Received: 13 March 2017 | Revised: 24 April 2017 | Accepted: 6 May 2017
DOI: 10.1002/aoc.3905

FULL PAPER

WILEY Applied Organometallic Chemistry

Fe_3O_4-Methylene diphenyl diisocyanate-guanidine (Fe_3O_4–4, 4′-MDI-Gn): A novel superparamagnetic powerful basic and recyclable nanocatalyst as an efficient heterogeneous catalyst for the Knoevenagel condensation and tandem Knoevenagel-Michael-cyclocondensation reactions

Razieh Maleki | Nadiya Koukabi | Eskandar Kolvari

Department of Chemistry, Semnan University, P.O. Box 35195-363, Semnan, Iran

Correspondence
Eskandar Kolvari, Department of Chemistry, Semnan University, P.O. Box 35195-363, Semnan, Iran.
Email: kolvari@semnan.ac.ir

In this paper, guanidine groups (Gn) supported on modified magnetic nanoparticles (Fe_3O_4–4,4′-MDI) were synthesized for the first time. The catalyst synthesized was characterized by various techniques such as SEM (Scanning Electron Microscopy), TEM (Transmission electron microscopy), XRD (X-ray Diffraction), TGA (Thermogravimetric ananlysis), EDS (Energy-dispersive X-ray spectroscopy) and VSM (vibrating sample magnetometer). The catalyst activity of modified MNPs–MDI-Gn, as powerful basic nanocatalyst, was probed through the Knoevenagel and Tandem Knoevenagel–Michael-cyclocondensation reactions. Conversion was high under optimal conditions, and reaction time was remarkably shortened. This nanocatalyst could simply be separated and recovered from the reaction mixture by simple magnetic decantation and reused many times without significant loss of its catalytic activity. Also, the nanocatalyst could be recycled for at least seven (Knoevenagel condensation) and six (Knoevenagel and Tandem Knoevenagel–Michael-cyclocondensation) additional cycles after they were separated by magnetic decantation and, washed with ethanol, air-dried, and immediately reused.

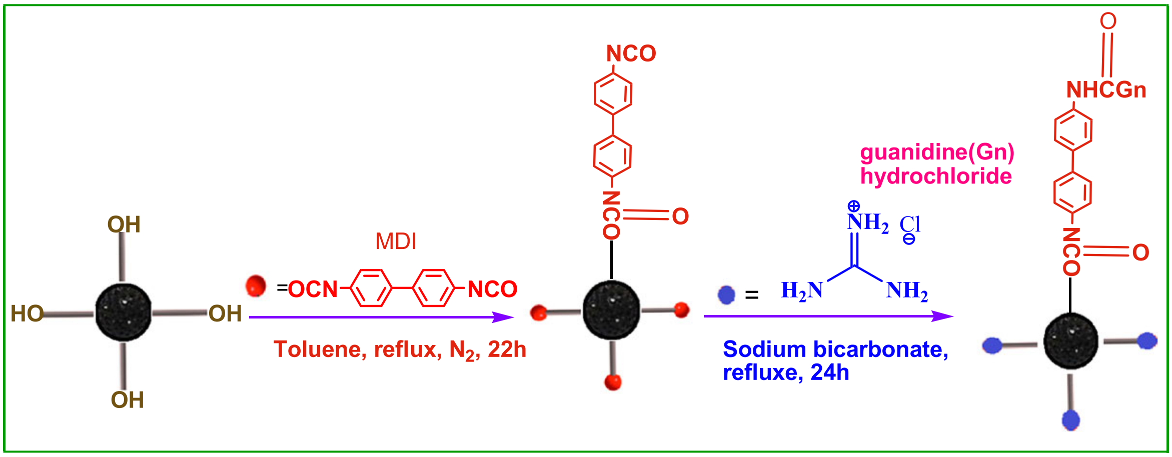
KEYWORDS
basic nanocatalyst, Fe_3O_4-Methylene diphenyl diisocyanate-guanidine, Knoevenagel condensation, nanocatalyst, tandem Knoevenagel–Michael-cyclocondensation reaction

1 | INTRODUCTION

Heterogeneous catalysts have been widely involved in various organic reactions, because the reuse of catalysts is highly favourable for economy.[1] Solid-supported catalysts are a significant and growing arena in heterogeneous catalysis.[2] The nano-magnetic catalyst may be a better choice of heterogeneous catalyst because the magnetic separation generally avoids loss of catalyst and increases its reusability in comparison to filtration or centrifugation.[3] Magnetic nanoparticles have been studied widely for disparate biological and medical applications.[4] Efficient catalysts that can be easily and simply separated from the reaction media were produced. It is known that iron oxides, magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3), are intrinsically biocompatible and are amenable to post-synthesis surface modification, which makes them great candidates for many important applications.[5] The insoluble and paramagnetic nature of the nano magnetic enables trouble-free separation of this catalyst from the reaction mixture by using an external magnet, which eliminates the necessity of catalyst filtration. Although iron oxide magnetic nanoparticles are non-toxic and could be easily synthesized by co-precipitation methods,[6] their applications have been limited due to low chemical and thermal stability in environmental conditions. Thus, the coating of these nanoparticles with an oxygen-impermeable scabbard is a necessary prerequisite for their potential use in biomedical and catalyst support applications.[7] Magnetite-supported catalysts have emerged as the viable alternatives to existing solid-supported heterogeneous catalysts, as they are inert, inexpensive, easy to prepare, and most importantly could be separated by an external magnet and reused multiple times for the several reaction cycles.[8] In addition, because of their large ratio of surface area to volume, superparamagnetic behaviour, and low toxicity, magnetic nanoparticles have attracted much attention in manifold technological fields. The magnetically separable nanocatalysts are valuable addition to sustainable methodologies as the demand for benign nanocatalyst and their applications in synthesis is on the rise. For example MNPs supported catalysts are used in asymmetric synthesis of organic compounds.[9]

