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Nanomagnetic zirconia-based sulfonic acid (Fe₃O₄@ZrO₂-Pr-SO₃H):a new, efficient and recyclable solid acid catalyst for the protection of alcohols via HMDS under solvent free conditions

Azadeh Tadjarodi^{a,*}, Rahim Khodikar^a, Hosssein Ghafuri^a

In the present work, sulfonic acid functionalized nanomagnetic zirconia is prepared by the reaction of (3-mercaptopropyl)trimethoxysilane and nanomagnetic zirconia. Then, nanomagnetic zirconia-based sulfonic acid (Fe₃O₄@ZrO₂-Pr-SO₃H) is synthesized through direct oxidation of thiol group by hydrogen peroxide and H₂SO₄ subsequently. The catalyst was charactrized by fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FE-SEM) image, energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), measurement and vibrational sample magnetometry (VSM). It was used as an effective nanocatalyst with high catalytic activity for the protection of alcohols using hexamethyldisilazane (HMDS) under solvent-free conditions at room temperature. The solid nanocatalyst can easily be separated and reused several times without significant loss of its catalytic activity. Also, morethan inexpensive and simplicity of separation process, this heterogeneous catalyst has shown a good chemoselectivity in the reactions.

Introduction

During the last decade, over 90% organic reaction processes have employed catalysts. These catalysts play an important role in the organic synthesis and transformations¹. Catalysts can be classified into two categories: homogenous² and heterogeneous³. Homogeneous acid catalysts such as HCl, H_2SO_4 , HNO₃, HClO₄ and HF are considerably used in the industrial processes but these catalysts have drawbacks in handling, having toxic waste and corrosiveness. In recent years, there has been a growing interest in developing heterogeneous acid catalyst in the organic reactions. Solid acid catalysts supply few opportunities for recovering and recycling catalysts from organic reaction. Also these catalysts are environmental friendly.

In this context, a heterogeneous catalyst based on nanoparticle (ZrO₂) has been introduced, which is an inorganic material with chemical inertness. Also zirconia has a powerful resistance in comparison with alkalis and acids. Therefore, it can be used as suitable core for coating nanoparticle $Fe_3O_4^{4-7}$. Also in this work, magnetic zirconia functionalized sulfonic acid as heterogeneous solid acid catalyst used for carried various organic reactions.

The protection of alcohols is one of important and necessary process for multistep organic synthesis. Generally, protection of alcohols has been carried out by different reagents such as alkylsilanes^{8,9,10} and bis(trimethylsilyl)amine (HMDS)¹¹ in the presence of a suitable catalyst¹². However, all above mentioned agents except HMDS suffered from serious problems such as toxicity, low yield of product, low selectivity, but HMDS are the useful and more popular compound for the protection of hydroxyl functional group by transforming silylether. Bis(trimethylsilyl)amine (HMDS), a cheap and stable reagent, can be used as an alternative silylating agent for preparation of silylethers from -OH alcohols compound^{13,14}. The main problem is the low silylating power and unsatisfactory yield¹⁵. Therefore, asuitable catalyst in the reactions should be used¹⁶. Lately, some catalysts used for the protection of alcohols reaction such as, $(CH_3)_3SiCl^{17}$, $ZnCl_4^{18}$, $LiClO_4^{19}$, $MgBr_2.OEt_2^{20}$, $LaCl_3^{21}$, sulfonic acid-functionalized nanoporous²². These catalysts are effective, however, they have some significant drawbacks such as poor silylating power, moisture-sensitive, long reaction time, wearisome workups, solvent usage and difficulty in the recovery of catalyst, severe reaction condition and high cost²³.

