ORIGINAL PAPER



Application of structurally enhanced magnetite cored polyamidoamine dendrimer for knoevenagel condensation

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Received: 5 May 2020 / Accepted: 18 September 2020 © Iranian Chemical Society 2020

Abstract

In this paper, the synthesis of magnetic cored amino group terminated dendrimer ($Fe_3O_4@SiO_2@PAMAM-G_2$) through covalent bonding was described. This catalyst was characterized by FT-IR, XRD, FE-SEM, TEM, and TGA detection methods. Next, the catalytic activity of this catalyst was investigated for the Knoevenagel condensation reaction of aldehydes with malononitrile under mild and solvent-free conditions. The $Fe_3O_4@SiO_2@PAMAM-G_2$ could be separated from the reaction mixture by an external magnet and reused five times.

Keywords Modified polyamidoamine dendrimer · Silica-coated magnetic nanoparticles · Knoevenagel condensation · Green chemistry

Introduction

Much attention has already been paid to the development of heterogenizing homogeneous catalysts to merging the benefits of homogeneous and heterogeneous catalysts [1]. Heterogenized catalysts can be readily dissociated from the solution reaction, but they have a difficulty of low reactivity and selectivity toward their homogeneous counterparts. For solving this problem, nanoparticles have been used because they possess a high specific surface area and can be easily controlled in the reaction mixture [2-4]. Recently, magnetic Fe₃O₄ nanoparticles have been used to make core-shell particles, and the surface of magnetic nanoparticles were protected by various organic and inorganic materials such as silica, polymers, biomolecules, and metals [5–7]. Among them, silica was considered as one of the best materials for coating Fe_3O_4 magnetic nanoparticles, due to its unique properties such as chemical diversity in surface modification, stability, and biocompatibility [8, 9]. The main advantages of using silica are; (i) to prevent the oxidation of Fe_3O_4 magnetic nanoparticles, and (ii) for linking to different functional groups and surface modification.

Dendrimers are monodispersed macromolecules including an initial core, radial branches with end-group and interior spaces in branches [10, 11]. The core, type, the number of branches, and end-groups can be changed, so their chemical properties and structure can be controlled. The stepwise growth of the dendrimer, will provide more active sites for conjugation of many biological molecules such as enzymes, proteins, genes, and drugs because the number of surface amino groups will be doubled. In this regards, the polyamidoamine (PAMAM) dendrimer, a highly branched dendritic macromolecule, possesses a unique surface with amine chain ends, and the number of surface groups can be precisely controlled by choosing the appropriate synthetic generation. These excellent properties of the dendrimer have led to the use of that in the synthesis of polyamidoamine (PAMAM) dendrimer functionalized magnetic nanoparticles. Hence, magnetic nanoparticles coated with the PAMAM dendrimer have attracted a lot of attention due to their many functional groups and applications [12–21].

The Knoevenagel condensation is a powerful method for the synthesis of α , β -unsaturated compounds. This condensation has attracted much attention due to its economical, cleanliness, and efficiency in the synthesis of different organic material. There are diverse synthetic strategies for the Knoevenagel reaction like utilization of various catalysts such as Rare-earth (RE) exchanged NaY zeolite [RE(72%)NaY] [22], cetyltrimethyl ammonium bromide (CTMAB) [23], MgO/ZrO₂ [24], Zn²⁺ exchanged Hß (Znß)

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[25], poly(vinyl chloride) supported tetraethylenepentamine (PVC-TEPA) [26], Na₂S/Al₂O₃ [27], magnesium fluoride (MgF₂) [28], Ni–SiO₂ [29], Ceria-zirconia (C/Z-30/70) [30], La₂O₃–MgO/KOH [31], guanidine supported on magnetic nanoparticles Fe₃O₄ (Fe₃O₄@guanidine) [32], BEA or TS-1 or CuBTC or FeBTC [33], gallium chloride (GaCl₃) [34], polyvinyl amine coated Fe₃O₄@SiO₂ (Fe₃O₄@SiO₂-PVAm) [35], Fe₃O₄@UiO-66-NH₂ [36], N-(3-trimethoxysilylpropyl) diethylenetriamine) coated (Fe₃O₄@SiO₂-3N) [37], Fe₃O₄@ P4VP@ZIF-8 [38], magnetic Fe₃O₄@SiO₂@Ni-Zn-Fe layered double hydroxide (LDH) (Fe₃O₄@SiO₂@Ni-Zn-Fe LDH) [39], and fiber (PAN_PF-3) [40]. Although most of the reported methods have practical synthetic procedures, they endure some disadvantages such as using expensive organic solvents, harsh and hazardous reaction conditions, long reaction times, unacceptable yields, and tedious workup procedure. Therefore, a simple method which utilizes mild and effective catalysts under green conditions is still a favorite topic.