Guanidines are important classes of compound that are found throughout nature that also have many uses with inorganic chemistry commonly as organic bases.[10] During the recent increasing interest in the field of organocatalysis, guanidines have also been shown to act as organic bases and nucleophilic catalysts.[11] However, the major disadvantage of catalysts based on guanidines is their separation from the product, which needs solid–liquid or liquid–liquid techniques in many reactions. This problem can be overcome by immobilizing these catalysts on MNPs, which can be easily removed from the reaction mixture by magnetic separation.

On the other hand, organic reactions should be fast and facile, and the target products should be easily separated and purified in high yields.[12] One-pot multicomponent reaction strategies propose significant advantages over conventional linear-type syntheses by virtue of their convergence, productivity, facile execution, and high yield.[13] In the other hand, condensation reaction is a chemical reaction in which two, three or four molecules or moieties, often functional groups, combine to form a larger molecule, together with the loss of a small molecule.[14] Condensation reactions, known to be catalysed by base, are of great



SCHEME 1 Preparation of MNPs–MDI-Gn nanocatalyst

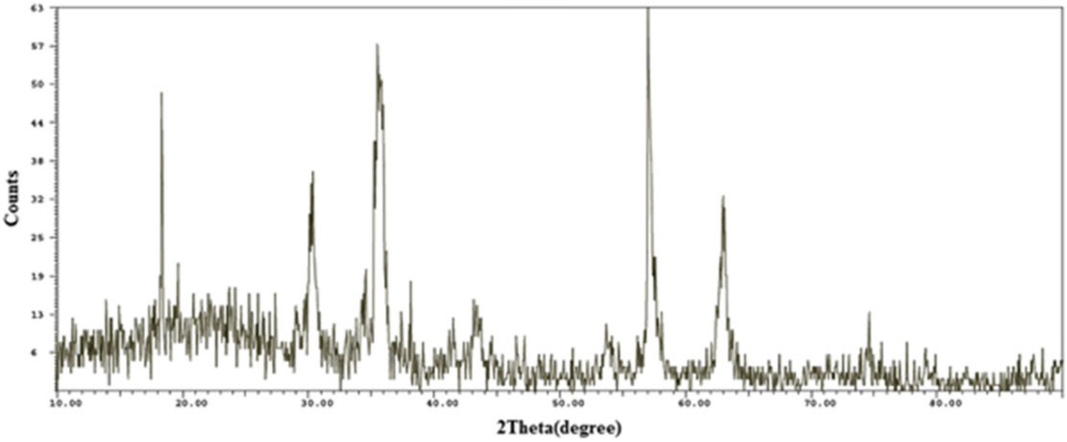


FIGURE 1 XRD spectrum of MNPs–MDI-Gn

importance for the synthesis of pharmaceutical and fine chemicals.

Herein, we have applied 4,4′-Methylene diphenyl diisocyanate (4,4′-MDI) as a coupling agent which is a type of bifunctional-group organic chemicals and guanidine hydrochloride which is a feasible amination reagent and report a catalytic system based on magnetic nanocatalyst with 4,4′-MDI and guanidine, which proved to be highly efficient for low temperature Knoevenagel and MCRs reactions. Catalyst can be easily separated with an external magnet, without using extra organic solvents.

TABLE 1 Scherrer data information for MNPs-MDI-Gn nanocatalyst

Crystal size (nm)	cos $_B$	$B_{1/2}$ (rad)	$B_{1/2}$ (°)		2	Sample
10	0.951872	0.01396	0.80	17.8481	35.6962	

2 | EXPERIMENTAL

2.1 | Materials and instruments

All starting materials were purchased from Merck and Sigma-Aldrich and used as received without further purification. Thermogravimetric analyses (TGA) was done using a DUPONT 951 thermal analysis Instruments heated from 25 °C to 1000 °C at ramp 5 °C/min under N_2 atmosphere. The morphology of the catalyst were studied using scanning electron microscopy (SEM) with a Philips XL30 field

