Revised: 27 September 2018

#### FULL PAPER



## SO<sub>3</sub>H-functionalized nano-MGO-D-NH<sub>2</sub>: Synthesis, characterization and application for one-pot synthesis of pyrano[2,3-*d*]pyrimidinone and tetrahydrobenzo[*b*]pyran derivatives in aqueous media

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Behrooz Maleki, Department of Chemistry, Faculty of Sciences, Hakim Sabzevari University, 96179–76487, Sabzevar, Iran. Email: malekibehrooz@gmail.com An SO<sub>3</sub>H-functionalized nano-MGO-D-NH<sub>2</sub> catalyst has been prepared by multifunctionalization of a magnetic graphene oxide (GO) nanohybrid and evaluated in the synthesis of tetrahydrobenzo[*b*]pyran and pyrano[2,3-*d*]pyrimidinone derivatives. The GO/Fe<sub>3</sub>O<sub>4</sub> (MGO) hybrid was prepared via an improved Hummers method followed by the covalent attachment of 1,4-butanesultone with the amino group of the as-prepared polyamidoamine-functionalized MGO (MGO-D-NH<sub>2</sub>) to give double-functionalized magnetic nanoparticles as the catalyst. The prepared nanoparticles were characterized to confirm their synthesis and to precisely determine their physicochemical properties. In summary, the prepared catalyst showed marked recyclability and catalytic performance in terms of reaction time and yield of products. The results of this study are hoped to aid the development of a new class of heterogeneous catalysts to show high performance and as excellent candidates for industrial applications.

#### **KEYWORDS**

dendrimer, magnetic, pyrano[2,3-*d*]pyrimidinones, SO<sub>3</sub>H-functionalized nano-MGO-D-NH<sub>2</sub>, tetrahydrobenzo[*b*]pyrans

## **1** | INTRODUCTION

The growing need to eliminate hazardous materials at their source has become a great motivation for careful design and selection of appropriate substances that are environmentally more benign and simultaneously avoid the necessity of the reduction or disposal of the generated wastes during the chemical process. This goal which falls within the scope of green chemistry has been brought into the spotlight of intensive researches over the past few decades and has the double advantage of economic benefits and environmental protection by decreasing the usage of toxic materials and increasing the overall efficiency. Among the most important aspects of green chemistry, catalysis has been identified as a fundamental tool which is directly linked to the synthesis of chemical products and plays a pivotal role in the development of cleaner technologies and chemical manufacturing processes. Catalytic science may fulfil the essential requirements of green chemistry by the development of novel catalysts which have the benefits of lower input energies, higher selectivity and decreasing toxic agents during the synthesis of certain chemicals which leads to the implementation of facile and simpler separation and recycling processes.<sup>[1-6]</sup>

In organic transformations, catalysts play a significant role, and most of these are acid catalysts. The most commonly used acidic catalysts are sulfuric, hydrochloric, nitric and phosphoric acids. However, corrosive properties, inability to be reused and tough separation are their drawbacks. Heterogeneous catalysts are superior to homogeneous ones with regard to several important characteristics such as costeffectiveness, recyclability and catalytic performance. Consequently, a great deal of attention has been directed towards the design and performance analysis of these catalysts in the last few decades and this topic is still a matter of scientific interest.<sup>[7–11]</sup> An efficient method for the fabrication of solid acid catalysts is the attachment of catalytically active compounds onto the surface of various supporting materials such as inorganic molecules or nanostructures which leads to the formation of catalytically active hybrid materials.<sup>[12,13]</sup> This idea dates back to the pioneering work of Hara and co-workers who prepared a carbon-based solid acid catalyst through incomplete carbonization of sulfonated aromatic compounds, which was further generalized by the interesting work of Wang and co-workers who covalently attached sulfonic acid-containing aryl radicals to mesoporous carbon and obtained a highly active catalyst with an acid density of 1.93 mmol  $H^+ g^{-1}$ .<sup>[14,15]</sup>

