

New magnetic nanocatalyst containing a bis-dicationic ionic liquid framework for Knoevenagel condensation reaction

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Abstract

Bis[(3-aminopropyl)triethoxysilane]dichloride immobilized on magnetic nano- γ -Fe₂O₃@SiO₂ has been prepared. After characterization, the reagent was used for efficient promotion of the Knoevenagel reaction, achieving high reaction rates and yields. Also, the recovery and reusability of the catalyst were excellent for the studied reaction.

Keywords Bis-dicationic magnetic nanoparticles \cdot Nano- γ -Fe₂O₃ \cdot Arylidene malononitriles \cdot Ethyl-3-aryl-2-cyanoacrylates \cdot Water-mediated reaction

Introduction

In recent decades, magnetic nanoparticles have received attention due to their important properties such as superparamagnetism, coercivity, high surface area, and low Curie temperature [1]. These properties make them suitable for use in the fields of drug delivery and magnetic resonance imaging (MRI) [2], biosensors [3], and other fields, especially catalysis [4, 5].

Usually, nanoparticles are covered with organic (such as starch [6], alginates [7], chitosan [8] polyacrylic acid [9], polyethyleneimine [10], and polyethylene glycol [11]) or inorganic (including silver [12], gold [13], graphene oxide [14–16], silicon and silica [17]) coatings, to extend their ability and increase their surface.

Various iron oxides have important applications in industry as pigments, polishing agents, and catalysts as well as in electrochemical cells [18]. Moreover, iron oxide nanoparticles have properties distinct from the bulk material. The applications

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of iron oxide nanoparticles have led to the introduction of various methods for their synthesis and characterization. One of the most famous methods for preparation of coated γ -Fe₂O₃ is the modified Stöber method, using which the size of the resulting nanoparticles can be tuned by adjusting the pH, solvent, temperature, and concentrations of the starting materials [19].

Even though ionic liquids have many benefits, their use also has some disadvantages. Their high viscosity prevents their high surface from taking part in reactions. Their separation and reusability (especially in homogeneous catalysis) are also difficult. Also, use of large amounts of ionic liquids is not affordable [20, 21]. Because heterogeneous catalysts are preferred in chemical industry to achieve required reactions, use of supported ionic liquids represents a good method to benefit from their advantages as well as heterogeneous catalysis [22]. These advantages increase when the catalyst can be separated using an external magnet, to reduce the cost of separation and obtain highly pure products [23].

Knoevenagel condensation is one of the most important reactions for C–C bond formation [24–27]. From the viewpoint of green chemistry, this reaction is ecofriendly because its byproduct is water [28]. This reaction has been used to obtain fine chemicals and many other useful compounds [29]. This reaction plays a key role in synthesis of some bioactive compounds [30, 31]. Also, the Knoevenagel reaction is one of the key steps in preparation of some medicines such as entacapone [32] and atorvastatin [33]. Because of the importance of the Knoevenagel condensation of an aldehyde and malononitrile (or ethyl cyanoacetate) as a basic and key step to obtain more important molecules, various methods and catalysts have been reported to promote this reaction [34–39].

In spite of their considerable advantages, these methods are accompanied by drawbacks such as high toxicity, low reusability, use of large amounts of catalyst, use of organic solvents, high cost, long reaction time, and low yield. Therefore, introduction of new methods to avoid such disadvantages has received attention from many researchers in organic chemistry.

Experimental

Materials

All chemicals were purchased from Merck, Aldrich, and Fluka chemical companies and used without any further purification. All products were separated and characterized based on their physical properties and comparison with reported values. Both purity determination of the substrates and reaction monitoring were carried out by thin-layer chromatography (TLC) using silica gel SIL G/UV 254 plates. Melting points were determined using a Büchi B-545 apparatus. Fourier-transform infrared (FT-IR) spectra were recorded using a PerkinElmer (USA) Spectrum BX series spectrophotometer (KBr disks). Field-emission scanning electron microscopy (FESEM) was performed using a TESCAN (Czech Republic) MIRA III instrument. X-ray diffraction (XRD) patterns of samples were recorded on a Philips (The Netherlands) PW1730. Thermogravimetric analysis (TGA) was carried out on a TA (USA) model Q600 instrument. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded using a Bruker (Germany) Ultrashield 400 MHz instrument with deuterated dimethylsulfoxide (DMSO) as solvent. Vibrating sample magnetometer (VSM) was recorded on a Lakeshore 7200 (USA) instrument.