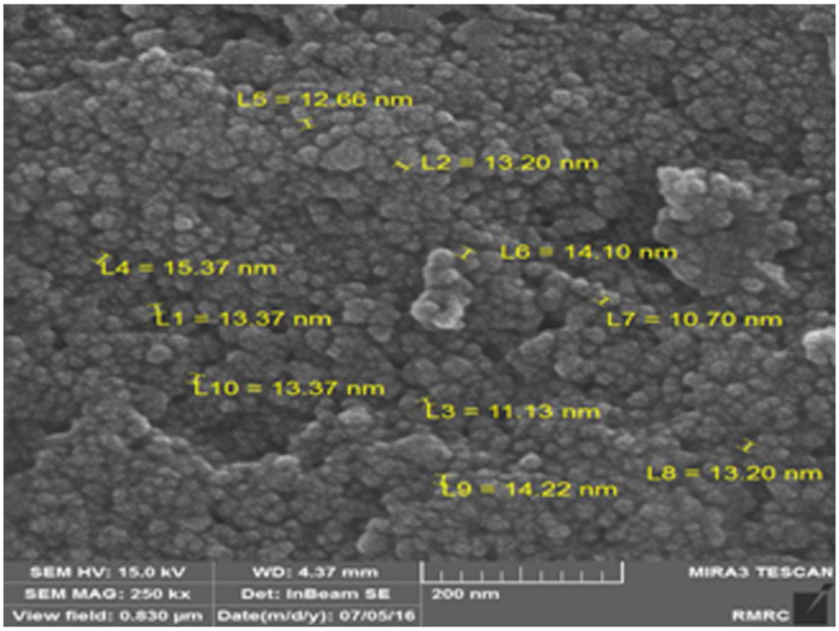


FIGURE 2 SEM spectrum of MNPs–MDI-Gn

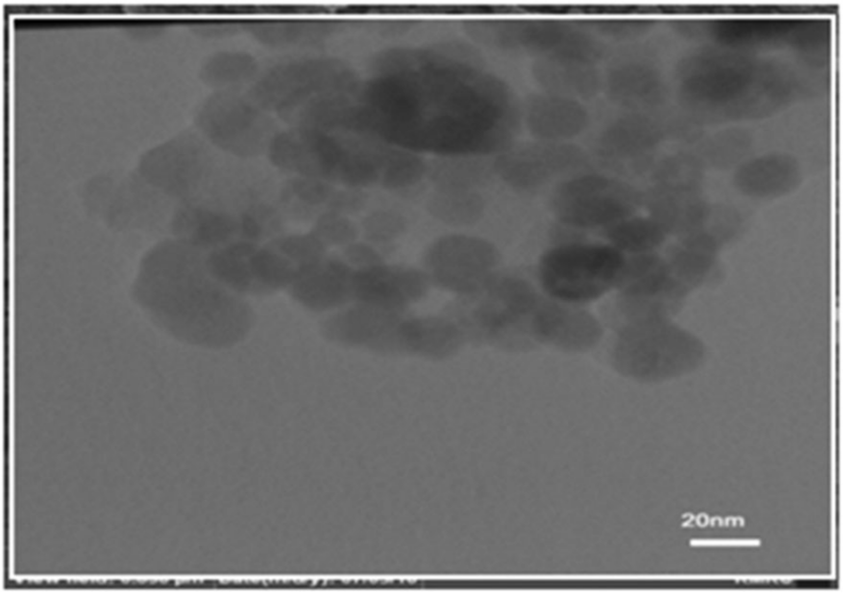


FIGURE 3 TEM spectrum of MNPs–MDI-Gn

emission scanning electron microscope (Royal Philips Electronics, Amsterdam, the Netherlands) instrument operating at 25 kV and transmission electron microscopy (TEM, CM30, Philips, the Netherland). The magnetic measurements were carried out in vibrating sample magnetometer (VSM, Lakeshore 7407) at room temperature. The energy dispersive X-Ray spectroscopy (EDS or EDX) (Philips XL-30) was used for determination of elemental composition of catalyst. Wide-angle X-ray diffraction (XRD) measurements were performed at room temperature on a Siemens D5000 (Siemens AG, Munich, Germany) using Cu-Ka radiation of wavelength 1.54 °A. The purity of products was checked by thin layer chromatography (TLC) on commercial plates coated with silica gel 60 F254 using n-hexane/ethyl acetate mixture as mobile phase. Melting points were recorded on THERMO SCIENTIFIC 9100 Instrument.

2.2 | Preparation of the magnetic Fe_3O_4 nanoparticles

The Fe_3O_4 magnetic nanoparticles were synthesized by reduction–precipitation method according to the previously reported procedure.[15] 3 ml $FeCl_3$(2 M dissolved in 2 M HCl) was added to 10.33 ml double distilled water, and 2 ml Na_2SO_3 (1 M) was added to the former solution dropwise in 1 min under magnetic stirring. Just after mixing of Fe^{3+} and SO_3^{-2}, the colour of the solution in the smaller beaker could be seen to alter from light yellow to red, indicating formation of complex ions. This solution was added to 80 ml NH_3 solution (0.85 M) under vigorous stirring when the colour changed from red to yellow again. A black precipitate quickly formed, which was allowed to crystallize completely for another 30 min under magnetic stirring. The resulting black MNPs were isolated by applying an external magnet, washed several times with deionized water until the pH was less than 7 and then dried under vacuum at 60 °C for 12 h.

2.3 | Functionalization of magnetic nanoparticles with MDI

A mixture of 1.5 g of synthesized Fe_3O_4 nanoparticles was dispersed in 15 ml of dried toluene. Then 2.25 g of MDI was added and placed in an ultrasonic bath for 15 min. Then, the reaction mixture was maintained at the temperature of

