Nano-Fe₃O₄ Encapsulated-Silica Particles Bearing 3-Aminopropyl Group as a Magnetically Separable Catalyst for Efficient Knoevenagel Condensation of Aromatic Aldehydes with Active Methylene Compounds

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Knoevenagel condensation of aromatic aldehydes with active methylene compounds such as malononitrile, ethylcyanoacetate, benzimidazol-2-acetonitrile and benzothiazole-2-acetonitrile proceeded very smoothly, catalyzed by nano-Fe₃O₄ encapsulated-silica particles supported primary amine. Both reaction time and yield are satisfying. The advantages of this catalyst are ease of preparation, non-toxicity, low cost, ease of handling and recyclability.

Keywords magnetic nanoparticle, Knoevenagel condensation, recyclability, magnetic separation

Introduction

The Knoevenagel reaction involves the condensation of aldehydes with a C-H acidic methylene group activated by one or two electron-withdrawing group, such as nitrile, acyl, and nitro.^[1-3] It has been used for the synthesis of important intermediates or products for cosmetics, perfumes, pharmaceuticals, calcium antagonists and functional polymers.^[4-7] Traditionally, Knoevenagel condensation is performed under homogeneous conditions in the presence of bases or acids, such as primary or secondary amines and salts.^[8,9] Using these catalysts, however, has numerous drawbacks such as the use of toxic solvents, long reaction time and in some reactions the catalysts are not efficient and cannot be reused. Recently, ionic liquids (ILs) have become of growing interest due to their unique chemical and physical properties of nonvolatility, nonflammability, thermal stability, and controlled miscibility. Consequently, many kinds of ionic liquids have been used as solvents and catalysts for Knoevenagel condensation.^[10-12] Our group also synthesized several ionic liquids to catalyze Knoevenagel condensation reaction with wonderful effects.^[13-16] Although the ability of ILs has been demonstrated successfully in many reactions, the chemical industry still prefers to use heterogeneous catalyst system due to its ease of handling and regenerability.

In recent years, many efforts have been made to prepare heterogeneous catalysts based on solid materials. Literature survey reports various heterogeneous catalysts, such as zeolite catalyst,^[17] Ni-SiO₂,^[18] fly ash supported calcium oxide,^[19] porous polybenzimidazoles,^[20] Carbon Nitride materials,^[21] polycarbosilanesupported titanium(IV) catalyst,^[22] silica gel or mesoporous SBA-15 functionalized with imidazolium or pyridinium based ionic liquids,^[23,24] and different types of amine immobilized catalysts based on polyacrylamide or silica gel.^[25-27] Immobilization of the organocatalysts to insoluble materials allows an easy separation by filtration, which is a conventional way to make catalysts recovery and the work-up procedure simple. However, many heterogeneous catalysts tend to need harsh conditions to prepare.

Nowadays, magnetic nanoparticles (MNPs) have appeared as a new kind of catalyst support because of their good stability, easy synthesis and functionalization, high surface area, facile separation by magnetic forces, low toxicity and cost.^[28] MNP catalysts can be recovered by an external magnetic field and their catalytic efficiency remains after repeated reactions. However, ultrafine magnetic nanoparticles always tend to undergo agglomeration due to the large surface area-to-volume ratio and the magnetic dipole-dipole attractions between particles. It has been demonstrated that the formation of a passive coating of inert materials such as silica on the surfaces of iron oxide nanoparticles could help prevent their aggregation in liquid and improve their chemical stability.^[29,30]

Driven by the unique properties of magnetic nanoparticles and the interest in the preparation and use

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of solid catalysts, herein, we report a novel silica-coated Fe_3O_4 nanoparticle bearing 3-aminopropyl group and its application as a highly efficient and magnetically recoverable catalyst for Knoevenagel condensation between aromatic aldehydes and active methylene compounds in water under mild conditions. The experiments result in high yields. The water stable catalyst can be easily recycled from the reaction system using external magnet and can be reused several times without loss of activity, which provides a green route for Knoevenagel reactions.

Experimental

Reagents

All aldehydes, active methylene compounds, (3-aminopropyl)triethoxysilane, tetraethyl orathosilicate (TEOS), FeCl₂•4H₂O, FeCl₃•6H₂O, NH₄OH solution (25%) and the other reagents used were analytical grade and employed without further purification. Water was deionized.

Apparatus and instruments

¹H NMR and ¹³C NMR spectra were recorded on a Bruker 400 MHz spectrometer. FT-IR spectra were registered with a Nicolet 5700 Fourier infrared spectrophotometer. Magnetization curves were performed by using a SQUID magnetometer. X-ray diffraction (XRD) was detected by Bruker D8 X-ray diffractometer, transmission electron microscope (TEM) was examined by Tecnai G2 F20 transmission electron microscope. Thermogravimetric analysis (TGA) was examined by SDT Q600 simultaneous thermal analyzer.