Based on our research interests [41, 42], herein, we report an efficient synthesis of 2-benzylidenemalononitriles in the presence of $Fe_3O_4@SiO_2@PAMAM-G_2$ at 50 °C (Scheme 1).

Experimental

Materials and instruments

The chemical materials and solvents were purchased from Merck and Aldrich Chemical Companies and were employed without further purification. The IR spectra were recorded on a Bruker IFS-88 instrument using KBr disks in the region of 400-4000 cm⁻¹. The ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker AC-300 spectrometer using tetramethylsilan as an internal standard. X-ray powder diffraction (XRD) data were collected on an XD-3A diffractometer using Cu Ka radiation, and with the scanning rate set to 3° min⁻¹. Thermogravimetric analyses were performed on the TGA-50 Shimadzu thermal analyzer in the flowing air atmosphere with the heating rate of 10 °C min⁻¹ in the temperature region of 50-650 °C. The transmission electron microscopy (TEM) analysis was performed with a nitrogen flow using a Zeiss EM-900 instrument at an acceleration voltage of 80 kV. To study the morphology and distribution of particles, the synthesized catalyst was used from a field emission scanning electron microscopy (FE-SEM) Hitachi model S-4160.

Preparation of the magnetic cored amino group terminated dendrimer (Fe₃O₄@SiO₂@PAMAM-G₂)

The synthesis of the $Fe_3O_4@SiO_2@PAMAM-G_2$ was accomplished according to the procedure described in detail in the literature [14]. However, a retread on the main aspects of the synthesis route would be beneficial to clearly illustrate the underneath.

Preparation of nanomagnetic Fe₃O₄

The precursors of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ with a molar ratio of 1: 2 were dissolved in 20 ml of deionized water. The pH of the solution was increased to 10 by adding a dropwise 5 ml of NH₃. The resulting solution is stirred vigorously at room temperature for 1 h. The final nanoparticles were extracted by an external magnetic field. Separated nanoparticles were washed several times with ethanol, deionized water, and then were dried in a vacuum oven at 60° C for 8 h.

Preparation of silica-coated nanomagnetic (Fe₃O₄@SiO₂)

After ultra-sonication of iron nanoparticles for 30 min, a 5 ml of tetraethyoxysilane (TEOS) added to the Fe_3O_4 solution. The solution is stirred vigorously at room temperature for 5 h. After completing the reaction, the nanoparticles were collected by an external magnet field. The product was washed three times with deionized water, ethanol, and then dried in a vacuum oven at 60 °C for 12 h.

Preparation of the amino functionalized silica-coated magnetic nanoparticles ($Fe_3O_4@SiO_2@Pr-NH_2$)

1 g of silica-coated nanoparticles was dispersed in 20 ml of dry toluene. After the ultra-sonication of the solution, 0.25 ml (3-aminopropyl) tri-methoxysilane (APTES) and 5 drops of glacial acetic acid were added gradually under mechanical stirring. The solution was refluxed at 60 °C for three days. After cooling to room temperature, the magnetic nanoparticles were separated by an external magnetic field.



Finally, the nanoparticles were washed three times with the dry methanol and dried in the oven for 24 h.

Preparation of magnetic cored esteric group terminated dendrimer

1 g of amino-functionalized magnetic nanoparticle (Fe₃O₄@ SiO₂@Pr-NH₂) was dispersed in a 15 ml of anhydrous methanol and was sonicated for 30 min. Then, a 1.5 ml of methyl acrylate was added and the mixture was heated at 60 °C for 3 days. Afterward, the mixture was cooled down to room temperature. The particles were separated by applying an external magnetic field and washed several times with the dry methanol and dried under a vacuum for 24 h. The prepared product was denoted as (Fe₃O₄@SiO₂@PAMAM-G_{0.5}). Similarly, the Fe₃O₄@SiO₂@PAMAM-G₁ using the same procedure.

