synthesized nanomagnetic catalyst. The hysteresis loop of Fe₃O₄@CeO₂/SO₄²⁻ obtained using limited field from -1,000 to 1,000 Oe is shown in Figure 6. According to this figure, the amount of saturation magnetization decreased from 7 emu/g for Fe₃O₄@CeO₂ to 2 emu/g for Fe₃O₄@CeO₂/SO₄²⁻ due to the coating of surface of Fe₃O₄@CeO₂ by sulfate. Also, the results show that the calcination of the prepared magnetic nanocatalyst should be done in a N₂ atmosphere and in an air atmosphere (O₂), and the magnetic properties were perished through reduction of Fe₃O₄ nanoparticles (blue).



FIGURE 3 SEM images of catalyst $Fe_3O_4@CeO_2/SO_4^{2-}$ (a) and the distribution chart of particle size (b)

2.8 | Product characterization

FT-IR spectroscopy is the best technique for characterization of the products in the protection reaction. First, the reagents have a sharp peak at 3,200–3,400 cm⁻¹ for the OH group of alcohol and after the protection, this peak completely disappeared and a sharp peak appeared at 1,100–1,200 cm⁻¹ (1,182 cm⁻¹), which is ascribed to the Si–O bond. The spectra related to the protection of octanol and the disappearance of the OH peak clearly show the completion of the protection reaction. (Figure 7)

3 | EXPERIMENTAL

3.1 | Materials and methods

All chemicals were purchased from Merck and utilized without further purification. FT-IR spectra were recorded using KBr pellets on a Shimadzu-8400s in the range 400–4,000 cm⁻¹. The XRD pattern was recorded using a STOE powder diffractometer with Co k α (λ = 1.789 Å) irradiation, and the morphology of the catalyst was studied using SEM. The images



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FIGURE 4 EDX analysis of (a) $Fe_3O_4@CeO_2$ (b) $Fe_3O_4@CeO_2/SO_4^{2-}$

TABLE 3 Calculation of the Hammett acidity function (H_0) of Fe₃O₄@CeO₂/SO₄^{2- a}

Entry	Catalyst	A_{\max}	[I]s (%)	$[IH^{+}]_{s}(\%)$	Н
1	—	2.147	100	0	_
2	Fe ₃ O ₄ @CeO ₂ /SO ₄ ²⁻	1.255	62.95	37.05	1.21

^a Conditions for UV–visible spectrum measurement: solvent, CCl₄; indicator, 4-nitroaniline (pK(I)aq: (0.99), 1.44×10^{-4} mol/L, catalyst, Fe₃O₄@CeO₂/SO₄²⁻, 20 mg, 25 °C.

were taken using a Hitachi S4160. Magnetic properties were tested using a VSM (lake shore 7,410). The protection products were studied using a gas chromatograph (Shimadzu) equipped with a HP-5 capillary column.



FIGURE 5 Absorption spectra of 4-nitroaniline (indicator; curve a) and $Fe_3O_4@CeO_2/SO_4^{2-}$ (catalyst; curve b) in CCl4



FIGURE 6 VSM results for $Fe_3O_4@CeO_2$ and $Fe_3O_4@CeO_2/SO_4^{2-}$ in air and N_2 atmospheres



FIGURE 7 IR spectra of protected octanol in the presence of Fe₃O₄@CeO₂/SO₄²⁻ as a catalyst



FIGURE 8 Recyclability of the $Fe_3O_4@CeO_2/SO_4^{2-}$ catalyst for the 4-iodobenzyl alcohol protection

3.2 | Preparation of Fe₃O₄ nanoparticles

Ferric acid and ferrous salts were employed as precursors for the synthesis of Fe_3O_4 nanoparticles. Briefly, $FeCl_3.6H_2O$ (12.2 g, 0.04 mol) and $FeCl_2.4H_2O$ (4.7 g, 0.02 mol) were dissolved in 100 mL distilled water under vigorous stirring. After 10 min, the solution was heated at 50 °C under a nitrogen atmosphere. Consequently, the ammonium hydroxide solution (25%) was added dropwise to the mixture to maintain the reaction pH about 9. Then, the mixture was cooled at room temperature and the black precipitate was collected TABLE 4 Comparison of the obtained results for Fe₃O₄@CeO₂/SO₄²⁻ with yields obtained using the recently reported catalysts

