

TiCl₄-functionalized nano-Fe₃O₄ encapsulated-silica particles as a recyclable and magnetic catalyst for the synthesis of perhydrotriazolotriazole derivatives

Leila Javadian

Laboratory of Organic Compound Research, Department of Organic Chemistry, College of Chemistry, University of Kashan, P.O. Box: 87317-51167, Kashan, Islamic Republic of Iran Email: Leilajavadian@ymail.com

Javad Safari

Laboratory of Organic Compound Research, Department of Organic Chemistry, College of Chemistry, University of Kashan, P.O. Box: 87317-51167, Kashan, Islamic Republic of Iran Email: Safari@kashanu.ac.ir

Abstract

A robust magnetic nanocatalyst was prepared by the immobilization of TiCl₄ on the surface of Fe₃O₄@SiO₂ nanoparticles and characterized using energy dispersive X-ray analysis, scanning electron microscopy, transmission electron microscopy, vibrating sample magnetometer, and Fourier transform-infrared spectroscopy. The catalytic activity of this nanocomposite was investigated via the synthesis perhydrotriazolotriazoles using a condensation reaction of azine derivatives as 1,3-heterodienes with potassium thiocyanate in [3 + 2]cycloaddition at ambient temperature. This catalytic system offers several advantages such as simplicity, short reaction times, excellent yields and recyclable catalyst.

Keywords: TiCl₄-functionalized Fe₃O₄@SiO₂ nanoparticles, [3+2] cycloaddition, perhydrotriazolotriazoles, nanocatalyst.

Introduction

The term "criss-cross" cycloaddition appeared in 1917 by Bailey and McPherson. They described the cycloaddition of cyanic acid to benzalazine (Verner and M. Pot'a'cek, 2006). Criss-cross cycloaddition reactions are a procedure for the synthesis of fused heterocyclic rings in an one pot arrangement that offer two fused five-membered rings (Zachov'a et al, 2009). 1,3-Dipolar cycloaddition reaction is fundamental processes that offers a synthetic methodology to achieve five-membered heterocyclic compounds. These compunds was described by Huisgen in 1963 as the result of two following [3+2] cycloaddition reaction. Since then, some papers have published [3+2] cycloaddition reactions of aldazines with different dipolarophiles (Kumar, 2002; Safari et al, 2012). The 1,3-dipolar aldazines are 1,3-heterodiene compounds and have double 1, 3-dipolar sites. In addition to aldazines, [3+2] cycloaddition reactions or 1,3-dipolar cycloaddition have been reported for ketazines and

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glyoxalimines with many types of compounds including alkenes. As our knowledge, there are a few reports of the condensation of azines with thiocyanates. But there are several drawbacks such as high catalyst loading and drastic conditions.

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In recent decades, Fe_3O_4 nanoparticles has appeared as a kind of eco-friendly catalyst support due to ease of surface modification, unique physical properties and low toxicity (Reddy et al, 2012). The surface of the Fe_3O_4 MNPs is usually modified with a thin silica layer to prevent the aggregation of Fe_3O_4 MNPs. The surface silanol groups can easily react with various compounds to reach the certain purposes especially in the field of catalysis (Zhang et al, 2014; Sharma, 2014; Kolvari, 2014; Naeimi and Nazifi, 2013; Bamoniri Moshtael-Arani, 2015). Magnetic nanocatalysts have been used in various organic reactions such as multicomponent reactions, C–C couplings, oxidation and reductions with a high level of activity (Cheng, 2014; Cheng, 2013; Karimi, 2014). As a continuation of our works on the development of magnetic nanocatalyst, we herein report the preparation and characterization of Fe_3O_4 @SiO₂–TiCl₄ as a novel nanocatalyst and its utility for the synthesis of perhydrotriazolotriazole derivatives by the condensation of aldazine derivatives with potassium thiocyanate at room temperature.

Experimental

Preparation of magnetic Fe₃O₄@SiO₂-TiCl₄ MNPs

First, Fe_3O_4 nanoparticles were prepared by chemical co-precipitation method as described in the literature (Safari and Javadian, 2013). Second, Fe_3O_4 -SiO₂ composite were synthesized through the Stöber method (Bamoniri and Fouladgar, 2015). Briefly, 0.5 g of the Fe_3O_4 NPs was dispersed in 20 ml of distilled water and 50 ml of ethanol under ultrasound irradiation and then concentrated aqueous ammonia (3 ml) was added under continuous mechanical stirring. Finally, 0.2 ml of tetraethyl orthosilicate diluted in ethanol (10 ml) was added drop-wisely under continuous mechanical stirring. After stirring for 18 h, Fe_3O_4 -SiO₂ nanoparticles were collected by magnetic separation, washed with water/ethanol and dried at 70 °C.