 $Fe_3O_4@SiO_2@PAMAM-G_{1.5}$: 1 g of $Fe_3O_4@SiO_2@PAMAM-G_1$ was dispersed in a 30 ml of the anhydrous methanol and a 5 ml of the methyl acrylate.

Preparation of magnetic cored amino group terminated dendrimer

1 g of the magnetic cored esteric group terminated dendrimer ($Fe_3O_4@SiO_2@PAMAM-G_{0.5}$) was dispersed in 20 ml of anhydrous methanol and was sonicated for 30 min. Then, a 2.5 ml of the ethylene diamine was added and the mixture was heated at 60 °C for 3 days. Afterward, the mixture was cooled down to room temperature. The particles were separated by applying an external magnetic field and washed several times with the anhydrous methanol and dried under a vacuum for 24 h. The prepared product was denoted as ($Fe_3O_4@SiO_2@PAMAM-G_1$). Similarly, the $Fe_3O_4@$ $SiO_2@PAMAM-G_2$ was prepared from the $Fe_3O_4@SiO_2@$ PAMAM-G_{1.5} using the same procedure.

 $Fe_3O_4@SiO_2@PAMAM-G_2$: 1 g of the $Fe_3O_4@SiO_2@PAMAM-G_{1.5}$ was dispersed in a 40 ml of the anhydrous methanol and a 5 ml of the ethylene diamine.

General procedure for Knoevenagel condensation

A mixture of the aldehyde (1 mmol), malononitrile (1.2 mmol), and $Fe_3O_4@SiO_2@PAMAM-G_2$ (6 mg), was added to a bottom flask fitted with a reflux condenser (5 drops of ethanol was used as solvent for solid aldehydes). Then, the mixture was mechanically stirred at 50 °C in an oil bath under solvent-free condition. The reaction progress was monitored by the TLC and after the completion of this reaction, the catalyst was separated by an external magnet. The resulting solid product was poured onto ice and was isolated

by filtration and recrystallized from the ethanol (3 ml) to get 2-benzylidene malononitrile derivatives (**3a-k**).

2-Benzylidene malononitrile (3a) ¹H NMR (400 MHz, DMSO-d₆): δ 7.90 (d, 2H, J=7.0 Hz), δ 7.80 (s, 1H), δ 7.55 (m, 3H); ¹³C NMR (100 MHz, DMSO-d₆) δ (ppm): 82.54, 112.45, 113.64, 116.44, 124.33, 130.64, 130.74, 134.50, 159.98; IR (KBr, cm⁻¹): 2219, 1614, 1434, 750, 673.

2-(3-Nitrobenzylidene) malononitrile (3b) ¹H NMR (400 MHz, DMSO-d₆): δ 8.66 (s, 1H), δ 8.49 (d, 1H, J=8.0 Hz), δ 7.90 (s, 1H), δ 7.84 (d, 1H, J=8.0 Hz); δ 7.90 (s, 1H), δ 7.84 (d, 1H, J=8.0 Hz); ¹³C NMR (100 MHz, DMSO-d₆) δ (ppm): 81.55, 113.61, 114.78, 116.53, 122.26, 122.53, 131.08, 132.86, 158.30, 162.10; IR (KBr, cm⁻¹): 2225, 1593, 1525, 1350, 815, 669.

2-(4-Nitrobenzylidene) malononitrile (3c) ¹H NMR (400 MHz, DMSO-d₆): δ 8.40 (d, 2H, J = 8.8 Hz), δ 8.09 (d, 2H, J = 8.8 Hz), δ 7.90 (s, 1H); ¹³C NMR (100 MHz, DMSO-d₆) δ (ppm): 87.45, 111.58, 112.60, 116.38, 131.35, 135.78, 150.35, 156.95;; IR (KBr, cm⁻¹): 2225, 1577, 1514, 1344, 840, 678.

Results and discussion

Synthesis of catalyst

The synthesis of the Fe₃O₄@SiO₂@PAMAM-G₂ used in the present study is reported in the previous work [14]. In this research, for the first time, the catalytic efficiency of the Fe₃O₄@SiO₂@PAMAM-G₂ in the organic transformation is investigated. To the best of our knowledge, there are not reports on Fe₃O₄@SiO₂@PAMAM-G₂ in organic reaction. This is the first report of the catalytic application of the Fe₃O₄@SiO₂@PAMAM-G₂ in an organic transformation. Therefore, the first catalytic application of Fe₃O₄@SiO₂@ PAMAM-G₂ in knoevenagel condensation is the novelty of the present work.