Synthesis of the catalyst

The magnetic nanoparticle supported catalyst was prepared following the procedure shown in Scheme 1.

Scheme 1 Synthesis of the magnetic nanoparticle supported catalyst



Synthesis of silica-coated Fe₃O₄ nanoparticles (SiO₂@Fe₃O₄)

 Fe_3O_4 was prepared via a coprecipitation method according to the procedures reported in the literature.^[31] $FeCl_3 \cdot 6H_2O$ (11.0 g) and $FeCl_2 \cdot 4H_2O$ (4.0 g) were dissolved in 250 mL deionized water under nitrogen with mechanical stirring at 85 °C. A solution of concentrated aqueous ammonia (10 mL, 25 wt%) was added to the solution in a drop-wise manner using a dropping funnel. After continuous stirring for 4 h, the magnetite precipitates were washed using deionized water. The black precipitate (Fe₃O₄) was collected by a permanent magnet. Sonicating a dispersion of the above black precipitate (1.0 g) with ethanol (50 mL) for 30 min at room temperature, then conc. NH₃•H₂O (6 mL) and TEOS (2.0 mL) was added successively. After mechanical stirring for 24 h, the black precipitate (SiO₂@Fe₃O₄) was collected using a permanent magnet, followed by washing with ethanol several times and drying in a vacuum.

Procedure for the synthesis of AP-SiO₂@Fe₃O₄

1.0 g of SiO₂@Fe₃O₄ was dispersed in 50 mL ethanol by sonication for 1 h. 2.0 g of (3-aminopropyl)triethoxysilane was then added, and the reaction mixture was refluxed for 2 d under nitrogen. After cooling to room temperature, the catalyst AP-SiO₂@Fe₃O₄ was collected by a permanent magnet and rinsed with ethanol, then dried under vacuum. The loading amount of the 3-aminopropyl group on SiO₂@Fe₃O₄ was determined to be 0.64 mmol•g⁻¹ by elemental analysis.

General procedure for Knoevenagel condensation

A mixture of aldehyde (1 mmol), active methylene compound (1 mmol) and catalyst in water (2 mL) was stirred at room temperature. The reaction progress was monitored by TLC. After completion of the reaction, the catalyst was collected by a permanent magnet and washed with ethyl acetate (10 mL \times 3). The reaction mixture was extracted three times with ethyl acetate. The combined organic phases were concentrated and purified by column chromatography (petroleum etherethyl acetate). All of the products generated in this way were characterized by comparison of their spectral (¹H NMR, ¹³C NMR) and melting point data with those of the authentic samples.

Results and Discussion

Characterization of the catalyst

The magnetic properties of the AP-SiO₂@Fe₃O₄ and SiO₂@Fe₃O₄ were investigated at room temperature and up to external field of 20 kOe. As shown in Figure 1, the hysteresis loop for the samples was completely reversible, showing that the nanoparticles exhibit super-paramagnetic characteristics. The hysteresis loops of them reached saturation up to the maximum applied magnetic field. The saturation magnetization of samples changed from 15 to 6 emu•g⁻¹, due to the functionalization of 3-aminopropyl group. Both particles showed high permeability in magnetization and their magnetization was sufficient for magnetic separation with a conventional magnet.

In order to demonstrate the successful functionaliza-

tion of SiO₂@Fe₃O₄ with 3-aminopropyl group, IR was employed to give detailed investigation of the AP-SiO₂@Fe₃O₄ and SiO₂@Fe₃O₄ (Figure S1). In comparison with SiO₂@Fe₃O₄, Si-OH band (3447 cm⁻¹), Fe-O band (579 cm⁻¹) and Si-O bonds (964 and 1099 cm⁻¹) are the same, demonstrating the existence of SiO₂ components. In addition, at 2949 and 2872 cm⁻¹ (CH₂ stretching vibration), 1211 and 1153 cm⁻¹ (NH₂ stretching vibration) the new bands are observed, indicating the definite graft of 3-aminopropyl group.



Figure 1 Magnetic curves of SiO_2@Fe_3O_4 and AP-SiO_2@ Fe_3O_4.

The crystalline structure of SiO₂@MNP was characterized by X-ray diffraction (XRD). The diffraction pattern shows characteristic peaks and relative intensity matched well with the standard Fe₃O₄ nanoparticles (JCPDS file No. 19-0629, Figure 2). The broad peak from 2θ =20° to 30° shows the typical properties of amorphous silica shell on the surface of the MNPs.^[32] Moreover, transmission electron microscope (TEM) analysis displays that the particle size of the catalyst AP-SiO₂@Fe₃O₄ is similar to that of blank carrier SiO₂@MNP (Figure S2), with the average size range of 20-30 nm for dark Fe₃O₄ core which is surrounded by a grey silica shell of about 4-6 nm in thickness.