Therefore, this protocol is, the development of not extreme and selective method for protection of alcohols that is done without solvent and in a short time and also has simple recovery by magnet, and environmentally friendly at room temperature $(r.t)^{24}$. In this paper, the synthesis of chemically adsorbed sulfonic acid on Fe₃O₄@ZrO₂ was obtained by the reaction post-synthesis (grafting)²⁵ of (3-mercaptopropyl) trimethoxysilane and Fe₃O₄@ZrO₂. Then oxidation of thiols by H₂O₂ and 1 mL H₂SO₄ successfully was carried out²⁶. Catalyst Fe₃O₄@ZrO₂-Pr-SO₃H as a new catalyst has high efficiency for organic reactions and also it is useful as catalyst having bronsted acid properties for the preparation derivatives protection of alcohols. The characterization of Fe₃O₄@ZrO₂-Pr -SO₃H was performed with use of different techniques such as FT-IR, SEM, EDX, VSM and XRD ²⁷.

^{a.} Department of chemistry, Iran university of Science and Technology, Narmak, Tehran 16846-13114, Iran.

^{*}corresponding author: tajarodi@iust.ac.ir

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$$\frac{\text{Fe}_{3}\text{O}_{4}@\text{Zr}\text{O}_{2}\text{-Pr-SO}_{3}\text{H}}{\text{Solvent free, RT}} \rightarrow \frac{\text{ROSiMe}_{3} + \text{NH}_{3}}{\text{Solvent free, RT}}$$

was separated by magnet and washed three times with distilled water and acetone to get Fe_3O_4 @ZrO₂-Pr-SO₃H catalyst (Scheme 2).

 $\label{eq:scheme.1} \begin{array}{l} \mbox{The protection reaction of alcohol in the presence of synthesized magnetic acidic nanocatalyst (Fe_3O_4@ZrO_2-Pr-SO_3H) in room temperature and solvent free condition. \end{array}$

Experimental

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Chemical materials were purchased from Merck Co. and utilized without further purification. FT-IR spectra were recorded as KBr pellets on a Shimadzu-8400 sin the range 400-4000 cm⁻¹. The X-Ray diffraction (XRD) pattern was recorded using a STOE powder diffractometer with Co k α , (λ = 1.789 Å) irradiation.Also for studyingthe morphology of catalyst scanning electron microscopy (SEM), entire image were taken bya Hitachi S4160 FESM. Magnetic characteristic of the particle was assessed with a vibrating sample magnetometer (VSM, lake shore 7410). The protection products were analyzed with a gas chromatograph (Shimadzu) equipped with a HP-5 capillary column.

Preparation of Fe₃O₄@ZrO₂nanoparticle

Fe₃O₄ nanoparticles were synthesized utilizing massart's procedure²⁸ and then the core-shell Fe₃O₄@ZrO₂ was prepared according to the applying method reported previously²⁹⁻³³. Briefly, 0.2 g of Fe₃O₄ nanoparticles (NPs) homogenously were dispersed in HCl 0.1 M for 15 min in order to activate the nanoparticles surface. After magnetic particles were separated by magnet from aqueous solution. It was washed with distilled water two times. The nanoparticles again were dispersed in the mixture of 70 mL ethanol, 30 mL distilled water and 1 mL concentrated NH₃ solution (28%). Finally TEOS (0.05 g, 2.4 mmol) was added to the mixture and stirred for 6 h at r.t. Afterward, silica coated Fe₃O₄ was separated by magnet and washed with ethanol and distilled water at least three times. Nanoparticles coated in the previous step, in the mixture of 0.4 g (1.1 mmol) CTAB (as surfactants), 70 mL distilled water, 2 mL NH₃ and 70 mL ethanol for 30 min was stirred continuously until homogenized and uniform dispersion. Then zirconium nitrate Zr(NO₃)₄ (0.7 g, 3.03 mmol) dissolved in the water) was added drop-wise to the stirring mixture for 6 h at r.t. The final product was collected by magnet and washed with ethanol and distilled water. For removal of surfactant, the obtained particles were refluxed by acetone in the soxhelt extractor for 32 h. Afterward, it was separated, washed by distilled water and dried at 80 °C to get Fe₃O₄@ZrO₂.

Preparation of 3-mercaptopropyl magnetic Zirconia (MPMZ)

0.6 g of Fe₃O₄@ZrO₂ was added to 4 mL dry toluene, 2 mL (10.77 mmol) of (3-mercaptopropyl) trimethoxysilane, and the reaction mixture was refluxed for 18 h. The nanoparticles were separated by magnet and washed with hot toluene for 12 h in the continuous extraction. Then it was dried for overnight at 110 °C to achieve surface bond thiol from Fe₃O₄@ZrO₂-Pr-SH (MPMZ) group.