The divergent synthesis of the PAMAM- G_2 dendrimer on the silica coated amagnetic iron oxide nanoparticle is discussed. Initially, the Fe3O4 was prepared by the conventional coprecipitation method, subsequently the controlled silica coating was carried out on the Fe3O4 nanoparticle for a better protection and achieving the spherical morphology with the sustainable magnetic retentivity. It was further functionalized with the APTES to develop. The amino silanated material was labeled as the Fe₃O₄@SiO₂@Pr-NH₂ nanohybrid material with propylamine surface groups. Subsequently, the magnetic cored amino group terminated dendrimer (Fe₃O₄@SiO₂@PAMAM-G₂) was prepared by the consecutive repeating the Michael addition and amidation reactions (Scheme 2).

Catalyst characterizations

In the IR spectrum of Fe_3O_4 magnetic nanoparticles, peaks at 561, 1622, and 3418 cm⁻¹ corresponding to Fe–O and hydroxyl groups on the surface of Fe_3O_4 (Fig. 1A). The peak around 1094 cm⁻¹ in Fig. 1B is assigned to the Si–O



bond. In Fig. 1C, the peaks 1558 and 2932 cm⁻¹ correspond to the methylene -CH₂ group, and the C-H chain and the peak at about 1104 cm⁻¹ belong to the Si–O-Si bond. Also, in the IR spectrum of the Fe₃O₄@SiO₂@PAMAM-G_{0.5} (G_{0.5}) and Fe₃O₄@SiO₂@PAMAM-G_{1.5} (G_{1.5}), bands at 1737 and 1732 cm⁻¹, are related to the carbonyl group of esters. In generations Fe₃O₄@SiO₂@PAMAM-G₁ (G₁) and Fe₃O₄@SiO₂@PAMAM-G₂ (G₂), this peak (C=O) is removed. The characteristic band 1625 cm⁻¹ is



Fig. 1 FT-IR spectra of (**A**) Fe₃O₄, (**B**) Fe₃O₄@SiO₂, and (**C**) Fe₃O₄@SiO₂@Pr-NH₂ in the left; Fe₃O₄@SiO₂@ PAMAM-G2 in different generations from $G_{0.5}$ - G_2 in the right





Fig. 2 XRD spectrum of a Fe_3O_4 , b fresh $Fe_3O_4@SiO_2@PAMAM-G_2$ and c $Fe_3O_4@SiO_2@PAMAM-G_2$ after five cycles

for the group –CO–NH. These results indicated that the Michael addition and amidation reactions were successfully performed, and the PAMAM dendrimer through the covalent bonding was successfully grafted onto magnetic nanoparticles.

The X-ray powder diffraction analyses of nanoparticles were performed to identify the crystal structure. All reflection peaks in the Fe₃O₄@SiO₂@PAMAM-G₂ within the 2θ range 25–65° were recorded (Fig. 2b). The characteristic peaks at $2\theta = 30.1^{\circ}$, 35.4° , 43.1° , 53.4° , 57.0° , and 62.6° were observed, which are in agreement with the XRD peaks of Fe₃O₄ nanoparticles. Also, the X-ray diffraction (XRD) pattern of recycled Fe₃O₄@SiO₂@PAMAM-G₂ is shown in Fig. 2c. To confirm that the Fe_3O_4 is stable, after five runs of recyclability, we compared the XRD of fresh and reused Fe₃O₄@SiO₂@PAMAM-G₂ after five runs with the XRD of standard Fe₃O₄ (Fig. 2a). The results shows XRD of fresh Fe₃O₄@SiO₂@PAMAM-G₂ is similar to XRD of standard Fe₃O₄, and also there is almost no change after five performance run compared to peaks of standard Fe₃O₄, in terms of position and intensity of peaks.

The TEM analysis was used to investigate the morphology, size and distribution of the $Fe_3O_4@SiO_2@PAMAM-G_2$. The TEM image of the catalyst in Fig. 3 clearly shows core–shell structure, with $Fe_3O_4@SiO_2$ as the core and



Fig. 3 a TEM image of Fe₃O₄@SiO₂@PAMAM-G₂. b TEM image of Fe₃O₄@SiO₂@PAMAM-G₂ after five cycles





Fig. 5 TGA analysis of $Fe_3O_4@SiO_2@PAMAM-G_2$

polyamidoamine (PAMAM) dendrimer as the shell. The effect of recycling process on nanoparticle distribution was also investigated via TEM analysis (Fig. 3b). The results revealed that recycling process has not changed the morphology and size of the nanoparticles.