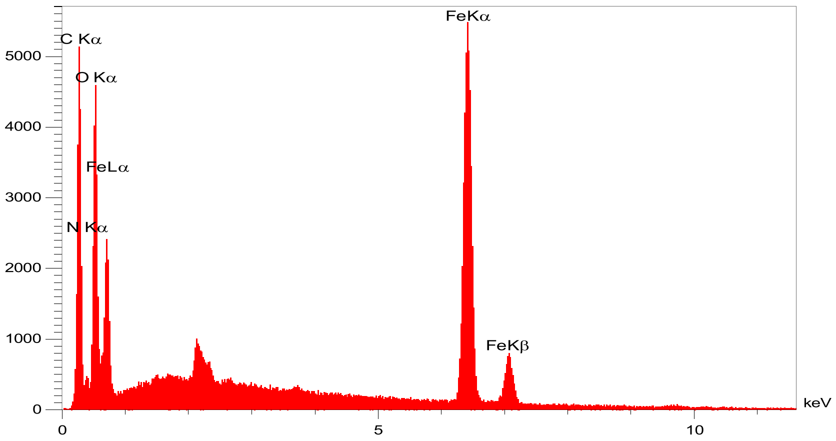


FIGURE 4 EDS spectrum of MNPs–MDI-Gn

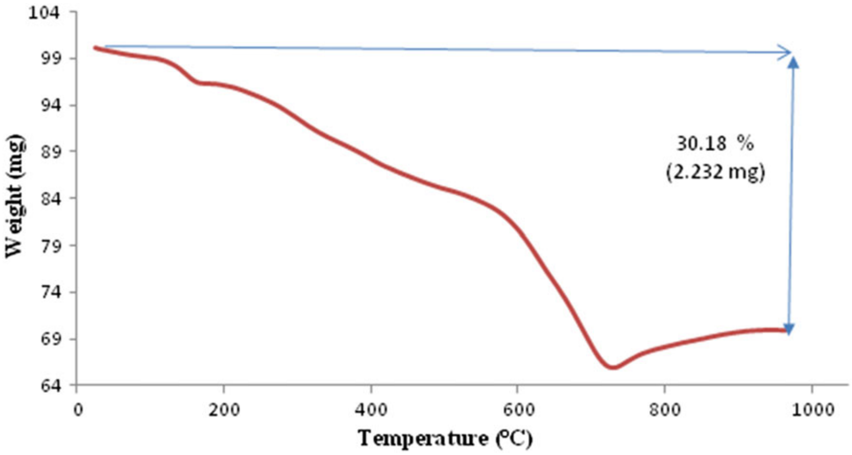


FIGURE 5 TGA spectrum of MNPs–MDI-Gn

100 °C and refluxed for 22 h under nitrogen atmosphere. The modified nanoparticles with MDI were magnetically separated and washed with dried toluene to remove the unreacted MDI. The product was dried in a vacuum at 100 °C for 8 h.

2.4 | Preparation of magnetic nanocatalyst (n-Fe_3O_4-MDI-Gn)

The modified nanoparticles with MDI (0.75 g) were dispersed in dry toluene (10 ml) by ultrasonication for 15 min. Subsequently, guanidine hydrochloride (0.3 g,) and sodium bicarbonate (0.5 g) were added and the mixture was refluxed for 24 h. Then, the final product, which named as Fe_3O_4-MDI-Gn, was separated by magnetic decantation and washed twice by dry CH_2Cl_2, MeOH and CH_2Cl_2 respectively. The synthesized nanocatalyst was dried in a vacuum at 70 °C for 6 h.

2.5 | General procedure for the Knoevenagel condensation by using of (n-Fe_3O_4-MDI-Gn)

A mixture of aldehyde (0.5 mmol), malononitrile (0.5 mmol) or dimedone (0.5 mmol) and (n-Fe_3O_4-MDI-Gn (0.05 g) in round bottom flask containing 1 ml ethanol:water was stirred at RT using a magnetic stirrer for the time specified. After terminus of the reaction monitored by TLC, the catalyst was separated magnetically. The reaction mixture was placed at room temperature until solidification occurred. In order to further purification, the solid was recrystallized from 96% ethanol.

2.6 | General procedure for the synthesis of tetrahydrobenzo[b]pyrans using of (n-Fe_3O_4-MDI-Gn)

A mixture of aldehyde (0.5 mmol), malononitrile (0.5 mmol), dimedone (0.5 mmol) and (n-Fe_3O_4-MDI-Gn (0.05 g) in