With the emergence of nanostructures, many scientists have been intrigued by the fascinating properties of these materials, such as excellent chemical and mechanical properties, and a great deal of effort has been made to take advantage of these properties in developing novel materials in various scientific fields. In this regard, graphene and its derivatives such as an oxidized form of graphene - so-called graphene oxide (GO) - have drawn considerable attention because of their superior chemical and mechanical properties.<sup>[16-19]</sup> As a chemically modified graphene sheet, GO has been considered as an efficient alternative to pristine graphene in a wide range of applications. Because of the presence of hydrophilic functional moieties such as epoxide, hydroxyl and carboxylic groups in addition to its very large aromatic surface, GO has the double advantage of both retaining the excellent mechanical and thermal properties of graphene while alleviating the dispersibility problem of pristine graphene sheets in aqueous media. Consequently, graphene and its oxidized analogues have been introduced as efficient materials for the preparation of hybrid composites through introduction of a wide variety of functionalities which have gained marked popularity in the literature, both theoretically and experimentally, and offer promising potential in scientific fields such as energy research,<sup>[20,21]</sup> catalysis<sup>[22,23]</sup> and electrochemical analysis.<sup>[24]</sup> Several studies have pointed out the synergistic interactions that GO can have with a wide class of biomolecules such as enzymes and organic dyes through covalent or non-covalent linkages and reported improved performances in conversion and yields.<sup>[25-28]</sup> In work by Ji et al., sulfonated groups were covalently attached to the surface of GO and the reactivity of this solid acid catalyst was evaluated in the catalytic hydrolysis of ethyl acetate. It was found that the activity of the catalyst

remained unchanged after several sets of experiments with an average hydrolysis rate of 64% at 70°C for 6 h.<sup>[29]</sup> GO-based composites can also be fabricated through the attachment of bifunctional linkers to the surface of GO. These linkers, such as dendrimers, which play the role of molecular bridges will provide reactive sites for anchoring of guest molecules such as acid catalysts and enhance the overall efficiency and lifetime of the prepared composites.

Dendrimers are characterized as manufactured, to a great degree branched, nano-sized and mono-scatter structure.<sup>[30,31]</sup> with globular macromolecules а Dendrimers are known as types of artificial polymers with unique structural features such as structural homogeneity, host-guest potential, high internal porosity, integrity, controlled composition and biocompatibility. They have also been broadly investigated for their applications in cancer diagnosis,<sup>[32]</sup> drug delivery,<sup>[33]</sup> catalysis,<sup>[34]</sup> electrochemical sensors,<sup>[35]</sup> gene therapy,<sup>[36]</sup> adsorption<sup>[37]</sup> and other areas.<sup>[38]</sup>

Due to the diverse biological properties associated with pyranopyrimidinones and tetrahydrobenzo[b]pyrans, there is an extensive interest in the synthesis of such compounds. Tetrahydrobenzo[b]pyrans and their derivatives are an important class of heterocyclic compounds which have prominent biological and pharmacological properties such as antitumour,<sup>[39,40]</sup> antibacterial,<sup>[41]</sup> antihypertensive, hepatoprotective, cardiotonic,<sup>[39,42]</sup> vasodilatory and bronchodilatory<sup>[43]</sup> activities, and hence are introduced as ideal enhancers having a wide range of therapeutic applications. In this regard, the objective of the work presented here was to synthesize a novel solid acid catalyst based on GO which meets the criteria of green chemistry and to aid the efficient synthesis of tetrahydrobenzo[b]pyrans and pyrano[2,3-d]pyrimidinones via a domino Knoevenagel cyclocondensation reaction. We utilized magnetic GO as the supporting material and polyamidoamine (PAMAM) dendrimers which act as the bifunctional linker for the anchoring of alkylsultone as the acid catalyst. Further information regarding the incorporated chemicals and synthesis route as well as the evaluation procedures are thoroughly discussed in the following sections.