Catalyst preparation

Preparation of γ-Fe₂O₃ NPs

To a solution of FeCl₂·4H₂O (4 g), FeCl₃·6H₂O (6.35 g), and HCl (1.7 mL) in deionized water (50 mL), NH₃ solution (1.5 M, 250 mL) was added dropwise under argon atmosphere at room temperature to reach pH 11. The resulting black mixture was stirred at room temperature for 1 h until its color changed to brown. The synthesized magnetic nanoparticles were separated from the reaction medium using an external magnet, then washed with deionized water to reach pH 7. Finally, the residue was placed in an oven at 250 °C for 3 h to obtain reddish-brown powder of γ -Fe₂O₃ nanoparticles [40, 41].

Preparation of γ-Fe₂O₃@SiO₂ NPs

First, 1.0 g of synthesized γ -Fe₂O₃ nanoparticles was dispersed by sonication in a solution of ethanol and water (80.0 mL) [4:1], then tetraethylorthosilicate (3.0 mL) and ammonia 28 % (3.0 mL) were slowly added to it, and the reaction mixture was stirred for 8 h at room temperature. After that, the obtained solid was separated using an external magnet, washed several times with deionized water and ethanol, and dried in an oven at 60 °C for 12 h. The synthesized silica-coated nano- γ -Fe₂O₃ was characterized by FT-IR spectroscopy, XRD analysis, FESEM, and TGA, whose results are presented in the next sections [42].

Preparation of bis-dicationic ionic liquid N^1 , N^4 -bis(3-(triethoxysilyl)propyl) butane-1,4-diaminium dichloride, [Bis-APTES]Cl₂

In a 50-mL round-bottomed flask, a mixture of (3-aminopropyl)triethoxysilane (10.0 mmol) and 1,4-dichlorobutane (5.0 mmol) was stirred in refluxing acetonitrile (10 mL) for 12 h. During this process, a white solid gradually settled out. After that, the white precipitate was filtered and washed with ethanol, and dried at 70 °C for 12 h.

Preparation of γ-Fe₂O₃@SiO₂@[Bis-APTES]Cl₂ NPs

In a 50-mL round-bottomed flask, 1.0 g γ -Fe₂O₃@SiO₂ was dispersed in dry toluene (20 mL) by sonication, then 1.1 g of synthesized N^1 , N^4 -bis(3-(triethoxysilyl)propyl)butane-1,4-diaminium dichloride was added to it and stirred for 48 h at reflux



Scheme 1 Preparation of γ-Fe₂O₃@SiO₂@[Bis-APTES]Cl₂ NPs



Fig. 1 Stepwise preparation of γ -Fe₂O₃@SiO₂@[Bis-APTES]Cl₂ NPs

temperature. Finally, the brown precipitate was separated using an external magnet, washed with ethanol several times, and dried at 70 °C for 12 h (Scheme 1; Fig. 1).

Preparation of products

Preparation of arylidene malononitrile and ethyl-3-aryl-2-cyanoacrylate derivatives

In a 10-mL round-bottomed flask, a mixture of aldehyde (1.0 mmol), malononitrile (or ethyl cyanoacetate) (1.1 mmol), and γ -Fe₂O₃@SiO₂@[Bis-APTES]Cl₂ NPs (5 mg) in water (3.0 mL) was stirred at 80 °C for appropriate time. After reaction completion as monitored by TLC [*n*-hexane:EtOAc (7:3)], the precipitate was dissolved in ethanol or acetone (20 mL). Then, the nanocatalyst was removed using an external magnet. After that, the solvent was evaporated and the solid residue was washed with a few drops of cold ethanol and washed with water. The expected product was obtained in high yield purity without need for any extra purification steps.