Entry	Catalyst	Cat. (mg)	T (min)	Solvent	Yield (%)	Temp. (°C)	Ref.
1	Trichloroisocyanuricacid (TCCA)	24	240	CH_2Cl_2	90	r.t.	[38]
2	$H_3PW_{12}O_{40}$	29	23	Neat	90	55-60	[45]
3	ZrCl ₄	5	1	CH ₃ CN	95	r.t.	[46]
4	ZrO(OTf) ₂	20	1	CH ₃ CN	92	r.t.	[45]
5	LaCl ₃	49	180	CH_2Cl_2	91	r.t.	[47]
6	Poly(N-bromobenzene-1,3-disulfonamide)	20	90	CH_2Cl_2	90	r.t.	
7	$Fe_{3}O_{4}@CeO_{2}/SO_{4}^{2-}$	7	6	Neat	95	r.t.	This work

using an external magnet and washed several times with ethanol and distilled water. In the final step, nanoparticles were dried at 60 $^{\circ}$ C in an oven.

3.3 | General procedure for the synthesis of Fe₃O₄@CeO₂/SO₄²⁻

Initially, 12 g of Ce(NO₃)₃ were dissolved in 100 mL solution (Ethylene Glycol) EG: H₂O (1:1) for 5 min to form a homogeneous solution. Next, aqueous ammonia (25%) was added dropwise under vigorous stirring until the pH of the solution reached 4. Then, 1 g of Fe₃O₄ was added to the mixture under sonication and aqueous ammonia (28%) was added dropwise until pH reached 9.7. After 24 hr, the solution was filtered and the obtained solid was dipped in (3 mol/L) aqueous solution of (NH₄)₂SO₄ at room temperature for 24 hr. After filtering and drying at 100 °C, the calcination was carried out at 550 °C for 2 hr under N₂ atmosphere conditions.

3.4 | General procedure for the protection of alcohol (preparation of trimethyl silyloxy group)

Alcohols or phenols (1 mmol) were added to a stirred mixture of $Fe_3O_4@CeO_2/SO_4^{2-}$ (10 mg) and HMDS (0.7 mmol) at room temperature. The reaction progress was monitored using TLC. After the completion of the reaction, the nanocatalyst was simply separated from the reaction mixture using an external magnetic field. The product was characterized using IR and ¹H-NMR spectroscopy.

3.5 | Catalyst recovery and reusability

The catalyst can be reutilized for more than four successive runs under the same reaction conditions, which shows its excellent recyclability. For its reusability, the catalyst was recovered using an external magnet and then washed with acetone and distilled water and dried at 110 °C for 30 min. These results exhibit the highest stability and any change in the activity of the catalyst as shown in Figure 8.

To show the efficiency of $Fe_3O_4@CeO_2/SO_4^{2-}$ in the protection reaction, this method was compared with other catalysts such as trichloroisocyanuric acid (TCCA),^[43] H₃PW₁₂O₄₀,^[44] ZrO(OTf)₂,^[45] sulfonic acid@nanoporoussilica,^[46] and LaCl₃.^[47] The results are given in Table 4. According to Table 4, this reaction will be considered as a most suitable reaction among others.

4 | CONCLUSIONS

In this study, $Fe_3O_4@CeO_2/SO_4^{2-}$ was synthesized as a heterogeneous solid acid catalyst and used for the protection of alcohols and phenols via HMDS under solvent-free conditions. The synthesized nanomagnetic catalyst was characterized using FT-IR, SEM, energy dispersive X-ray spectroscopy (EDX), XRD, and VSM techniques. Our synthesized bifunctional nanocatalyst as a new strong solid acid catalyst can be used in a wide range of reactions that are catalyzed by acid catalysts. The existence of two Bronsted and Lewis acid sites cause to carry out the reaction under different conditions. Also, easy separation of the nanocatalyst from the reaction mixture is possible with its excellent magnetic properties. In addition, the application of this nanocatalyst for a wide range of alcohols such as aliphatic, aromatic, and benzylic alcohols shows its potential to be employed in the protection reactions. High yields of product, simple recovery, easy workup, solvent-free conditions, environmentally benign, inexpensive catalyst, and high selectivity between -OH and -NH groups are outstanding advantages of this method.

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