#### 2 | EXPERIMENTAL

#### 2.1 | Materials and instrumentation

TLC was conducted using glass plates coated with silica gel 60 F254 with *n*-hexane–ethyl acetate mixture as the mobile phase to determine the purity of the products. Melting point measurements of the synthesized samples were carried out using a Thermo Scientific 9100

apparatus. Fourier transform infrared (FT-IR) spectroscopic measurements were carried out with a Shimadzu 8400 spectrometer in the wavenumbers range 400– 4000 cm<sup>-1</sup> using KBr pellets. NMR spectra were recorded with a Bruker DRX-400 AVANCE (MA, USA) spectrometer at 400.13 and 100.61 MHz. Field-emission scanning electron microscopy (FE-SEM) images were obtained with a MIRA3 XMU instrument operating at 25 kV to study the morphology of samples. Also the MIRA3 XMU scanning electron microscope was equipped with energy-dispersive X-ray (EDX) analysis facility for elemental analysis. Finally, thermogravimetric analysis (TGA) of the samples was performed with a DuPont 2000 thermal analysis system within the range 30–600°C using a heating rate of 5°C min<sup>-1</sup> under air atmosphere.  $\mathcal{N}_{\mathbf{I}}$   $\mathbf{F}_{\mathbf{Y}}$   $- \mathbf{Q}_{\mathbf{r}}$  ganometallic -

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#### 2.2 | Preparation of GO/Fe<sub>3</sub>O<sub>4</sub> (MGO)

By oxidizing graphite with a modified Hummers method, GO was prepared.<sup>[44,45]</sup> Using an effective chemical precipitation method, a magnetic GO (GO/Fe<sub>3</sub>O<sub>4</sub> or MGO) nanocomposite was synthesized. An amount of 30 mg of GO was added to 10 ml of distilled water and sonicated for 20 min to form a fully dispersed suspension. The resulting suspension was heated to 50°C in a nitrogen atmosphere to remove O<sub>2</sub>. Then, a solution of FeCl<sub>2</sub>·4H<sub>2</sub>O (80 mg) and FeCl<sub>3</sub>·6H<sub>2</sub>O (216 mg) was added to the suspension under ultrasonication for 30 min. After complete mixing, 1 ml of NH<sub>3</sub>·H<sub>2</sub>O solution was added dropwise to the mixture under nitrogen. The mixture was continually stirred for 40 min at 50°C to continue



SCHEME 1 Preparation of modified PAMAM denrimer (G2)

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the reaction and the resulting mixture was cooled to room temperature. The obtained product was thoroughly washed with double-distilled water and the resulting MGO nanoparticles were separated using a magnet.

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# 2.3 | Preparation of modified PAMAM dendrimer

The synthesis of the modified PAMAM dendrimer was accomplished according to a procedure described in detail in our previous work.<sup>[37]</sup> However, a recap of the main

aspects of the synthesis route would be beneficial, as illustrated in Scheme 1.

### 2.4 | Functionalization of MGO with modified PAMAM dendrimer (MGO-D-NH<sub>2</sub>)

MGO (0.3 g) was dispersed in 200 ml of deionized water by sonication for 30 min. Then, 1-ethyl-3-(3dimethylaminopropyl)carbodiimide hydrochloride (EDC. HCl; 0.052 g) and *N*-hydroxysuccinimide (NHS; 0.015 g) were added to the solution and stirred for 10 min to



SCHEME 2 Procedures for the preparation of GO/Fe<sub>3</sub>O<sub>4</sub>NCs with modified PAMAM dendrimer (MGO-D-NH<sub>2</sub>)

activate the carbonyl groups of MGO. Finally, the modified PAMAM dendrimer (3 ml) was added dropwise to the system, and the reaction was allowed to proceed for 24 h at room temperature. The precipitate was collected using an external magnetic field, washed with deionized water and ethanol several times and dried in a vacuum at 70°C. The resulting dark-brown precipitates of MGO-D-NH<sub>2</sub> were ready to use (Scheme 2).