Physical and spectral data of newly synthesized compound

2-((1-Methyl-1*H***-pyrrol-2-yl)methylene)malononitrile** Yellow crystals; m.p. 156–158 °C; IR (KBr, cm⁻¹): 3386, 3118, 3032, 2924, 2854, 2212, 1586, 1491, 1402, 1318, 1183, 1170, 752; ¹H NMR (400 MHz, DMSO- d_6) δ (ppm)=3.80 (s, 3H), 6.46 (ddd, J_1 =4.4 Hz, J_2 =2.0 Hz, J_3 =0.4 Hz, 1H), 7.40 (dd, J_1 =4.4 Hz, J_2 =1.2 Hz, 1H), 7.51 (t, J=1.2 Hz, 1H); ¹³C NMR (100 MHz, DMSO- d_6) δ (ppm)=34.0, 67.7, 112.6, 115.2, 115.9, 119.0, 127.2, 134.3, 145.

Results and discussion

Various catalysts have been designed and introduced for chemical reactions by our research group over more than two decades, each showing at least one distinguished advantage in comparison with other introduced ones [43–47]. Among them, nano-catalysts and nanomagnetic catalysts are a unique field for our research group [48, 49]. In continuation of these studies and for the first time, we introduce herein a bis-dicationic acidic ionic liquid using an aliphatic spacer and its immobilization on sil-ica-coated magnetic nano- γ -Fe₂O₃ for efficient promotion of synthesis of arylidene malononitrile and ethyl-3-aryl-2-cyanoacrylate derivatives.

Characterization of γ-Fe₂O₃@SiO₂@[Bis-APTES]Cl₂ NPs

FT-IR spectroscopy

The FT-IR spectrum of γ -Fe₂O₃ (a) showed a peak centered at 3424 cm⁻¹ related to hydroxyl groups of the surface of γ -Fe₂O₃ and adsorbed water. Strong stretching vibrations of Fe–O appeared at 559 cm⁻¹ and 638 cm⁻¹, while these peaks were weakened in the FT-IR spectrum of γ -Fe₂O₃@SiO₂ (b). Also, for this compound, the strong broad stretching peak in the region of 1000–1300 cm⁻¹, which is related to Si–O bonds, shows that γ -Fe₂O₃ was successfully coated by silica. In the FT-IR spectrum of the obtained N^I, N^4 -bis(3-(triethoxysilyl)propyl)butane-1,4-diaminium dichloride (c), the broad peak at 1000–1300 cm⁻¹ is related to Si–O stretching vibrations. In this spectrum, peaks at 2800–3000 cm⁻¹ are related to stretching C–H vibrations. N–H stretching vibration is indicated at 3433 cm⁻¹. Also, acidic vibrations related to H⁺ cause peak broadening at 2600–3300 cm⁻¹, which proves the acidic nature of the IL and its successful preparation. The FT-IR spectrum of γ -Fe₂O₃@SiO₂@[Bis-APTES]Cl₂ NPs (d) shows the Fe–O stretching medium vibration peaks at 565 cm⁻¹ and 640 cm⁻¹. In this spectrum, the broad peak at 1000–1300 cm⁻¹ is due to Si–O–Si symmetric and asymmetric stretching vibrations. Overall, these results clearly show that, in the FT-IR spectrum of Fe₂O₃@SiO₂@ [Bis-APTES]Cl₂ NPs, peaks related to the bis-dicationic link are added to the FT-IR peaks of Fe₂O₃@SiO₂ (Fig. 2).

XRD analysis

Figure 3 shows the XRD patterns of γ -Fe₂O₃@SiO₂ (a) and γ -Fe₂O₃@SiO₂@[Bis-APTES]Cl₂ (b). Peaks at around 2θ =30.4°, 35.8°, 43.5°, 54.0°, 57.5°, and 63.2°, which can be assigned to (220), (311), (400), (422), (511), and (440), are readily recognized from the XRD patterns. Observed diffraction peaks match well with the structure of maghemite. The broad peak from 2θ =19° to 28° is attributed to amorphous-phase silica in the shell of the silica-coated γ -Fe₂O₃ manoparticles (γ -Fe₂O₃@SiO₂) (a). Certainly, this peak for γ -Fe₂O₃@SiO₂@[Bis-APTES]Cl₂ NPs is broader, indicating the presence of ionic liquid in the catalyst structure (b) [50] (Fig. 3).