The chemical identity of $Fe_3O_4@SiO_2@PAMAM-G_2$ was confirmed by EDX analysis (Fig. 4). The EDX spectrum shows peaks of elements Fe (24.27%), Si (9.46%), O (41.89%), N (4.09%), and C (20.3%) which is given in Fig. 4 as components of the synthesized $Fe_3O_4@SiO_2@$ PAMAM-G₂.

The thermal stability of magnetic cored amino group terminated dendrimer was evaluated by TGA (Fig. 5). As it is seen in this curve, at the range of 50-700 °C, there are

Table 1Optimization ofReaction Conditions for 3a

Entry	Catalyst (g)	Conditions	Time (min)	Yield ^a (%)
1	Fe ₃ O ₄ @SiO ₂ @PAMAM-G ₂ (0.006 g)	Solvent-free/50 °C	30	95
2	Fe ₃ O ₄ @SiO ₂ @PAMAM-G ₂ (0.006 g)	Water/50 °C	30	40
3	Fe ₃ O ₄ @SiO ₂ @PAMAM-G ₂ (0.006 g)	Toluene/50 °C	30	10
4	Fe ₃ O ₄ @SiO ₂ @PAMAM-G ₂ (0.006 g)	Ethanol/50 °C	30	64
5	Fe ₃ O ₄ @SiO ₂ @PAMAM-G ₂ (0.006 g)	Solvent-free/rt	30	40
6	Fe ₃ O ₄ @SiO ₂ @PAMAM-G ₂ (0.006 g)	Solvent-free/40 °C	30	79
7	Fe ₃ O ₄ @SiO ₂ @PAMAM-G ₂ (0.006 g)	Solvent-free/60 °C	30	95
8	Fe ₃ O ₄ @SiO ₂ @PAMAM-G ₂ (0.005 g)	Solvent-free/50 °C	30	86
9	Fe ₃ O ₄ @SiO ₂ @PAMAM-G ₂ (0.004 g)	Solvent-free/50 °C	30	75
10	Fe ₃ O ₄ @SiO ₂ @PAMAM-G ₂ (0.007 g)	Solvent-free/50 °C	30	93
11	$Fe_3O_4@SiO_2 (0.006 g)$	Solvent-free/50 °C	30	_b
12	_c	Solvent-free/50 °C	30	_b

^aIsolated yield; ^bNo product **3a** observed; ^cThis reaction was carried out in the absence of $Fe_3O_4@SiO_2@PAMAM-G_2$

several decomposition steps for the composition of Fe₃O₄@ SiO₂@PAMAM-G₂. The loss of weight at the temperature of 150 to 570 °C, is related to the decomposition of the PAMAM dendrimer from the Fe₃O₄@SiO₂ surface. At the first decomposition step (at the temperatures under 150 °C), a weight loss of 3.5% can be assigned to the removal of physically adsorbed water and surface hydroxyl groups. A second steady mass loss (about 13 wt%) occurred between 150 and 570 °C possibly attributed to the organic group's decomposition.

Catalytic study

After synthesis and characterization of the magnetic cored amino group terminated dendrimer ($Fe_3O_4@SiO_2@PAMAM-G_2$), its catalytic performance was investigated in reaction condensation between aldehydes with malononitrile. For this purpose, 0.006 g of magnetic nanocatalyst was added to a mixture of benzaldehyde (1 mmol) and malononitrile (1.2 mmol) at 50 °C under solvent-free conditions. Then, the mixture was stirred for an appropriate time in an oil bath, and the reaction was monitored by TLC. After the completion of the reaction, the product was purified (experimental section). In order to obtain the best conditions for our reaction, we optimized the parameters as listed in Table 1. The excellent route was in the presence of 0.006 g of magnetic nanocatalyst under the solvent-free condition at 50 °C (Table 1, entry 1). No product was found in the absence of the catalyst (Table 1, entry 11) which confirms catalyst plays an important role in the reaction progress.