Third, functionalization of Fe_3O_4 - SiO_2 composite nanoparticles was performed by adding 0.10 g of Fe_3O_4 -SiO₂ MNPs to 10 ml of CHCl₃ under ultrasound irradiation for 20 min. After that, 1 ml of titanium tetrachloride was dissolved in CHCl₃ (30 ml) and was added in drops to the suspension of Fe_3O_4 - SiO₂ composite nanoparticles under vigorous magnetic stirring. Subsequently, the reaction mixture was stirred for 1 h at room temperature. The suspension successively magnetically collected, washed with CHCl₃ and then dried.

General procedure for the synthesis of tetrahydro-[1,2,4] triazolo [1,2-a][1,2,4]triazole-1,5-dithiones

In a typical experiment, KSCN (2 mmol), AcOH (3 mmol, 0.18 mL), CH₃CN (10 mL) and catalytic amount of Fe_3O_4 -SiO₂ -TiCl₄ nanocomposite (0.03 g) were stirred at room temperature. After stirring for 5 min, aldazine (1 mmol) was added to this mixture and the contents were stirred for an appropriate period while the progress of the reaction was followed by TLC. After completion of the reaction, the nanocatalyst was removed by an external magnet and reused. Then, cold water (30 mL) was added and the solid product was collected by filtration, was washed with CHCl₃, dried and recrystallized from ethanol.



Scheme 1. Synthesis of perhydrotriazolotriazole derivatives by Fe₃O₄@SiO₂-TiCl₄ as a nanocatalyst.

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Results and discussion

The objectives of the present study are: (i) to catacterization of nanoparticles (Fe_3O_4 , $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2$ -TiCl₄) and (ii) to prepare tetrahydro-[1,2,4] triazolo [1,2-a][1,2,4]triazole-1,5-dithiones in the presence of $Fe_3O_4@SiO_2$ -TiCl₄ MNPs.

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characterization of magnetic nanocatalyst

The magnetization curve for synthesized materials from Fe_3O_4 to $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2$ -TiCl₄ nanoparticles were recorded in figure 1. The saturation magnetization of the Fe_3O_4 NPs was 55.6 emu/g, which decreased to 46.5 emu/g after supporting Fe_3O_4 with SiO₂. Also, the saturation magnetization of the $Fe_3O_4@SiO_2$ decreased to 16.5 emu/g after linking of TiCl₄ on the surface of $Fe_3O_4@SiO_2$. It confirms the presence of TiCl₄ as a diamagnetic shell.



Figure 1. Magnetization curves for the Fe₃O₄, Fe₃O₄-SiO₂ and Fe₃O₄-SiO₂-TiCl₄ MNPs.

The molecular structures of magnetic Fe₃O₄, Fe₃O₄@SiO₂, and Fe₃O₄@SiO₂-TiCl₄ nannoparticles were determined by FT-IR analysis. Nano- Fe₃O₄ was identified by band at 570 cm⁻¹ due to Fe–O vibration. The FT-IR spectrum of Silica coated magnetite nano particles displays characteristic The peaks at 1073 and 850 cm⁻¹ corresponds to the symmetrical and asymmetrical vibrations of Si–O–Si. Also, the band at 451 cm⁻¹ corresponds to the Si–O–Fe stretching vibrations. The linking of the TiCl₄ on the surface of Fe₃O₄@SiO₂ MNPs was confirmed by the appearance of a band at 929 cm⁻¹ (Fig. 2).



Figure 2. FT-IR spectra of (a) Fe₃O₄, (b) Fe₃O₄@SiO₂ and (c) Fe₃O₄@SiO₂-TiCl₄ MNPs.

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The EDAX image of nanocatalyst provided the presence of the expected elements in the structure of $Fe_3O_4@SiO_2$ -TiCl₄ (Figure 3). It confirmed the presence of TiCl₄ on the $Fe_3O_4@SiO_2$ MNPs. The elemental compositions of $Fe_3O_4@SiO_2$ -TiCl₄ were found to be 30, 5, 19, 14 31 wt % for Fe, Si, Ti, Cl and O, respectively.



Figure 3. The energy dispersive X-ray (EDAX) of Fe₃O₄@SiO₂-TiCl₄ nanocatalyst.

The phase of the synthesized materials from Fe₃O₄ to Fe₃O₄@ SiO₂- TiCl₄ MNPs were investigated by XRD patterns. The diffraction peaks in the XRD pattern of Fe₃O₄ (2θ =30.1, 35.5, 43.2, 53.5, 57.0, 62.8 and 74.3°) can be in accord with standard pattern of an inverse cubic spinel. Magnetic Fe₃O₄@SiO₂ NPs exhibited a broadened at 2θ = 20-30 due to the non-crystalline nature of silica layer. The XRD pattern of nanocatalyst (Fe₃O₄@SiO₂-TiCl₄) exhibited a much broader diffraction pattern and increased the noise to that of Fe₃O₄@SiO₂ NPs, indicating that the linking of the TiCl₄ on the surface of Fe₃O₄@SiO₂ (Fig. 4).