TGA

The TGA curve of γ -Fe₂O₃@SiO₂ shows two distinguished weight loss peaks. First, a decrease in weight (2 %) related to desorption of surface water is observed from room temperature to 130 °C. In continuation, 3 % weight loss is seen between 130 and 700 °C, which indicates the thermal stability of the compound (a). In the case



Fig. 2 FT-IR spectra of γ -Fe₂O₃ (a), γ -Fe₂O₃@SiO₂ NPs (b), [Bis-APTES]Cl₂ (c), and γ -Fe₂O₃@SiO₂@ [Bis-APTES]Cl₂ NPs (d)



Fig. 3 XRD patterns of γ -Fe₂O₃@SiO₂ NPs (a) and γ -Fe₂O₃@SiO₂@[Bis-APTES]Cl₂ NPs (b)

of γ -Fe₂O₃@SiO₂@[Bis-APTES]Cl₂ NPs, decomposition started at 340 °C and 18 % weight loss was observed up to 700 °C, which in comparison with γ -Fe₂O₃@SiO₂ (5 %) is a higher amount to the same temperature. This difference is caused by decomposition of ionic liquid on the surface of the catalyst, confirming successful immobilization of the organic part on Fe₂O₃@SiO₂ (b) [50] (Fig. 4).



Fig. 4 TGA curves of γ -Fe₂O₃@SiO₂ NPs (a) and γ -Fe₂O₃@SiO₂@[Bis-APTES]Cl₂ NPs (b)



Fig. 5 FESEM image of γ -Fe₂O₃ NPs



Fig. 6 FESEM image of γ -Fe₂O₃@SiO₂ NPs

FESEM analysis

Field-emission scanning electron microscopy (FESEM) revealed γ -Fe₂O₃ and γ -Fe₂O₃@SiO₂ microspheres with size of around 18 and 35 nm, respectively (Figs. 5, 6). Comparison between γ -Fe₂O₃@SiO₂ and γ -Fe₂O₃@SiO₂@[Bis-APTES]Cl₂ NPs showed that, in the case of the prepared catalyst, the free state of the particles was changed, becoming interconnected and attached (Figs. 7, 8). This shows that ionic liquid links are successfully formed between the γ -Fe₂O₃@SiO₂ nanoparticles. Also, these results indicate that the particles were connected in different directions.

Vibrating-sample magnetometry (VSM) analysis

The synthesized nanomagnetic catalyst possessed a high superparamagnetic characteristic. Magnetic measurements were performed in an applied magnetic field at room temperature, sweeping the field from -12,000 to +12,000 Oe using a VSM to measure the magnetic properties. The magnetic saturation of γ -Fe₂O₃@SiO₂@[Bis-APTES]Cl₂ NPs was found to be 40 emu/g. The catalyst showed high magnetization ability, sufficient for magnetic separation using a conventional magnet (Fig. 9).



Fig.7 FESEM image of $\gamma\text{-}Fe_2O_3@SiO_2@[Bis-APTES]Cl_2$ NPs, revealing a severe change in surface morphology



Fig. 8 FESEM image of γ -Fe₂O₃@SiO₂@[Bis-APTES]Cl₂ NPs, indicating their size



Fig. 9 Magnetization curve of γ -Fe₂O₃@SiO₂@[Bis-APTES]Cl₂ NPs

New magnetic nanocatalyst	containing a	bis-dicationic ionic
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Entry	Catalyst (mg)	Solvent	Temp.	Time (min.)	Yield (%) ^c
1	_	_	80 °C	150	15 ^a
2	5	-	80 °C	120	25 ^a
3	5	CHCl ₃	Reflux	120	35 ^a
4	5	CH ₃ CN	Reflux	120	60 ^a
5	5	EtOH	RT	120	55 ^a
6	5	EtOH	Reflux	100	75 ^b
7	5	H ₂ O	RT	55	81 ^b
8	5	H ₂ O	50 °C	20	85 ^b
9	5	H ₂ O	70 °C	6	90 ^b
10	5	H ₂ O	80 °C	1	98 ^b
11	5	H ₂ O	90 °C	1	90
12	2	H ₂ O	80 °C	3	95 ^b
13	8	H ₂ O	80 °C	1	96 ^b
14	5	H ₂ O/EtOH (1:1)	Reflux	3	88 ^b