Preparation of solid Fe₃O₄@ZrO₂ -based sulfonic acid

MPMZ was oxidized by 5 mL H_2O_2 and 1 mL H_2SO_4 in the 20 mL methanol for 12 h at r.t and washed three times with distilled water. In order to ensure complete protonation, the solid catalyst will be suspended in the H_2SO_4 solution 20% for 5 h. After that, the mixture



Scheme. 2 Preparation of catalyst Fe₃O₄@ZrO₂-Pr-SO₃H

FT-IR analysis

FT-IR spectra of Fe_3O_4 , Fe_3O_4 @ZrO₂ and Fe_3O_4 @ZrO₂-Pr-SO₃H samples are shown in Fig.1. In Fig.1a, there are the peaks at 1635 and 3452 cm⁻¹, which related to –OH bending and stretching vibrations of the absorbed water molecules, respectively.

There is the peak at 584 cm⁻¹ that showing the presence of Fe-O. Also the peaks at 1054 and 630 cm⁻¹ belong to vibrations Si-O and Zr-O, respectively (Fig.1b). The vibrational peak of S-H is seen at 2559 cm⁻¹ as shown in Fig.1c. Because of weak dipole vibration of thiol bonds, observed peak is weak^{34, 35}. The appeared peaks at 1045, 1089 and 1188 cm⁻¹ were attributed to the O=S=O asymmetric, symmetric and S-O vibrations of the (-SO₃H) groups, respectively^{36,37} (Fig.1d). In addition, the CH stretching vibrations were observed at 2842 and 2929 cm⁻¹.



Fig. 1 FT-IR spectra of (a) Fe_3O_4 , (b) $Fe_3O_4@ZrO_2$, (c) $Fe_3O_4@ZrO_2$ -Pr-SH and (d) $Fe_3O_4@ZrO_2$ -Pr-SO_3H

XRD patterns

X-ray diffraction patterns (XRD) for Fe₃O₄, Fe₃O₄@ZrO₂ and Fe₃O₄@ZrO₂-Pr-SO₃H are given in Fig.2. As well as XRD of the magnetic nanoparticles of Fe₃O₄ in the cubic phase is a good agreement with (PDF no: 01-075-0499) as shown in Fig.2a. Also the XRD patterns of Fe₃O₄@ZrO₂ and Fe₃O₄@ZrO₂-Pr-SO₃H are similar with XRD pattern for Fe₃O₄^{30,31} as given in Fig.2b and 2c. It demonstrates that the modification has not considerable effect on the

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phase of Fe₃O₄. For this reason, ZrO_2 is amorphous. Organic groups and nanoparticles available in amorphous structure have no effect in the crystal structure of compounds. Due to this fact, XRD patterns of Fe₃O₄@ZrO₂ and Fe₃O₄@ZrO₂-Pr-SO₃H are similar.



Fig. 2 XRD patterns of (a) Fe₃O₄, (b) Fe₃O₄@ZrO₂ and (c) Fe₃O₄@ZrO₂-Pr-SO₃H

FE-SEM analysis

The FE-SEM images for the pure $Fe_3O_4@ZrO_2$ and $Fe_3O_4@ZrO_2$ Pr-SO₃H are illustrated in Fig.3. According to this chart, the particle size bare $Fe_3O_4@ZrO_2$ distribution is narrow and the size of most of the particles is about 20-70 nm (Fig.4a) and (Fig.3). Then, the powder is aggregated because of modification by sulphate and form strong hydrogen bonds between the-SO₃H groups (Fig.4b).