A probable mechanism for the reaction is indicated in Scheme 3. The Knoevenagel condensation is occurred by nucleophilic attack of activated malononitrile to iminium ion to produce the 2-benzylidenemalononitrile [37].

To illustrate the applicability of this reaction, the direct reaction worked well with a variety of aryl aldehydes including those bearing electron-donating and electron-withdrawing groups such as OH, Me, OMe, Cl, $(Me)_2N$, and NO₂, and the desired compounds were obtained in high-to-excellent yields (Table 2). Furthermore, the heteroaromatic and aliphatic aldehyde reacted smoothly with malononitrile in the presence of Fe₃O₄@SiO₂@PAMAM-G₂ (Table 2, entries 12–14). Encouraged by the observations, the condensation was studied using terephthalaldehyde. The bis-substituted derivative was produced in 90% yield, when 2.5 mmol of malononitrile was used (Table 2, entry 15).

Reusability study

The reusability of the $Fe_3O_4@SiO_2@PAMAM-G_2$ was studied in the model reaction under optimized conditions. At the end of the reaction, the catalyst was separated by an external magnetic field and then was washed with ethanol and dried. Results indicated that the recycled nanocatalyst was reused in at least five condensation reaction runs



without significant loss of its catalytic activity as shown in Fig. 6.

Scheme 3 Possible mechanism for the synthesis of benzylidene

malononitrile derivatives in the presence of $Fe_3O_4@SiO_2@$

PAMAM-G₂

Finally, the catalytic performance of $Fe_3O_4@SiO_2@$ PAMAM-G₂ was compared to catalysts previously reported for similar condensation (Table 3). As it can be seen, this catalyst has equal or slightly higher efficiency than other catalysts.

Table 2Catalytic efficiency ofthe magnetic cored amino groupterminated dendrimer (Fe₃O₄@SiO₂@PAMAM-G₂) for thesynthesis of 2-benzylidenemalononitrile derivatives undersolvent-free condition

Entry	Products	Yield ^a (%)	Time (min)	mp (°C)		
				Found	Lit.	
1	CN CN	95	30	80-81	81-82 ²³	
2 ^b	$(3a)$ $O_2N \xrightarrow{CN} CN$	92	30	102–104	101–103 ²⁷	
3 ^b	(3b) CN CN CN	89	30	159–161	161–162 ²⁷	
4	(3c) (3c) MeO	93	30	114–115	113–114 ²⁷	
5	(3d) MeO CN CN	88	20	101–103	102–104 ⁴⁰	
6	(3e) CN CN OMe	83	25	79–80	80-81 ²⁷	
7 ^b	(3f) (C) $(3f)$ (C)	84	25	85–87	84-86 ³²	
8 ^b	(3g) CI CN	90	20	164–166	162–163 ²³	
	(3h)					

Table 2 (continued)

Entry	Products	Yield ^a (%)	Time (min)	mp (°C)		
				Found	Lit.	
9 ^b	HO CN	80	40	147–149	148–150 ⁴⁰	
10	(3i) Me CN	83	50	134–136	137–138 ²⁷	
11 ^b	(3j) (Me) ₂ N CN	85	50	180–182	179–180 ²³	
12	$(3k)$ $(S) \rightarrow CN$ CN	89	20	96–97	95–96 ³⁷	
13	(3I) $(3I)$ (CN)	87	25	83-85	84–86 ⁴⁰	
14	(3m)	82	50	124–125	122–123 ²⁷	
15 ^{b,c}	(3n) CN NC CN CN	90	25	266–268	260–262 ³⁹	
	(30)					

^aIsolated yields; ^b5 drops of ethanol was used; ^cterephthalaldehyde (1 mmol), and malononitrile (2.5 mmol) were used

Conclusions

In conclusion, we have developed a novel, efficient, and green method for synthesis of benzylidene malononitrile derivatives by magnetic $Fe_3O_4@SiO_2@PAMAM-G_2$ which

is confirmed with FT-IR, XRD, FE-SEM, EDS, TGA, and TEM. The benefits of this reaction including; good to excellent yields, decrease reaction times, simple work-up, and reusable for five times without any significant loss of activity.