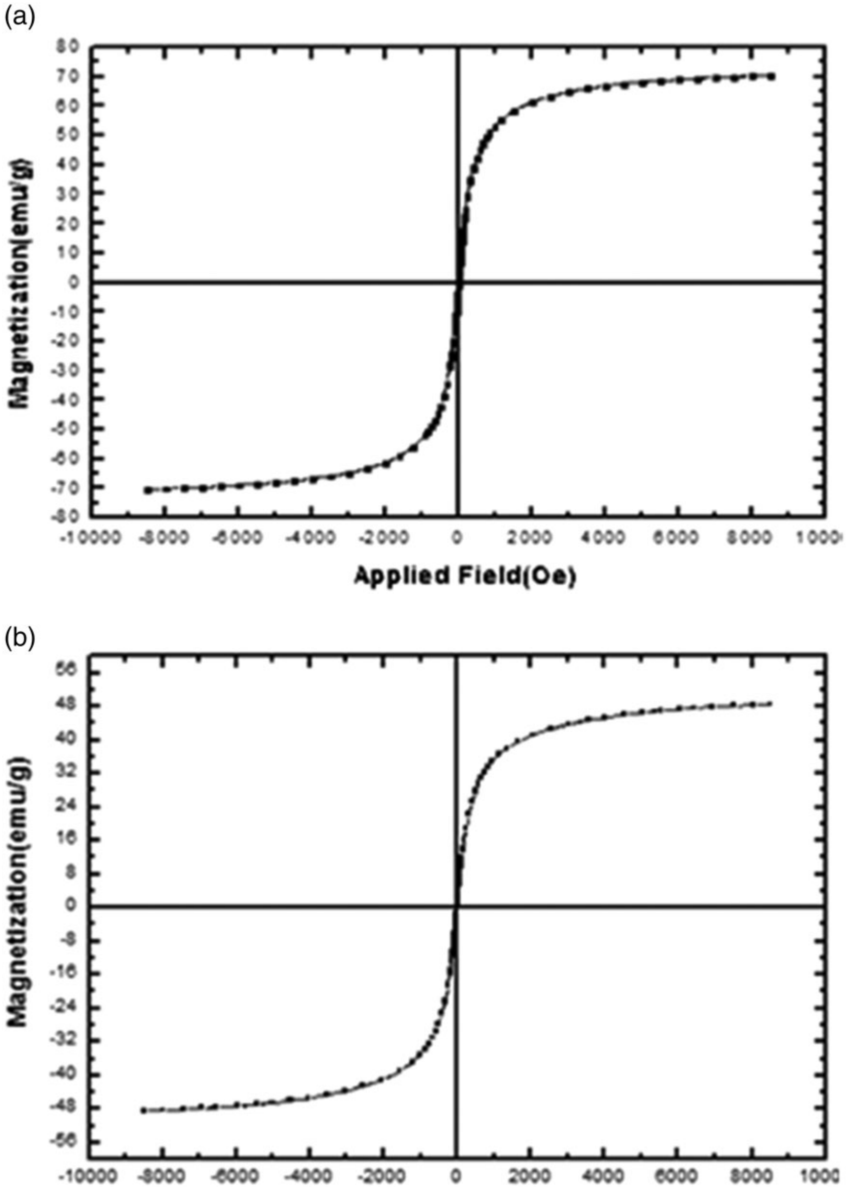


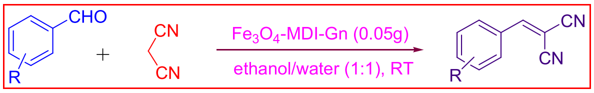
FIGURE 6 (a) Room-temperature magnetization curve of magnetic Fe_3O_4. (b) Room-temperature magnetization curve of MNPs–MDI-Gn

TABLE 2 Optimization of Knoevenagel condensation reaction conditions

Entry	Solvent	Catalyst (g)	Temp (°C)	Yield (%)
1	Solvent free	0.05	50	Trace
2	Solvent free	0.05	80	Trace
3	Ethanol	0.05	50	45
4	Water	0.05	90	30
5	Ethanol	0.05	70	30
6	Ethanol: Water(2:1)	0.02	RT	50
7	Ethanol: Water(2:1)	0.03	RT	63
8	Ethanol: Water(2:1)	0.04	RT	78
9	Ethanol: Water(2:1)	0.05	RT	95
10	Ethanol: Water(2:1)	0.06	RT	96
11	Dichloromethane	0.05	40	-----
12	Ethanol: Water	0.02	50	40
13	Ethanol: Water	0.04	50	47
14	Acetonitrile	0.05	70	-----

TABLE 3 Optimization of tandem Knoevenagel-Michael-cyclocondensation reaction conditions

Entry	Solvent	Catalyst (g)	Temp. (°C)	Yield (%)
1	Solvent free	0.05	60	36
2	Solvent free	0.05	90	72
3	Ethanol	0.05	50	45
4	Water	0.05	90	30
5	Ethanol	0.05	70	48
6	Ethanol: Water	0.02	RT	44
7	Ethanol: Water	0.03	RT	62
8	Ethanol: Water	0.04	RT	80
9	Ethanol: Water	0.05	RT	95
10	Ethanol: Water	0.06	RT	96
11	Dichloromethane	0.05	45	-----
12	Ethanol: Water	0.02	50	49
13	Ethanol: Water	0.04	50	64



SCHEME 2 Fe_3O_4–MDI-Gn catalyzed Knoevenagel condensation of aromatic aldehydes with malononitrile in ethanol/water

round bottom flask containing 1 ml ethanol:water was stirred at RT by using of a magnetic stirrer for the time specified. Upon completion of the reaction (monitored by TLC), the catalyst was separated by employing an external magnet. The reaction mixture was decanted and eluted using hot ethanol (5 ml). The products were obtained by recrystallization using ethanol solution.

3 | RESULTS AND DISCUSSION

3.1 | Preparation and characterization of MNPs–4,4′-Methylene diphenyl diisocyanate-guanidine (MNPs–MDI-Gn) nanocatalyst

The MNPs–MDI-Gn was synthesized according to the concise route outlined in Scheme 1. Firstly, magnetic Fe_3O_4 nanoparticles were prepared through reduction–precipitation method and subsequently were coated with MDI to achieve functionalized magnetic nanoparticles. Next, MNPs–MDI-Gn nanoparticles were synthesized by the reaction between free guanidine and functionalized magnetic nanoparticles (Scheme 1). This nanocatalyst was characterized using a variety of different techniques such as SEM, TEM, XRD, TGA, FT-IR, EDX and VSM.

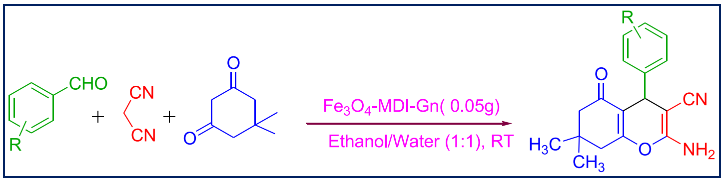
XRD was used to recognize the crystal structure of the superparamagnetic nanocatalyst. The XRD pattern of MNPs–MDI-Gn is shown in Figure 1 and Table 1. The diffraction signals, positions and relative intensities of all peaks are confirmed with the standard XRD pattern of Fe_3O_4.