Figure 4. XRD patterns of (a) Fe_3O_4 (b) $Fe_3O_4@SiO_2$ (c) $Fe_3O_4@SiO_2$ -TiCl₄.

The TEM was recorded to understand the surface morphology and also shape of the particles. As demonstrated in Fig. 5a, Fe₃O₄ MNPs have a mean diameter lower than 15 nm a nearly spherical shape. Figure 5b shows that Fe₃O₄@SiO₂ nanoparticles keep the morphological properties of Fe₃O₄ MNPs except for a larger particle size and smoother surface, which silica are uniform coated on the Fe₃O₄ MNPs to form silica shell. The TEM image of Fe₃O₄@SiO₂-TiCl₄ nanoparticles are displayed in Figure 5c. According to this image, the nanocatalyst is nearly spherical with more than 35 nm in size.



Figure 5. a) The TEM of Fe₃O₄ MNPs, b) Fe₃O₄-SiO₂ and c) Fe₃O₄-SiO₂-TiCl₄ MNPs.

Investigation of catalytic property of Fe₃O₄-SiO₂-TiCl₄ MNPs

In order to evaluation of the effect of $Fe_3O_4@SiO_2-TiCl_4$ MNPs, catalytic activity of $Fe_3O_4@SiO_2-TiCl_4$ was investigated on the model reaction. The results in Table 1 exhibited that the corresponding product was obtained in low yield and long reaction time in the absence of nanocatalyst. The cycloaddition reaction was carried out with high yields the presence of catalytic amount of $Fe_3O_4@SiO_2-TiCl_4$. Also the results indicated the optimum amount of the nanocatalyst was 0.03 g at room temperature and the increase of the nanocatalyst did not decrease time of reaction.

Table 1. The synthesis of tetrahydro-3,7-diphenyl-[1,2,4] triazolo [1,2-a][1,2,4] triazole-
1,5-dithione under different amounts of the magnetic catalyst. ^a

Entry	Fe ₃ O ₄ @SiO ₂ -TiCl ₄ (g)	Time (min)	Yield(%)
1	blank	60	47
2	0.01	27	76
3	0.02	20	89
4	0.03	15	97
5	0.04	15	95

^a Reaction condition: KSCN (2 mmol), AcOH (0.18 mL), aldazine (1 mmol), Fe₃O₄-SiO₂- TiCl₄ (0.03 g) and CH₃CN (10 mL).

In order to examine the generality of this procedure in the mentioned cycloaddition reaction, a number of aldazines containing different groups in the ortho, meta and para position were used with potassium thiocyanate and acetic acid in the presence of $Fe_3O_4@SiO_2-TiCl_4$ as a nanocatalyst in acetonitrile. As can be seen from Table 2, benzaldazine bearing ortho substituent afford lower yield than meta or para substituted benzaldazines. There is more steric hindrance for the 2-substituted benzaldazine on the product formation than the 3- or 4-substituted benzaldazines. So, this is due to the steric effect.

Table 2. Synthesis of tetrahydro-[1,2,4] triazolo [1,2-a][1,2,4] triazole-1,5-dithiones in the presence of Fe₃O₄@SiO₂-TiCl₄ MNPs.^a

Entry	R	Product	Time (min)	Yield (%)
1	C ₆ H ₅	3a	15	97
2	$3-NO_2 C_6H_4$	3b	28	85
3	4-OCH ₃ C ₆ H ₄	3c	13	96
4	$2-\text{Cl }C_6\text{H}_4$	3d	38	72
5	$3-\text{Cl} C_6 H_4$	3e	19	90
6	$4-\text{Cl }\text{C}_6\text{H}_4$	3f	14	92
7	3-OH C ₆ H ₄	3g	22	89
8	3-OH, 4-OCH ₃ C ₆ H ₃	3h	18	94

^a Reaction condition: KSCN (2 mmol), AcOH (0.18 mL), aldazine (1 mmol), Fe_3O_4 -SiO₂- TiCl₄ (0.03 g) and CH₃CN (10 mL).



From a green chemistry perspective, the stability of the nanocatalyst has been studied by the possibility of reusability. Thus, after the completion of the reaction, the catalyst was separated by an external magnet, washed with chloroform several times and dried at room temperature without further purification to use for the next run. The obtained results showed that the magnetic catalyst could be reused for four times without any appreciable loss of its activity (Table 3).