#### 2.5 | Preparation of *n*-butylsulfonatefunctionalized MGO-D-NH<sub>2</sub>

MGO-D-NH<sub>2</sub> (1 g) was dispersed in 25 ml of toluene by sonication for 30 min. Then, 0.7 g of 1,4-butanesultone was added to the solution and the reaction mixture was mixed at 100°C for 48 h. Finally, through an external magnetic field, the resultant particles were separated. The obtained particles were thoroughly rinsed with toluene and acetone in order to eliminate the unreacted 1,4-butanesultone, and finally vacuum-dried at 70°C for 24 h (Scheme 3).

### 2.6 | General procedure for one-pot synthesis of tetrahydrobenzo[b]pyrans and pyrano[2,3-d]pyrimidinone derivatives

*n*-Butylsulfonate-functionalized MGO-D-NH<sub>2</sub> (MGO-D-NH-( $CH_2$ )<sub>4</sub>-SO<sub>3</sub>H; 0.02 g) was added to a mixture of aldehyde (1 mmol), malononitrile (1.2 mmol), 1,3-cyclic



SCHEME 3 Procedures for the preparation of N-Butylsulfonate-functionalized MGO-D-NH<sub>2</sub>

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diketone (1 mmol) and 5 ml of water–ethanol (4:1, v/v) in a 10 ml round-bottom flask. Then, the resulting mixture was stirred at room temperature (see Tables 2 and 3). The reaction progress was monitored using TLC. After completion of the reaction process, the obtained product was dissolved by the addition of hot ethanol to the mixture. The incorporated magnetic catalyst was separated from the product by the application of a 1.4 T magnetic field followed by pouring the reaction product onto crushed ice for 10 min. The resulting product was then filtered and recrystallized from 96% ethanol (3 ml) to afford tetrahydrobenzo[*b*]pyran and pyrano[2,3-*d*]pyrimidinone derivatives.

#### 2.7 | Selected spectral data

#### 2.7.1 | 2-Amino-4-(4-chlorophenyl)-7,7dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*chromene-3-carbonitrile (4d)

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ , δ, ppm): 0.98 (s, 3H), 1.05 (s, 3H), 2.15–2.26 (m, 2H), 2.40 (s, 2H), 4.12 (s, 1H), 6.60 (brs, 2H, D<sub>2</sub>O exchangeable), 7.13 (d, 2H), 7.46 (d, 2H). FT-IR (KBr, ν, cm<sup>-1</sup>): 3370,3175, 2190, 1670, 1628, 1500, 1490, 1380.

#### 2.7.2 | 2-Amino-7,7-dimethyl-4-(2-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*chromene-3-carbonitrile (4e)

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 0.86 (s, 3H), 1.02 (s, 3H), 1.90–2.21 (m, 2H), 2.33–2.46 (m, 2H), 4.94 (s, 1H), 7.20 (brs, 2H, D<sub>2</sub>O exchangeable 2H), 7.32– 7.45 (m, 2H), 7.62–7.68 (m, 1H), 7.80–7.84 (dd, 1H). FT-IR (KBr disc,  $\nu$ , cm<sup>-1</sup>): 3400, 3306, 2200, 1692, 1592, 1505, 1462, 1378.

#### 2.7.3 | 2-Amino-7,7-dimethyl-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*chromene-3-carbonitrile (4f)

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 1.04 (s, 3H), 1.18 (s, 3H), 2.26–2.51 (m, 2H), 2.59 (s, 2H), 5.26 (s, 1H), 6.12 (brs, 2H, D<sub>2</sub>O exchangeable), 7.56 (d, 2H), 8.09 (d, 2H). FT-IR (KBr disc,  $\nu$ , cm<sup>-1</sup>): 3401, 3307, 2200, 1690, 1598, 1498, 1468, 1375.

#### 2.7.4 | 7-Amino-5-(2-chlorophenyl)-2,4dioxo-1,3,4,5-tetrahydro-2*H*-pyrano[2,3-*d*] pyrimidine-6-carbonitrile (6l)

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ , δ, ppm): 4.65 (s, 1H), 7.03 (s, 2H), 7.28–7.35 (m, 4H), 10.90 (s, 1H), 11.94 (s, 1H). FT-

IR (KBr disc,  $\nu$ , cm<sup>-1</sup>): 3502, 3306, 3170, 2199, 1720, 1668, 1612.