Table 1	Optimization	of typical	Knoevenagel	reaction
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Reaction conditions: 4-chlorobenzaldehyde (1.0 mmol), malononitrile (1.1 mmol), solvent (3.0 mL), and required amount of catalyst

^aReaction not completed

^bYields refer to isolated products



Catalytic activity

Optimization and derivation steps

After preparation and on the basis of the results obtained from the structural studies, we investigated the catalytic ability of γ -Fe₂O₃@SiO₂@[Bis-APTES]Cl₂ NPs in reactions needing acceleration using an acidic catalyst. For this purpose, Knoevenagel reaction between various aldehydes and malononitrile (or ethyl cyanoacetate) in presence of this reagent was studied.

Optimization step

First, to optimize the conditions, the reaction of 4-cholorobenzaldehyde and malononitrile was selected as a model. Performing this reaction in absence of catalyst and solvent and in refluxing chloroform did not result in a remarkable product. Carrying out the reaction in refluxing acetonitrile and room-temperature ethanol did not lead to reaction completion, while use of refluxing ethanol led to reaction completion but after long reaction time. Replacement of the organic solvent with water led to the best result at 80 °C. Using a mixture of water and ethanol (1:1) caused a slight decrease in the reaction rate and yield. Also, alteration of the amount of catalyst showed that the optimum amount was 5 mg for 1 mmol scale reaction (Table 1).

After the optimization step and determination of the best conditions (Scheme 2), various aldehydes with electron-donating or electron-withdrawing groups were used for this reaction, all leading to corresponding products. No noticeable difference was observed between the various types of aldehydes in this reaction, but the reaction rate and yield were lower when malononitrile was replaced with ethyl cyanoacetate (Table 2).

Reusability of catalyst

Figure 10 shows the magnetic property of the catalyst which facilitates the recycling process.

To determine the reusability of γ -Fe₂O₃@SiO₂@[Bis-APTES]Cl₂ NPs, as one of its distinguished advantages, reusability curves were prepared for the mentioned reaction. First, a typical reaction (Table 2, entry 4) was selected. After completion of the reaction, the product was dissolved by addition of ethanol or acetone and heating. Then, the flask was placed on an external magnet, and the solution was poured into a beaker while the catalyst remained in the flask. The same reaction was performed in the same flask without addition of extra catalyst. This test was repeated for six times for this reaction. The results confirmed the excellent recyclability and reusability of the catalyst in the studied reaction (Fig. 11).

Comparison of catalytic activity

To illustrate the catalytic ability of the synthesized nanoparticles in the mentioned reactions, the results obtained from the reaction of 4-chlorobenzaldehyde and malononitrile in presence of γ -Fe₂O₃ @SiO₂@[Bis-APTES]Cl₂ NPs are compared with some other catalysts introduced in literature in Table 3. In all cases, γ -Fe₂O₃@SiO₂@[Bis-APTES]Cl₂ NPs showed one or more advantages. Meanwhile, the high reusability of the nanocatalyst introduced herein with respect to many other types is also noticeable.

Reaction mechanism

The proposed mechanism begins with activation of both aldehyde and nitrile compounds using acidic hydrogen of the catalyst. After that, the activated aldehyde is attacked by the activated nitrile compound to obtain intermediate **I**. Then, with the

P (Ar		Time (mir.)	Yield (%) ^a	M.P (°C)	
Entry		Product	Time (min.)		(Obs.)	(Lit.) [ref.]
1	C ₆ H ₅	CN CN	3	89	77-79	78-80 [35]
2	2-Cl- C6H5		2	91	90-92	92-93 [37]
3	3-Cl- C ₆ H ₅	CI CN	1	93	95-97	95-96 [51]
4	4-Cl- C ₆ H ₅		1	98	160-162	160-162 [52]
5	2-NO2-C6H5		2	90	140-141	139-140 [52]
6	3-NO ₂ -C ₆ H ₅	O ₂ N CN CN	2	93	102-104	101-103 [35]
7	4-NO ₂ -C ₆ H ₅	O ₂ N CN	3	92	156-158	158-159 [51]
8	2-OH-C6H5	OH CN CN	5	88	100-102	99-101 [35]
9	4-OH-C6H₅	HO	4	87	183-185	186-188 [35]
10	2-OCH3-C6H5	OCH3 CN	4	90	83-85	81-82 [35]
11	4-OCH3-C6H5	H ₃ CO	5	88	114-116	115-117 [35]
12	4-CH ₃ -C ₆ H ₅	H ₃ C	5	92	133-135	136-137 [35]