Fig. 6 Reusability of Fe₃O₄@SiO₂@PAMAM-G₂

Table 3 Comparison of

References

- 1. C.E. Song, S.G. Lee, Chem. Rev. 102, 3495 (2002)
- 2. B. Cornils, W.A. Herrmann, J. Catal. 216, 23 (2003)
- J. Govan, Y.K. Gun'ko, Nanomaterials 4, 222 (2014) 3.
- 4. B. Maleki, M. Chahkandi, R. Tayebee, S. Kahrobaei, H. Alinezhad, S. Hemmati, Appl. Organomet. Chem. 33, e5118 (2019)
- 5. K.Y. Shin, J.Y. Hong, J. Jang, J. Hazard. Mater. 190, 36 (2011)
- 6. L. Zhang, T. Wu, X. Xu, F. Xia, H. Na, Y. Liu, H. Qiu, W. Wang, J. Gao, J. Alloys Compd. 628, 364 (2015)
- 7. B. Maleki, H. Alinezhad, H. Atharifar, R. Tayebee, A.V. Mofrad, Org. Prep. Proced. Int. 51, 301 (2019)
- 8. B. Maleki, H. Eshghi, M. Barghamadi, N. Nasiri, A. Khojastehnezhad, S.S. Ashrafi, O. Pourshiani, Res. Chem. Intermed. 42, 3071 (2016)
- 9. B. Maleki, N. Nasiri, R. Tayebee, A. Khojastehnezhad, H.A. Akhlaghi, RSC Adv. 6, 79128 (2016)
- 10. K. Esumi, Dendrimers for nanoparticle synthesis and dispersion stabilization, in Colloid Chemistry II (Springer, Berlin, Heidelberg, 2003), pp. 31-52

Table 3 Comparison of Methods for the Synthesis of	Entry	Conditions	Time (min)	Yield (%)
benzylidene malononitrile	3 a	Fe ₃ O ₄ @SiO ₂ @PAMAM-G ₂ /Solvent-free/50 °C (Present work)	30	95
derivatives		RE(72%)NaY/CH ₃ CN/rt ²²	720	78
		CTMAB/H ₂ O/rt ²³	90	91
		MgO/ZrO ₂ /Solvent-free/60°C ²⁴	20	93
		Znß/Solvent-free/140°C ²⁵	360	16
		PVC-TEPA/EtOH/reflux ²⁶	60	75
		Na ₂ S/Al ₂ O ₃ /CH ₂ Cl ₂ /reflux ²⁷	20	90
		MgF ₂ /EtOH/rt ²⁸	150	93
		Ni-SiO ₂ /Toluene/reflux ²⁹	900	100
		C/Z-30/70/EtOH/reflux ³⁰	50	82
		Fe ₃ O ₄ @UiO-66-NH ₂ -3/DMF/80°C ³⁶	60	73
		$Fe_3O_4@SiO_2-3N/Water/75^{\circ}C^{37}$	12	93
		Fe ₃ O ₄ @P4VP@ZIF-8/Toluene/23°C ³⁸	120	99
		Fe ₃ O ₄ @SiO ₂ @Ni-Zn-Fe/EtOH/reflux ⁴⁰	90	92
	3d	Fe ₃ O ₄ @SiO ₂ @PAMAM-G ₂ /Solvent-free/50 °C (Present work)	30	93
		CTMAB/H ₂ O/rt ²³	90	88
		MgO/ZrO ₂ /Solvent-free/60°C ²⁴	20	68
		PVC-TEPA/EtOH/reflux ²⁶	60	91
		Na ₂ S/Al ₂ O ₃ /CH ₂ Cl ₂ /reflux ²⁷	10	94
		MgF ₂ /EtOH/rt ²⁸	90	94
		Ni–SiO ₂ /Toluene/reflux ²⁹	900	75
		La ₂ O ₃ -MgO/KOH/Solvent-free/rt ³¹	60	90
		Fe ₃ O ₄ @guanidine/PEG:H ₂ O/rt ³²	300	95
		Fe ₃ O ₄ @SiO ₂ -3N/Toluene/75°C ³⁷	30	88
		Fe ₃ O ₄ @P4VP@ZIF-8/Toluene/23°C ³⁸	120	87
		Fe ₃ O ₄ @SiO ₂ @Ni-Zn-Fe/EtOH/reflux ⁴⁰	90	97