# 2.8 | Recyclability evaluation of MGO-D-NH-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H

The synthesis of 2-amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile was used to evaluate the recyclability of MGO-D-NH-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H, under optimized conditions. At the end of the reaction, the catalyst was separated using an external magnetic field and washed thoroughly with ethanol and acetone to eliminate any trace of synthesized compound on the catalyst surface. Finally, the catalyst was dried at 70°C for 1 h.

#### **3** | **RESULTS AND DISCUSSION**

Based on our interest in the synthesis of novel recoverable heterogeneous nanocatalysts, we report a novel experimental protocol for the preparation of MGO-D-NH-(-CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H. Scheme 3 shows the preparation of the nanocatalyst. First, nano-MGO was synthesized using a modified Hummers strategy.<sup>[44,45]</sup> In the following step, the surface of MGO was functionalized using a modified PAMAM dendrimer. The hydroxyl groups of carboxylic acid on the surface of nano-MGO reacted with NH<sub>2</sub> groups of the modified PAMAM dendrimer to form amide groups. Finally, MGO-D-NH-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H was formed by the reaction between 1,4-butanesultone with the NH<sub>2</sub> groups of MGO-D-NH<sub>2</sub> via a ring-opening process. The catalyst was characterized using FT-IR spectroscopy, EDX analysis, FE-SEM, TGA and acid–base titration.

#### 3.1 | Characterization of MGO-D-NH-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H

#### 3.1.1 | FT-IR spectroscopy

The successful attachment of functional groups onto the surface of the GO was assessed at each step of the catalyst synthesis through FT-IR spectra as shown in Figure 1. The FT-IR spectrum of GO which is illustrated in Figure 1a shows a broad peak between 3000 and  $3600 \text{ cm}^{-1}$  corresponding to the vibration of O–H groups and two sharp peaks in the region  $1635-1740 \text{ cm}^{-1}$  which can be attributed to the bending and stretching vibrations of O–H and C=O of –COOH groups, respectively. Moreover, the peaks at 1415 and 1131 cm<sup>-1</sup> correspond to the C–O stretching of carboxylic acid and C–OH of alcohol, respectively, confirming the presence of oxygen



**FIGURE 1** FT-IR spectra: (a) GO; (b) MGO; (c) MGO-D-NH<sub>2</sub>; (d) MGO-D-NH-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H

functionalities within the structure of the synthesized GO. The FT-IR spectrum of GO/Fe<sub>3</sub>O<sub>4</sub> (Figure 1b) shows the specific peak at 595  $\text{cm}^{-1}$  relating to the stretching vibration of the Fe-O bond. In the FT-IR spectrum of MGO-D-NH<sub>2</sub> (Figure 1c), the peaks at 2923 and 2863 cm<sup>-1</sup> are assigned to C–H stretching of the alkyl group in the modified PAMAM component. The characteristic peaks of MGO-D-NH2 at 1639, 1547 and 1434 cm<sup>-1</sup> are attributed to NH deformation vibration of primary amine, the coupling of N-H bending and C–N stretching of amide. Also, the peak at 3435  $cm^{-1}$ indicates the presence of nitrogen-containing functional groups.<sup>[65]</sup> Two significant peaks at 1037 and 1213 cm<sup>-1</sup> confirm the reaction of MGO-D-NH<sub>2</sub> with 1,4butanesultone that correspond to the symmetric and asymmetric stretching vibrations of S=O, respectively (Figure 1d). The effective functionalization of 1,4butanesultone onto the surface of MGO-D-NH<sub>2</sub> is evidenced by the FT-IR results.<sup>[66]</sup>

#### 3.1.2 | FE-SEM and EDX analyses

To study the surface of  $MGO-D-NH_2$ , FE-SEM analysis was used (Figure 2). Figure 2a shows a typical FE-SEM image of GO obtained using a modified Hummers method. GO presents a sheet-like structure with large

thickness, smooth surface and wrinkled edge. After the combination with  $Fe_3O_4$  nanoparticles to form MGO (Figure 2b), there is a much rougher surface, revealing that many small magnetic nanoparticles had been assembled on the surface of GO layers with a high density. The FE-SEM image of MGO-D-NH<sub>2</sub> (Figure 2c) confirms the grafting of organic compounds on MGO by increasing particle sizes.