 Table 2
 Synthesis of arylidene malononitrile and ethyl-3-aryl-2-cyanoacrylate derivatives

able 2	(continued)					
13	4-Br-C ₆ H ₅	Br	2	97	155-157	156-158 [35]
14	4-F-C ₆ H ₅	F CN CN	1	95	120-122	122-124 [35]
15	4-SCH3-C6H5	H ₃ CS	5	88	152-154	155-157 [35]
16	2-Furyl	€ CN CN	6	90	69-71	68-69 [54]
17	2-Thionyl	S CN	9	87	99-101	102-104 [55]
18	N-Methyl-pyrrole-2	H ₃ C N CN	7	90	156-158	New product
19	C ₆ H ₅	CN CO2Et	12	77	46-48	49-51 [52]
20	C ₆ H ₅	CI CN CN	10	91	88-90	89-90 [52]
21	C ₆ H ₅	O ₂ N CO ₂ Et	15	90	166-168	169-170 [52]
22	C ₆ H ₅	O ₂ N CN CN	15	93	132-133	132-134 [52]
23	C ₆ H ₅	CO ₂ Et	10	88	98-100	97 [52]
24	C ₆ H ₅	H ₃ CO CN	22	86	75-77	79-81[52]

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*Yields refer to isolated products



Fig. 10 Recycling catalyst using external magnet



Fig. 11 Reusability curves for preparation of arylidene malononitrile derivative (Table 2, entry 4)

Entry	Catalyst [Ref.]	Amount of catalyst (mg)	Condition	Time (min)	Yield (%)	Product
1	Fe ₃ O ₄ @SiO ₂ @ CuO–Fe ₂ O ₃ [34]	30	H ₂ O/reflux	7	91	
2	Fe ₃ O ₄ @SiO ₂ -3N [35]	50	Toluene/75 °C	20	90	
3	Ni NPs [36]	10	S.F.	45	95	
4	[TBA][Leu] [37]	9	H ₂ O/50 °C	60	97	
5	Taurine [38]	25	H ₂ O/reflux	7	98	
6	MNPs–Guanidine [52]	5	PEG/H ₂ O	150	96	
7	Melamine [53]	10	S.F. R.T	15	90	
8	This work	5	H ₂ O/80 °C	1	98	

Table 3 Comparison between some catalysts and $\gamma\mbox{-}Fe_2O_3@SiO_2@[Bis-APTES]Cl_2~NPs$ in the mentioned reaction



Scheme 3 Proposed mechanism for the mentioned reaction in presence of $\gamma\text{-}Fe_2O_3@SiO_2@[Bis-APTES]Cl_2~NPs$

interaction of the catalyst, a molecule of water is eliminated from intermediate **I**, leading to the corresponding product (Scheme 3).

Conclusions

Compounds containing triethoxysilane moiety have been used for many years as linkers to attach organic compounds to mineral supports. We used this reagent as both the cationic part and linker to prepare γ -Fe₂O₃@SiO₂@[Bis-APTES]Cl₂ NPs by immobilization of this reagent on the surface of γ -Fe₂O₃@SiO₂ NPs. After characterization using various techniques, the prepared compound was applied as a catalyst in synthesis of arylidene malononitrile and ethyl-3-aryl-2-cyanoacrylate derivatives. This reaction was catalyzed well in the presence of this new magnetic bis-dicationic reagent to give the desired target molecules. The results also confirmed the high efficiency and considerable reusability of the prepared catalyst is not a hygroscopic material, it is very suitable for use and storage in humid climates.

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