Fig. 3 Distribution chart of particles size



Fig. 4 FE-SEM images of (a) Fe₃O₄@ZrO₂ and (b) catalyst Fe₃O₄@ZrO₂-Pr-SO₃H

EDX analysis for Fe₃O₄@ZrO₂ and Fe₃O₄@ZrO₂-Pr-SO₃H

The EDX spectrum of Fe₃O₄@ZrO₂ (Fig.5a) displays the presence of iron, zirconium and oxygen elements. After modification of Fe₃O₄@ZrO₂, in the EDX spectrum of Fe₃O₄@ZrO₂-Pr-SO₃H (Fig.5b), some other elements such as sulphur and carbon were observed. The content of sulfur and carbon was 6.56 and 17.08 wt%, respectively. Also the reduction of iron peak intensity demonstrates that Fe₃O₄@ZrO₂ coated by (3-mercaptopropyl) trimethoxysilane, which confirms the synthesis process was successful.



Fig.5 EDX analysis of (a) Fe₃O₄@ZrO₂ and (b) Fe₃O₄@ZrO₂-Pr-SO₃H

Kel

Fe Ka

Back titration of Fe₃O₄@ZrO₂-PrSO₃H in aqueous media

Acidity $[H^+]$ of synthesized catalyst (Fe₃O₄@ZrO₂-PrSO₃H) was indicated by back titration method. The procedure of this titration include: 0.5 g of 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 h on a magnetic stirrer. After that, three drops Phenolphthalein was added to it and colour of mixture was pink. Then it was titrated with solution of HCl (0.1 M) until reached to neutral point. After calculations, pH value of catalyst was obtained 2.25.

Surface acidity studies

The acidity strength of an acid in organic solvents can be declared by the Hammett acidity function $(H_0)^{38,39}$. It can be calculated by the following equation:

$H_0 = pK(I)_{aq} + log([I]_s/[IH^+]_s)$

Here, '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 already known and can be acquired from more references (for example the pK(I)_{aq} value of 4-nitroaniline is 0.99). The value of $[I]_{s/}[IH^+]_s$ according to the Lambert-Beer's Law can be calculated using the UV-visible spectrum.

Here, we used 4-nitroaniline as the basic indicator and CCl_4 was chosen as the solvent. The maximal absorbance of the unprotonated form of 4-nitroaniline was observed at 329 nm in CCl_4 . As can be

10.00

resulted from Fig. 6, the indicator was partially in the form as $[IH^+]$ (The absorbance of the unprotonated form of the indicator in Fe₃O₄@ZrO₂-Pr-SO₃H was weak as compared to the sample of the indicator in CCl₄). The achieved results of the acidity strength of Fe₃O₄@ZrO₂-Pr-SO₃H are listed in Table 1 and Absorption spectra of 4-nitroaniline and Fe₃O₄@ZrO₂-Pr-SO₃H can be seen in Fig 6.

Table 1 Calculation of Hammett acidity function (H₀) of Fe₃O₄@ZrO₂-Pr-SO₃H^a

Entry	Catalyst	A _{max}	[I] _s (%)	$[IH^{+}]_{s}(\%)$	H_0	
1	-	2.147	100	0	-	
2	Fe ₃ O ₄ @ZrO ₂ -Pr-SO ₃ H	0.933	43.45	56.55	0.876	
^a Condition for UV-visible spectrum measurement: solvent, CCl ₄ ; indicator, 4-nitroaniline (pK(1) _{aq} : 0.99), 1.44 × 10 ⁴ mol/lit; catalyst, Fe ₃ O ₄ @ZrO ₂ -Pr-SO ₃ H, 20 mg, 25 C.						



Fig 6 Absorption spectra of 4-nitroaniline (indicator; curve A) and Fe_3O_4@ZrO_2-Pr-SO_3H (catalyst; curve B) in CCl_4.

Magnetic properties for Fe₃O₄@ZrO₂-Pr-SO₃H

Results of the VSM measurement for bare Fe₃O₄ and Fe₃O₄@ZrO₂-Pr-SO₃H have been reported (Fig.7). The hysteresis loop for Fe₃O₄@ZrO₂-Pr-SO₃H with limited filed from -1000 to 1000 Oe was shown in Fig. 7b. According to this figure, regarding to the first amount of magnetization saturation of Fe₃O₄ which was 61 emu/g, due to the coating of surface of Fe₃O₄ by propyl sulphate, the amount of magnetization saturation of Fe₃O₄@ZrO₂-Pr-SO₃H was decreased to 13.96 emu/g. This clearly has shown that the coating process successfully was carried out.