The EDX analysis of MGO-D-NH<sub>2</sub> and MGO-D-NH-(- $CH_2$ )<sub>4</sub>-SO<sub>3</sub>H confirmed the presence of C, S, N, Fe and O atoms (Figure 3).

#### 3.1.3 | Thermogravimetric analysis

TGA can be used to evaluate the thermal stability and bond formation of materials. The TGA results for MGO, MGO-D-NH<sub>2</sub> and MGO-D-NH-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H are shown in Figure 4 in the range 30–600°C. It can be seen from Figure 4a that MGO underwent a mild weight loss below 100°C which can be attributed to the loss of impurities such as residuals or absorbed solvent. At that point, two stages of weight loss happened at around 150 and 420°C, representing the decomposition and vaporization of several functional groups at different sites on GO. The TGA curve of MGO-D-NH<sub>2</sub> (Figure 4b) indicated a weight loss between 200 and 600°C which was assigned



FIGURE 2 FE-SEM images: (a) GO; (b) MGO; (c) MGO-D-NH<sub>2</sub>



FIGURE 3 EDX analysis: (a) MGO-D-NH<sub>2</sub>; (b) MGO-D-NH-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H

to the modified PAMAM dendrimer. In contrast to the observed situation for MGO and  $MGO-D-NH_2$  where the TGA curves showed an entirely descending trend,



**FIGURE 4** TGA curves: (a) MGO; (b) MGO-D-NH<sub>2</sub>; (c) MGO-D-NH-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H

the TGA curve of MGO-D-NH-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H as shown in Figure 4c exhibited an initial ascending behaviour as the consequence of the buoyancy effect of the instrument. Similar ascending trends in TGA curves have also been reported in several studies and explained in that this initial weight gain for the sample and platinum pan stems from the differences in heat capacity and thermal conductivity of the purging gas. The weight loss between 400 and 600°C originated from the decomposition of the modified PAMAM dendrimer and *n*-butyl– SO<sub>3</sub>H groups.

#### 3.1.4 | Analysis of pH of catalyst

The catalytic active sites of the synthesized MGO-D-NH- $(CH_2)_4$ -SO<sub>3</sub>H were determined by the method of

active-site titration. Following this aim, 100 mg of catalyst was selected and stirred with 10 ml of 1 M NaCl solution for 24 h at room temperature. After that, the pH was calculated to be about 2.1 which is equivalent to 0.06 mmol  $g^{-1}$  of SO<sub>3</sub>H groups within the structure of the catalyst.

#### 3.2 | Activity assessment of MGO-D-NH-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H catalyst

The activity of MGO-D-NH- $(CH_2)_4$ -SO<sub>3</sub>H nanoparticles was explored in the synthesis of pyrano[2,3-*d*]pyrimidinones and tetrahydrobenzo[*b*]pyrans by the three-component reaction of 1,3-dicarbonyl and malononitrile with various aromatic aldehydes (Scheme 4).

The reaction of 5,5-dimethylcyclohexane-1,3-dione (0.14 g, 1 mmol), benzaldehyde (0.106 g, 1 mmol) and malononitrile (0.079 g, 1.2 mmol) as a model reaction was selected to optimize the reaction conditions and investigated in the presence of several nanocatalysts such as GO, MGO, MGO-D-NH<sub>2</sub> and MGO-D-NH-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H in various solvents, and at different temperatures. The results are summarized in Table 1.

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The nanomagnetic MGO-D-NH- $(CH_2)_4$ -SO<sub>3</sub>H exhibited the best catalytic performance in comparison to the other catalysts according to the values of time and yield as presented in Table 1, and retained its optimal conditions. As can be perceived from the values of time and yield in Table 1, higher performance was achieved using 0.02 g of the catalyst at room temperature in water-ethanol (4:1, v/v) (entry 5). However, increasing the amount of catalyst and temperature did not lead to any improvements in the obtained results (entries 6 and 7).