Figure 2 XRD pattern of SiO₂@MNP.

TGA was used to study the thermal stability of $AP-SiO_2@Fe_3O_4$. The TG curve indicates several different mass loss (Figure S3). The first mass loss is

occurred below 150 °C, which is due to the loss of adsorbed solvent or trapped water from the catalyst. A mass loss of approximately 20% weight is seen between 150 and 500 °C, which is the loss of 3-aminopropyl group. What's more, the DTG curve shows that the decomposition of the organic structure mainly occurred from 250 to 500 °C, which is related to main weight loss of 17.5%. The peak in the DTG curve shows that the fastest loss of the 3-aminopropyl group occurred at 270 °C. Therefore, the catalyst is stable around or below 200 °C.

Optimization of the Knoevenagel reaction conditions

To optimize the reaction conditions, the condensation of benzaldehvde and ethvl cvanoacetate was used as a model reaction as depicted in Table 1. Initially, the reaction was carried out without catalyst using benzaldehyde (1 mmol) and ethyl cyanoacetate (1 mmol) in H₂O (2 mL) at room temperature. The reaction yield was 42% after 1.5 h. Then the reaction was carried out with various amounts of catalyst from 1 to 6 mol% in 1.5 h. As can be seen in Table 1 (Entries 2-6), there was a sharp increase in the yield from 76% to 90% when the catalyst loading increased from 1 to 5 mol%. When the amount of catalyst was increased from 5 to 6 mol%, no further increase in yield was observed. Therefore, a dosage of 5 mol% catalyst was selected for all subsequent reactions. Then the influence of solvent on the Knoevenagel condensation catalyzed by AP-SiO₂(a)Fe₃O₄ was investigated (Entries 8–13, Table 1). The reaction proceeded smoothly in the absence of

Table 1 Optimization of catalyst/organic solvent in Knoevena-
gel condensation reaction a

	CHO C	r. t.	ν + H ₂ Ο Et
Entry	Solvent	Catalyst ^b /mol%	Yield ^c /%
1	H_2O	0	42
2	H_2O	1	76
3	H_2O	2	79
4	H_2O	3	85
5	H_2O	4	89
6	H_2O	5	90
7	H_2O	6	90
8	—	5	81
9	CH ₃ CN	5	78
10	CHCl ₃	5	82
11	THF	5	81
12	ethanol	5	83
13	acetone	5	80

^{*a*} Reaction conditions: benzaldehyde (1.0 mmol) and ethyl cyanoacetate (1.0 mmol), AP-SiO₂@Fe₃O₄, room temperature, reaction time=90 min. ^{*b*} Based on the loading of 3-aminopropyl group. ^{*c*} Isolated yields.

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solvent with moderate yield. For solvents such as acetonitrile, CHCl₃, THF, ethanol, and acetone, moderate to good yield was obtained. When the reaction underwent in water, the reaction yield was more than 90%. Hence 5% catalyst in water is the most effective combination.

Knoevenagel condensation of various aromatic aldehydes with active methylene compounds

Various functionalized aromatic aldehydes including heterocyclic systems were reacted with active methylene compounds (malononitrile, ethyl cyanacetate) in water catalyzed by AP-SiO₂@Fe₃O₄ (Table 2). The method gave good results in terms of yield as well as time compared with many of the reported methods. Compared to ethyl cyanoacetate, malonontrile was more reactive. The effects of substituents at the aromatic ring on the Knoevenagel reaction were studied. The electronwithdrawing group (such as nitro, chloro group) substituted aromatic aldehydes with active methylene compounds converted smoothly to the corresponding products in high yields (Entries 2-4, 9-11, Table 2). Electron-donating group (such as methoxyl group) substituted aromatic aldehydes underwent Knoevenagel condensation smoothly and in good yield (Entries 5-7, 12-14, Table 2). In addition, Knoevenagel condensation of hetero aromatic aldehydes such as 2-thenal-

 Table 2
 Knoevenagel condensation reaction of active methylene compounds with functionalized aromatic aldehydes^a

 $Ar \stackrel{O}{\longrightarrow}_{H} + \begin{pmatrix} R \\ CN \\ Water, r.t. \end{pmatrix} Ar \stackrel{R}{\longrightarrow}_{CN} R$