Fig. 7 VSM curves of (a) the pure Fe₃O₄ and (b) Fe₃O₄@ZrO₂-Pr-SO₃H

Result and discussion

The trimethylsilylation of hydroxyl alcohols groups simply carried out in the not extreme conditions, solvent-free and room temperature in the presence catalyst $Fe_3O_4@ZrO_2-Pr-SO_3H$. The possible mechanism has been shown in Scheme 3. This mechanism is based-on bronsted acid and explains intractions between (-SO₃H) groups and nitrogen in HMDS that reactive silylating agent.



Scheme. 3 Suggested mechanism of protection alcohols

Alcohols or phenols (1 mmol) could be added to a stirring mixture of $Fe_3O_4@ZrO_2-Pr-SO_3H$ (10 mg) and HMDS (0.7 mmol) at r.t (Scheme 1). After accomplishment of the reaction, catalyst was separated simply from of reaction mixture by a magnet. The optimised catalyst amount was determined by mixing benzyl alcohol, HDMS and different amounts of the catalysts. The mixtures were stirred at room temperature and solvent free conditions. The results of this optimisation were presented in Table 2. According to results, the reaction can be carried out in the presence catalyst in the less time and the yields are outstanding. This catalyst has higher efficiency than previous reported ones. Also this reaction will be considered as a green reaction due to the solvent free conditions. According to Table 2; the optimized amount of catalyst was 10 mg.

Table 2 Optimization of the reaction condition for trimethysilylation of benzyl alcohol with HMDS^a

with minibb			
Entry	Amount of catalyst(mg)	Time (min)	Yield (%)
1	-	90	85
2	5	12	99
3	8	10	99
4	10	6	99
5	15	6	99

^a Reaction of benzyl alcohol (1 mmol) and HMDS (0.7 mmol, 0.112 g) in the present of different amounts of Fe₃O₄@ZrO₂-Pr-SO₃H at room temperature under solvent-free conditions.

In order to show productivity of Fe₃O₄@ZrO₂-Pr-SO₃H, various catalysts such as Trichloroisocyanuricacid (TCCA)⁴⁰, CuSO₄·5H₂O⁴¹, MgBr₂·OEt₂²⁰, Iodine⁴², H₃PW₁₂O₄₀⁴³, ZrCl₄¹⁸, ZrO(OTf)₂⁴⁴, Sulfonicacid@nanoporoussilica²², LaCl₃²¹, HCIO₄–SiO₂⁴⁵ and [V^{IV}(TPP) (OTf)₂]²³ were also used for protection of benzyl alcohol by HMDS. The results were given in Table 3. According to this table, Fe₃O₄@ZrO₂-Pr-SO₃H is very superior than the other catalysts because of solvent-free, simple recovery, and environmentally friendly method, low catalyst loading, high efficienty and reusability used.

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Table 3 Comparison of the obtained results for $Fe_3O_4@ZrO_2-Pr-SO_3H$ with Yields obtained by the recently reported catalyst.

Entry	Catalyst	Catalyst load (mg)	Time (min)	Solvent	Yield (%)	Temperature (°C)	Reference
1	Trichloroisocyanuric acid (TCCA)	24	240	CH ₂ Cl ₂	90	r.t	40
2	CuSO ₄ .5H ₂ O	20	12	CH ₃ CN	98	r.t	41
3	$MgBr_2 \cdot OEt_2$	50	5	Neat	98	r.t	20
4	Iodine	10	2	CH ₂ Cl ₂	98	r.t	42
5	$H_3PW_{12}O_{40}$	29	23	Neat	90	55-60	43
6	ZrCl ₄	5	1	CH ₃ CN	95	r.t	18
7	ZrO(OTf)2	20	1	CH ₃ CN	92	r.t	44
8	Sulfonicacid@nanop oroussilica	30	55	CH ₂ Cl ₂	99	r.t	22
9	LaCl ₃	49	180	CH ₂ Cl ₂	91	r.t	21
10	HClO ₄ –SiO ₂	15	2	CH ₃ CN	98	r.t	45
11	Poly(N- bromobenzene-1,3- disulfonamide)	20	90	CH ₂ Cl ₂	90	r.t	46
12	[V ^{IV} (TPP)(OTf) ₂]	10	1	CH ₃ CN	100	r.t	23
13	Fe ₃ O ₄ @ZrO ₂ -Pr- SO ₃ H	10	6	Neat	99	r.t	This work