- 11. B. Maleki, S. Sheikh, RSC Adv. 5, 42997 (2015)
- S. Chandra, M.D. Patel, H. Lang, D. Bahadur, J. Power Sources 280, 217 (2015)
- A. Zarei, S. Saedi, F. Seidi, J. Inorg. Organometal. Polym. Mater. 28, 2835 (2018)
- R. Abu-Reziq, H. Alper, D. Wang, M.L. Post, J. Am. Chem. Soc. 128, 5279 (2006)
- B. Maleki, M. Baghayeri, M. Ghanei-Motlagh, F.Z. Zonoz, A. Amiri, F. Hajizadeh, A.R. Hosseinifar, E. Esmaeilnezhad, Measurement 140, 81 (2019)
- F. Adibian, A.R. Pourali, B. Maleki, M. Baghayeri, A. Amiri, Polyhedron 175, 114179 (2020)
- S.H. Wang, X. Shi, M. Van Antwerp, Z. Cao, S.D. Swanson, X. Bi, J.R. Baker Jr., Adv. Funct. Mater. **17**, 3043 (2007)
- M. Tarahomi, H. Alinezhad, B. Maleki, Appl. Organomet. Chem. 33, e5203 (2019)
- H. Alinezhad, A. Amiri, M. Tarahomi, B. Maleki, Talanta 183, 149 (2018)
- M. Baghayeri, H. Alinezhad, M. Tarahomi, M. Fayazi, M. Ghanei-Motlagh, B. Maleki, Appl. Surface Sci 478, 87 (2019)
- M. Baghayeri, H. Alinezhad, M. Fayazi, M. Tarahomi, R. Ghanei-Motlagh, B. Maleki, Electrochim. Acta **312**, 80 (2019)
- 22. T.I. Reddy, R.S. Varma, Tetrahedron Lett. 38, 1721 (1997)
- 23. S. Wang, Z.J. Ren, W.G. Cao, W. Tong, Synth. Commun. **31**, 673 (2001)
- 24. M.B. Gawande, R.V. Jayaram, Catal. Commun. 7, 931 (2006)
- S. Saravanamurugan, M. Palanichamy, M. Hartmann, V. Murugesan, Appl. Catal. A Gen. 298, 8 (2006)
- 26. F. Dong, Y.Q. Li, R.F. Dai, Chin. Chem. Lett. 18, 266 (2007)

- M.M. Heravi, K. Bakhtiari, S. Taheri, H.A. Oskooie, J. Chin. Chem. Soc. 54, 1557 (2007)
- 28. R.M. Kumbhare, M. Sridhar, Catal. Commun. 9, 403 (2008)
- V.R. Pullabhotla, A. Rahman, S.B. Jonnalagadda, Catal. Commun. 10, 365 (2009)
- G. Postole, B. Chowdhury, B. Karmakar, K. Pinki, J. Banerji, A. Auroux, J. Catal. 269, 110 (2010)
- Y. Wei, S. Zhang, S. Yin, C. Zhao, S. Luo, C. Au, Catal. Commun. 12, 1333 (2011)
- 32. A. Rostami, B. Atashkar, H. Gholami, Catal. Commun. **37**, 69 (2013)
- M. Opanasenko, A. Dhakshinamoorthy, M. Shamzhy, P. Nachtigall, M. Horacek, H. Garcia, J. Cejka, Catal. Sci. Technol. 3, 500 (2013)
- 34. L. Muralidhar, C.R. Girija, J. Saud. Chem. Soc. 18, 541 (2014)
- 35. F. Zamani, E. Izadi, Chin. J. Catal. 35, 21 (2014)
- Y. Zhang, T. Dai, F. Zhang, J. Zhang, G. Chu, C. Quan, Chin. J. Catal. 37, 2106 (2016)
- J.B.M. de Resende Filho, G.P. Pires, J.M.G. de Oliveira Ferreira, E.E.S. Teotonio, J.A. Vale, Catal. Lett. 147, 167 (2017)
- Z. Miao, F. Yang, Y. Luan, X. Shu, D. Ramella, J. Solid, State Chem. 256, 27 (2017)
- 39. M. Gilanizadeh, B. Zeynizadeh, New J. Chem. 42, 8553 (2018)
- 40. G. Li, J. Xiao, W. Zhang, Green Chem. 13, 1828 (2011)
- B. Maleki, O. Reiser, E. Esmaeilnezhad, H.J. Choi, Polyhedron 162, 129 (2019)
- H. Alinezhad, M. Tarahomi, B. Maleki, A. Amiri, Appl. Organomet. Chem. 33, 4661 (2019)