Figure 2 shows the SEM image of the synthesized guanidine-functionalized magnetite nanocatalyst. According to, this Figure synthesized nanocatalyst has particle size about 10–20 nm.

TEM, as one of the most powerful techniques to investigate nanoparticles size, was used to further characterize the morphology of the synthesized MNPs–MDI-Gn. According to Figure 3, the size of nanoparticles in TEM image (within 10–20 nm) was in agreement with SEM image.

To identify the chemical composition of MNPs–MDI-Gn, EDS analysis was employed. According to Figure 4, chemical characterization of a typical sample shows that it is composed of iron, carbon and oxygen elements. The loading of the guanidine function on the magnetic nanocatalyst was specified by elemental analysis of nitrogen.

The TGA was used to determine the percent of organic functional groups chemisorbed onto the surface of magnetic nanoparticles. In the TGA curve of nanocatalyst (Figure 5).



SCHEME 3 Fe_3O_4–MDI-Gn catalyzed tandem Knoevenagel-Michael-cyclocondensation reaction of aromatic aldehydes with malononitrile and dimedone in ethanol/water

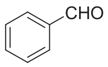
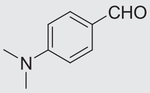
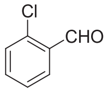
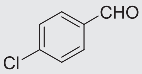
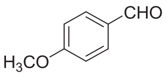
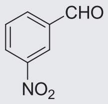
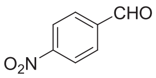
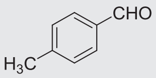
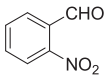
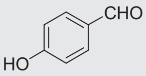
four stages were observed. The initial weight loss (below 200 °C) is likely because of the removal of physically adsorbed solvent or water and surface hydroxyl groups. The weight loss at temperatures about 200 to 600 °C (the second and third decomposition) was attributed to the decomposition of the 4,4′-Methylene diphenyl diisocyanate and the guanidine bases grafted onto the MNPs. The fourth decomposition step was identified at a temperature range of 710–1000 °C can be assigned to the oxidation reaction of magnetite to maghemite. These explanations show that the nanocatalyst was demonstrated to be thermally stable at the temperature used for the Knoevenagel and MCRs reactions.

The magnetic property of the final product was studied by VSM. Magnetization curve (Figure 6) measured at room temperature showed that MNPs–MDI-Gn is superparamagnetic. As expected, the Ms Value of MNPs–MDI-Gn compared to the naked MNPs (70 emu.g^{-1}) is decreased because of the organic materials coated to Fe_3O_4. The saturation magnetization value of the functionalized nanoparticles was 48 emu.g^{-1}. The images of the MNPs–MDI-Gn demonstrate the excellent and sufficient magnetization for its magnetic separation with a conventional magnetic.

3.2 | Applications of MNPs–MDI-Gn for the Knoevenagel condensation and Knoevenagel-Michael-cyclocondensation reaction

MNPs-MDI-Gn was investigated as basic magnetically separable heterogeneous nanocatalyst for the Knoevenagel

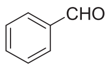
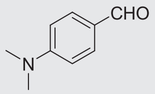
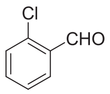
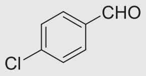
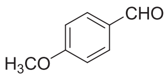
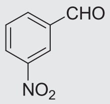
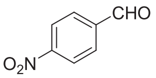
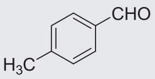
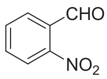
TABLE 4 Knoevenagel condensation reaction of different aromatic aldehydes with malononitrile[a]

Entry	Aldehyde	Yield(%)[b]	Time (min)	M.p)° C)	M.p. (reported) (°C)
1		95	10	83–85	82–85[16]
2		92	15	189–191	190–191[17]
3		93	10	92–95	94–95[18]
4		97	< 5	162–164	162–163[19]
5		98	5	113–115	113–114[6d]
6		96	15	106–108	102–103[20]
7		98	< 5	159–161	160[21]
8		91	< 10	135–137	134–135[22]
9		97	< 5	139–141	136–137[23]
10		90	20	187–189	187–188[19]

[a]Reaction conditions: Fe_3O_4–MDI-Gn (0.05 g), aromatic aldehydes(1 mmol), malononitrile(1 mmol), ethanol/water (1:1), RT.

[b]Yields are given for isolated products.

TABLE 5 Tandem Knoevenagel-Michael-cyclocondensation reaction of different aromatic aldehydes with malononitrile, and dimedone[a]

Entry	Aldehyde	Yield(%)[b]	Time	M.p)° C)	M.p. (reported) (°C)
1		93	10	228–230	228–229[6b]
2		96	< 15	172–174	171–173[3c]
3		91	< 15	211–213	212–213[3c]
4		93	10	237–239	236–238[2b]
5		95	15	195–197	194–196[2b]
6		94	10	202–204	200–201[6b]
7		98	< 5	175–177	178–179[6b]
8		92	< 20	233–234	232–234[3c]
9		97	< 10	196–197	195–197[3c]

[a] Reaction conditions: Fe_3O_4–MDI-Gn (0.05 g), aromatic aldehydes(1 mmol), malononitrile(1 mmol), dimedone(1 mmol), ethanol/water (1:1), RT.