Table 3. The cycloaddition reaction using t	the recycled Fe ₃ O ₄ -SiO ₂ -TiCl ₄ magnetic catalys
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Run	1	2	3	4	5
Yield (%)	97	96	96	95	90

Conclusion

In this research, we have been described the synthesis of tetrahydro-[1,2,4] triazolo [1,2-a][1,2,4] triazole-1,5-dithione derivatives *via* condensation of azines with potassium isothiocyanate using Fe₃O₄-SiO₂-TiCl₄ composite nanoparticles as a novel nanocatalyst. The reaction in the presence of recent magnetic catalyst indicated a lot of significant advantages such as low reaction times, simplicity of work-up, excellent product yields, eco-friendly and recyclable catalyst.

References

- A. Bamoniri and S. Fouladgar, (2015). SnCl₄-Functionalized nano-Fe₃O₄ encapsulated-silica particles as a novel heterogeneous solid acid for synthesis of 1,4-dihydropyridine derivatives, RSC Advances. Vol. 5. 78483-78490
- A. Bamoniri and N. Moshtael-Arani, (2015). Nano- Fe₃O₄ encapsulated-silica supported boron trifluoride as a novel heterogeneous solid acid for solvent-free synthesis of arylazo-1- naphthol derivatives, RSC Advances Vol. 5. 16911-16920
- T. Cheng, D. Zhang, H. Li and G. Liu, (2014). Magnetically recoverable nanoparticles as efficient catalysts for organic transformations in aqueous medium. Green Chemistry. Vol. 16. 3401–3427
- L. L. Cheng, N. Erathodiyil and J. Y. Ying, (2013). Nanostructured catalysts for organic transformations. Accounts of Chemical Research Vol. 46. 1825–1837
- B. Karimi, F. Mansouri and H. Vali, (2014). A highly water-dispersible/magnetically separable palladium catalyst based on a Fe₃O₄ @SiO₂ anchored TEG-imidazolium ionic liquid for the Suzuki–Miyaura coupling reaction in water. Green Chemistry. Vol. 16. 2587–2596
- E. Kolvari, N. Koukabi and O. Armandpour, (2014). A simple and efficient synthesis of 3,4-dihydropyrimidin-2-(1H)-ones via Biginelli reaction catalyzed by nanomagnetic-supported sulfonic acid, Tetrahedron. Vol. 70. 1383–1386
- H. Kumar, R. Goyal, S. Kaur, R. D. Anand, A. Parmar and B. Kumar, (2002). Synthesis of 1,5-substituted-*s*-triazolinodino[1,2-*a*]-*s*-triazolidine-3,7-dithione and 1,2,4- triazolidine-3-thione derivatives from azines. Indian Journal of Chemistry, Sect. B: 2182–2184
- H. Naeimi and Z.S. Nazifi, (2013). A highly efficient nano-Fe₃O₄ encapsulated-silica particles bearing sulfonic acid groups as a solid acid catalyst for synthesis of 1,8-dioxo-octahydroxanthene derivatives, Journal of Nanoparticle Research. Vol. 15. 2026-2037
- L. H. Reddy, J. L. Arias, J. Nicolas and P. Couvreur, (2012). Magnetic nanoparticles: design and characterization, toxicity and biocompatibility, pharmaceutical and biomedical applications Chemical Review Vol. 112. 5818–5878
- J. Safari, S. Gandomi-Ravandi and M. Ghotbinejad, (2012). New Synthesis of Perhydrotriazolotriazoles Catalyzed by TiCl₄ under Ambient Conditions. Journal of the Korean Chemical Society Vol. 56. 78–81
- J. Safari and L. Javadian, (2013). A one-pot synthesis of 5,5-disubstituted hydantoin derivatives using magnetic Fe₃O₄ nanoparticles as a reusable heterogeneous catalyst, Comptes Rendus Chimie. Vol. 16. 1165-1171
- R. K. Sharma, Y. Monga and A. Puri, (2014). Magnetically separable silica@ Fe₃O₄ core–shell supported nanostructured copper(II) composites as a versatile catalyst for the reduction of nitroarenes in aqueous medium at room temperature. Journal of Molecular Catalysis A: Chemical Vol. 393. 84–95
- J. Verner and M. Pot'a'cek, (2006). Criss-cross cycloadditions on ketazines derived from alicyclic ketones, Molecules. Vol. 11. 34–42

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- H. Zachov'a, S. Man, J. Taraba and M. Pot'a'cek, (2009). Rearrangement of fused tetracyclic heterocycles induced by alkyl halides and formation of a new type of 'proton sponge. Tetrahedron. Vol. 65. 792–797
 F. Zhang, M. Chen, X. Wu, W. Wang and H. Li, (2014). Highly active, durable and recyclable ordered
- F. Zhang, M. Chen, X. Wu, W. Wang and H. Li, (2014). Highly active, durable and recyclable ordered mesoporous magnetic organometallic catalysts for promoting organic reactions in water. Journal of Materials Chemistry A. Vol. 2. 484–491

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