Enter	۸r	R	Time/	Yield/	m.p./	Reported m.p./
Епиу	AI		min	%	°C	°C
1	C_6H_5	CN	60	93	79-81	80-82 ^[33]
2	$3-NO_2C_6H_4$	CN	30	96	103-104	$102 - 103^{[34]}$
3	$2-ClC_6H_4$	CN	30	94	92-93	92-94 ^[35]
4	$4-NO_2C_6H_4$	CN	20	98	158-160	159-160 ^[36]
5	2-OCH ₃ C ₆ H ₄	CN	60	92	79-80	79-80 ^[35]
6	3-OCH ₃ C ₆ H ₄	CN	60	95	105-107	$102 - 104^{[35]}$
7	4-OCH ₃ C ₆ H ₄	CN	60	94	113-115	115 ^[1]
8	C ₆ H ₅ C	COOEt	90	90	49-50	47-48[1]
9	3-NO ₂ C ₆ H ₄ (COOEt	60	94	130-131	132-134 ^[37]
10	$2-ClC_6H_4$ (COOEt	60	96	52-53	54-55 ^[38]
11	$4 - NO_2C_6H_4$ (COOEt	45	96	79-80	80-81[36]
12	2-OCH ₃ C ₆ H ₄ C	COOEt	90	86	75-76	72-74 ^[35]
13	3-OCH ₃ C ₆ H ₄ C	COOEt	90	88	53-54	52-54 ^[35]
14	4-OCH ₃ C ₆ H ₄ C	COOEt	90	83	79-81	80-81[39]
15	2-thienyl	CN	120	89	95-96	97-98 ^[40]
16	2-thienvl (COOEt	120	81	88-90	$94 - 98^{[41]}$

^{*a*} Reaction conditions: benzaldehyde (1.0 mmol) and ethyl cyanoacetate (1.0 mmol), AP-SiO₂@Fe₃O₄ (5 mol%), water (2 mL), room temperature. dehyde with active methylene compounds also underwent favourably (Entries 15, 16, Table 2).

Encouraged by the results above, we continued to study the reaction of aromatic aldehydes with complex active methylene compounds, such as benzimidazol-2-acetonitrile, benzothiazole-2-acetonitrile. The reaction smoothly proceeded to afford the corresponding products with moderate to good yield. From Table 2 and Table 3, we found that the acidity of methylene was the key factor influencing the reaction (Entries 1, 8, Table 2, Entries 1, 4, Table 3). Especially, the acidity of malononitrile methylene is apparently stronger than others and results in good effect.

 Table 3
 Knoevenagel condensation reaction of other active methylene compounds with functionalized aromatic aldehydes^a



^{*a*} Reaction conditions: benzaldehyde (1.0 mmol) and ethyl cyanoacetate (1.0 mmol), AP-SiO₂@Fe₃O₄ (5 mol%), water (2 mL), room temperature.

83

230-232

Recyclability studies

4-OCH₃ NH

4

6

Considering that the key feature of our catalyst was magnetic response, we investigated the reusability and the recycling use of the catalyst by carrying out repeated runs on the same batch of the used magnetic catalyst in Knoevenagel reaction of benzaldehyde and ethyl cyanoacetate. After each run, the catalyst can be easily collected by a magnet (Figure S4). The recovered catalyst was used directly for the next run after simply washing with ethyl acetate and removing the residue solvent under vacuum. The recovered catalyst still maintained similar activity after 4 cycles (Figure 3).

To demonstrate the stability of AP-SiO₂@Fe₃O₄, the FT-IR spectra of fresh catalyst and reused catalyst (5 times) were provided (Figure S5). No significant change in the catalyst occurred even after five times of reuse. TEM images (Figure S2b vs. S2c), also showed that the catalyst still maintained its nanostructure after repeated reuse. These observations suggested that the catalyst was perfectly stable during the Knoevenagel reaction and was readily recyclable from the reaction system.

 $218 - 220^{[45]}$







Figure 3 Reuse of catalyst for Knoevenagel condensation between benzaldehyde and ethyl cyanoacetate within 2 h.

Proposed mechanism

We proposed the mechanism reported in Scheme 2. The immobilized amino group extracts a proton from the active methylene compound, while the silanol group promotes the nucleophilic addition on the carbonyl compound via a hydrogen bond. The carbanion of active methylene attacks the carbocation to form the aldol intermediate. The aldol intermediate dehydrates and obtains the final product. The silica oxygen regenerates the amino function through hydrogen bonds.

Conclusions

AP-SiO₂@Fe₃O₄ is a good recyclable catalyst for the Knoevenagel condensation between active methylene compounds and aromatic aldehydes in water at room temperature. Compared with the reported methods, this method offers marked improvements in terms of simplicity, decreased reaction time, general applicability, low cost and no need for hazardous organic solvents and toxic catalysts. Thus, it provides a better and practical alternative to existing procedures.

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