[b] Yields are given for isolated products.

condensation and Knoevenagel-Michael-cyclocondensation reaction and compared the effect of different solvents and solvent-free conditions. Also, to investigate the optimized amount of catalyst in this case, the reaction was accomplished with various amounts of catalyst. Results are summarized in Tables 2–4. On the basis of these results it can be concluded that the best results can be obtained under the conditions shown in Scheme 2,3. As can be seen from Tables 2–4, the catalytic system worked exceedingly well in both Knoevenagel condensations and Knoevenagel-Michael-cyclocondensation reaction with wide range of substrates under the optimized reaction conditions. The expected products were prepared in short times and in excellent to high yields in both reactions.

To investigate the efficiency and applicability of this catalyst in the Knoevenagel condensation and Knoevenagel-Michael-cyclocondensation reactions, wide range of other substituted aldehydes under the optimized reaction conditions, were used. The expected products were obtained in short times and in good to high yields. All results are shown in Tables 4, 5.

After completion of the reaction, MNPs–MDI-Gn can be efficiently recovered easily and rapidly from the product by

TABLE 6 Recycling of Fe_3O_4–MDI-Gn for Knoevenagel condensation of benzaldehyde with malononitrile in ethanol/water and RT

Cycle	1st	2nd	3rd	4th	5th	6th	7th
Converted yield (%)	95	95	95	93	92	92	90

TABLE 7 Recycling of Fe_3O_4–MDI-Gn for tandem Knoevenagel-Michael-cyclocondensation reaction of benzaldehyde with malononitrile and dimedone in ethanol/water and RT

Cycle	1st	2nd	3rd	4th	5th	6th
Converted yield (%)	93	93	92	92	90	89

TABLE 8 Comparison of n-Fe_3O_4–MDI-Gn with some of the reportedcatalysts for tandem Knoevenagel-Michael-cyclocondensation

Entry	Catalyst	Reaction condition	Time(min)	Yield(%)	Ref
1	n-Pd	CH3CN/reflux	300	87	[24]
2	n-TiO2	Solvent-free/70 °C	35	92	[25]
3	n-Fe3O4	Solvent-free/100 °C	15	81	[26]
4	n-Fe3O4@SiO2@TiO2	Solvent-free/95 °C	20	93	[26]
5	n-SiO2	EtOH/r.t.	25	94	[27]
6	n-PbO	Grinding/r.t.	15	83	[28]
7	n-ZnO	EtOH:H2O/r.t.	210	86	[29]
8	n-Fe_3O_4–MDI-Gn	Ethanol/water, RT	10	93	This work

exposure to an external magnet. The remaining nanocatalyst was washed with EtOH, air-dried, and used directly for the next reaction without further purification to remove residual products. The recycled catalyst was used for up to seven for Knoevenagel condensation and six for Knoevenagel-Michael-cyclocondensation without significant loss of catalytic activity (Tables 6, 7).

In order to compare the efficiency of the prepared nanocatalyst with other reported catalysts as well as to exhibit the merit of the present work, our results are compared with some other previously reported studies in Table 8.

ACKNOWLEDGEMENTS

We are grateful to the University of Semnan Research Council for financial support of this work.

REFERENCES

[1] a) M. B. Gawande, P. S. Branco, R. S. Varma, *Chem. Soc. Rev.* **2013**, *42*, 3371; b) P. Barbaro, F. Liguori, N. Linares, C. M. Marrodan, *Eur. J. Inorg. Chem.* **2012**, *2012*, 3807.

[2] a) G. Kaupp, M. Reza Naimi-Jamal, J. Schmeyers, *Tetrahedron* **2003**, *59*, 3753; b) M. Seifi, H. Sheibani, *Catal. Lett.* **2008**, *126*, 275.

[3] a) H. Zhang, R. Qi, D. G. Evans, X. Duan, *J. Solid State Chem.* **2004**, *177*, 772; b) Y. Zhang, Y. Zhao, C. Xia, *J. Mol. Catal. A: Chem.* **2009**, *306*, 107; c) E. Tabrizian, A. Amoozadeh, *RSC Adv.* **2016**, *6*, 96606.

[4] a) L. Foppa, J. Dupont, C. W. Scheeren, *RSC Adv.* **2014**, *4*, 16583; b) J. Gao, H. Gu, B. Xu, *Acc. Chem. Res.* **2009**, *42*, 1097.

[5] a) S. Igder, A. R. Kiasat, M. R. Shushizadeh, *Res. Chem. Intermed.* **2015**, *41*, 7227; b) A. R. Kiasat, S. Nazari, *J. Mol. Catal. A: Chem.* **2012**, *365*, 80; c) M. B. Gawande, A. Velhinho, I. D. Nogueira, C. A. A. Ghumman, O. M. N. D. Teodoro, P. S. Branco, *RSC Adv.* **2012**, *2*, 6144; d) L. A. Mercante, W. W. M. Melo, M. Granada, H. E. Troiani, W. A. A. Macedo, J. D. Ardison, M. G. F. Vaz, M. A. Novak, *J. Magn. Magn. Mater.* **2012**, *324*, 3029; e) N. S. Chaudhari, S. S. Warule, S. Muduli, B. B. Kale, S. Jouen, B. Lefez, B. Hannoyer, S. B. Ogale, *Dalton Trans.* **2011**, *40*, 8003.

[6] a) A. Rostami, B. Atashkar, D. Moradi, *Appl. Catal., A* **2013**, *467*, 7; b) A. Rostami, B. Atashkar, H. Gholami, *Catal. Commun.* **2013**, *37*, 69; c) F. Osanlou, F. Nemati, S. Sabaqian, *Res. Chem. Intermed.* **2016**; d) F. Nemati, M. M. Heravi, R. Saeedi Rad, *Chin. J. Catal.* **2012**, *33*; 1825.