Results of these reactions with various alcohols were summrized in Table 4. According to this table, the different alcohols was used in this research such as benzylic, primary, secondary, and phenolic, and got the best result on the yields and time of the reaction. The achived results showed that electron-donating alcohols required less reaction times in comparision to electronwithdrawing alcohols. Also secondry alcohols reacted slowly at room temparature than primary alcohols (Table 4). In addition to, the results displays that aliphatic alcohols need more reaction time compared to aromatic alcohols. The reaction progress was monitored by TLC, GC and FT-IR in order to demonstrate complete protection of hydroxyl. The results showed that all reactions were perfect in the 6-10 min in the solventfree conditions and less reaction time for all alcohols and also the extraordinary yields at (r.t) were obtained. Also it has high efficiency chemoseletive for hydroxyl group but it was not successful to protect thiol and amine groups. Also recovered catalyst by magnet was washed with acetone and distilled water and then dried at 110 °C for 30 min. Afterward, reutilize for more 10 successive runs under same reaction conditions. These results exhibit the highest stability and also the least change in the activity of the catalyst as shown in Fig.8. One of the reasons for decreasing of the catalytic activities is reduction the acidities of catalyst. To prove this, the acidity was tested for each reaction using back titration. The results was indicated the little reduction in the catalyst acidity in each reaction.



Fig. 8 Recyclability of Fe₃O₄@ZrO₂-Pr-SO₃H catalyst for the protection

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Entry	Substrate	Product	Time (min)	Yield (%) ^b
1	CHrOH	CH_OSUMe3	6	99≥
2	CHSCHOH	CHCH ₂ OSiMe ₃	6	99≥
3	Meo CH ₂ OH	CH_OSIMe_	6	99≥
4	Me	CH4/SBM/sg	6	99≥
5	CH ₂ OH	CH ₂ OSiMe ₃	6	99≥
6	СНОН	CH_OSiMg	8	99≥
7	CH2OH	CH _k OSiMe ₃	8	99≥
8	O1N CH2OH	CIEOSDM9	9	99≥
9	CH ₂ OH	CH ₂ OSiMo ₃	9	99≥
10	OH	CSBMs3	7	99≥
11	ОН	OSiMo ₃	6	99≥
12			6	99≥
13	CI	CI CI	10	99≥
14	ныс	H ₅ C OSiMe ₃	6	99≥
15	OH NH ₂	OSiMe ₃	6	99≥
16	ОН	OSiMe3 COOH	7	99≥
17	OH CH ₃	OSiMe3	6	99≥
18	OH	OSiMe ₃	7	99≥
19	OH	OSiMe ₃	6	99≥
20	OH	OSIMe ₃	6	99≥
21	ОН	OSiMe ₃	7	99≥
22	ОН	OSiMe ₃	8	99≥
23	ОН	OSiMe ₃	8	99≥
24	HSOH	US OSiMe ₃	8	99≥

(a) Reaction conditions: alcohol (1 mmol), catalyst (10 mg), HMDS (0.7 mmol, 0.112 g), room temperature (RT). (b) Yield were determined by GC.

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Conclusion

In conclusion, Fe₃O₄@ZrO₂-Pr-SO₃H acid has been exhibited to be an efficient and suitable catalyst. Also green procedure for the protection of alcohols and phenols by HMDS in high yield, solventfree conditions, safe and environmentally benign method. To conclude, simple recovery, simple work up, mild conditions, short reaction time, inexpensive of catalyst and high efficiency make our method to be effective and appropriate for protection alcohols and aliphatic alcohols.

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