[7] a) C. W. Lim, I. S. Lee, *Nano Today* **2010**, *5*, 412; b) Y.-S. Li, J. S. Church, A. L. Woodhead, *J. Magn. Magn. Mater.* **2012**, *324*, 1543; c) A. Gupta, R. Jamatia, A. K. Pal, *New J. Chem.* **2015**, *39*, 5636.

[8] a) M. Gholinejad, M. Razeghi, A. Ghaderi, P. Biji, *Catal. Sci. Technol.* **2016**, *6*, 3117; b) R. K. Sharma, S. Dutta, S. Sharma, R. Zboril, R. S. Varma, M. B. Gawande, *Green Chem.* **2016**, *18*, 3184; c) J. Safaei Ghomi, S. Zahedi, *Ultrason. Sonochem.* **2017**, *34*, 916.

[9] A. Ying, S. Liu, Z. Li, G. Chen, J. Yang, H. Yan, S. Xu, *Adv. Synth. Catal.* **2016**, *358*, 2116.

[10] R. G. S. Berlinck, S. Romminger, *Nat. Prod. Rep.* **2016**, *33*, 456.

[11] a) Y. R. Su, S. H. Yu, A. C. Chao, J. Y. Wu, Y. F. Lin, K. Y. Lu, F. L. Mi, *Colloids Surf. Physicochem. Eng. Aspects* **2016**, *494*, 9; b) Y. Kudo, T. Yasumoto, D. Mebs, Y. Cho, K. Konoki, M. Yotsu-Yamashita, *Angew. Chem. Int. Ed.* **2016**, *55*, 8728.

[12] a) A. Puglisi, M. Benaglia, V. Chiroli, *Green Chem.* **2013**, *15*, 1790; b) M.-O. Simon, C.-J. Li, *Chem. Soc. Rev.* **2012**, *41*, 1415; c) E. Dezfoolinezhad, K. Ghodrati, R. Badri, *New J. Chem.* **2016**, *40*, 4575; d) R. B. N. Baig, R. S. Varma, *Chem. Commun.* **2013**, *49*, 752; e) R. B. Nasir Baig, R. S. Varma, *Green Chem.* **2013**, *15*, 398.

[13] a) H. Alinezhad, M. Tajbakhsh, N. Ghobadi, *Res. Chem. Intermed.* **2015**, *41*, 9979; b) A. Maleki, *Tetrahedron Lett.* **2013**, *54*, 2055; c) B. Wu, M. Santra, N. Yoshikai, *Angew. Chem.* **2014**, *126*, 7673.

[14] A. Ying, S. Liu, Y. Ni, F. Qiu, S. Xu, W. Tang, *Catal. Sci. Technol.* **2014**, *4*, 2115.

[15] Y.-k. Sun, M. Ma, Y. Zhang, N. Gu, *Colloids Surf. Physicochem. Eng. Aspects* **2004**, *245*, 15.

[16] H. R. Shaterian, M. Arman, F. Rigi, *J. Mol. Liq.* **2011**, *158*, 145.

[17] M. I. H. M. M. H. Bhuiyan, M. Ashraful Alam, M. M. Mahmud, *Chem. J.* **2012**, *2*, 31.

[18] Z. Ren, W. Cao, W. Tong, *Synth. Commun.* **2002**, *32*, 3475.

[19] N. M. Abd El-Rahman, A. A. El-Kateb, M. F. Mady, *Synth. Commun.* **2007**, *37*, 3961.

[20] X. C. Yang, H. Jiang, W. Ye, *Synth. Commun.* **2012**, *42*, 309.

[21] R. M. Kumbhare, M. Sridhar, *Catal. Commun.* **2008**, *9*, 403.

[22] R. M. H. A. Weinbergerr, *Can. J. Chem.* **1965**, 43.

[23] R. Malakooti, H. Mahmoudi, R. Hosseinabadi, S. Petrov, A. Migliori, *RSC Adv.* **2013**, *3*, 22353.

[24] M. Saha, A. K. Pal, *Adv. Nanopart* **2012**, *1*, 10.

[25] P. L. Anandgaonker, S. Jadhav, S. T. Gaikwad, A. S. Rajbhoj, *J. Cluster Sci.* **2014**, *25*, 483.

[26] A. Khazaei, F. Gholami, V. Khakyzadeh, A. R. Moosavi-Zare, J. Afsar, *RSC Adv.* **2015**, *5*, 14305.

[27] S. Banerjee, A. Horn, H. Khatri, G. Sereda, *Tetrahedron Lett.* **2011**, *52*, 1878.

[28] A. V. Borhade, B. K. Uphade, D. R. Tope, *J. Chem. Sci.* **2013**, *125*, 583.

[29] P. Bhattacharyya, K. Pradhan, S. Paul, A. R. Das, *Tetrahedron Lett.* **2012**, *53*, 4687.

How to cite this article: Maleki R, Koukabi N, Kolvari E. Fe_3O_4-Methylene diphenyl diisocyanate-guanidine (Fe_3O_4–4,4′-MDI-Gn): A novel superparamagnetic powerful basic and recyclable nanocatalyst as an efficient heterogeneous catalyst for the Knoevenagel condensation and tandem Knoevenagel-Michael-cyclocondensation reactions. *Appl Organometal Chem*. 2017;e3905. https://doi.org/10.1002/aoc.3905