Having found the optimized reaction conditions based on the data reported in Table 1, we aimed at assessing the performance and activity of MGO-D-NH- $(CH_2)_4$ -SO<sub>3</sub>H in the synthesis of various derivatives of tetrahydrobenzo[*b*] pyran (Table 2) and pyrano[2,3-*d*]pyrimidinone (Table 3) by reacting a wide range of arylaldehydes (1 mmol) with 5dimethylcyclohexane-1,3-dione (1 mmol) and malononitrile (1.2 mmol) in the presence of our synthesized catalyst.

To demonstrate the advantages of the synthesized catalyst, we compared the obtained results for the catalytic activity of MGO-D-NH- $(CH_2)_4$ -SO<sub>3</sub>H with other reported results for the synthesis of tetrahydrobenzo[*b*] pyrans and pyrano[2,3-*d*]pyrimidinones using various catalysts (Table 4). It is evident from Table 4 that

**SCHEME 4** MGO-D-NH-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H-catalyzed synthesis of tetrahydrobenzo[*b*]pyrans and pyrano[2,3*d*]pyrimidinones

**TABLE 1** Optimization of reaction conditions for synthesis of tetrahydrobenzo[b]pyran derivative 4a

Entry	Reaction conditions	Time (min)	Yield (%)
1	GO (0.02 g)/water/ethanol (4:1, v/v), 25°C	40	65
2	Fe <sub>3</sub> O <sub>4</sub> (0.02 g) water/ethanol (4:1, v/v), 25°C	75	50
3	MGO (0.02 g)/water/ethanol (4:1, v/v), 25°C	35	70
4	MGO-D-NH <sub>2</sub> (0.02 g)/water/ethanol (4:1, v/v), 25°C	10	75
5	MGO-D-NH-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.02 g)/water/ethanol (4:1, v/v), $25^{\circ}$ C	5	95
6	MGO-D-NH-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.03 g)/water/ethanol (4:1, v/v), $25^{\circ}$ C	5	95
7	MGO-D-NH-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.02 g)/water/ethanol (4:1, v/v), $35^{\circ}$ C	5	95
8	MGO-D-NH-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.02 g)/toluene, 100°C	120	Trace
9	MGO-D-NH-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.02 g)/DMF, 100°C	120	40
10	MGO-D-NH-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.02 g)/ethanol, 25°C	5	80
11	MGO-D-NH-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.02 g)/water, 25°C	60	62

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**TABLE 2** Synthesis of tetrahydrobenzo[b]pyran derivatives catalysed by MGO-D-NH-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H

Entry	Ar	Time (min)	R	M.p. (found) (°C)	Yield (%)	M.p. (lit.) (°C)
4a	$C_6H_5$	5	CH <sub>3</sub>	227-228	95	228-230 <sup>[46]</sup>
4b	$2\text{-ClC}_6\text{H}_4$	4	CH <sub>3</sub>	217-219	95	217-219 <sup>[47]</sup>
4c	$3-ClC_6H_4$	5	CH <sub>3</sub>	223-225	94	224-225 <sup>[48]</sup>
4d	$4-ClC_6H_4$	4	CH <sub>3</sub>	207–209	96	209-211 <sup>[46]</sup>
4e	$2-O_2NC_6H_4$	4	CH <sub>3</sub>	223-225	97	224-226 <sup>[49]</sup>
4f	$4-O_2NC_6H_4$	3	CH <sub>3</sub>	173–175	98	174–176 <sup>[50]</sup>
4g	$4\text{-BrC}_6\text{H}_4$	4	CH <sub>3</sub>	205–207	93	203-205 <sup>[51]</sup>
4h	4-(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	6	CH <sub>3</sub>	206-208	94	206-208 <sup>[52]</sup>
4i	$4-H_3CC_6H_4$	6	CH <sub>3</sub>	215-217	90	216-218 <sup>[47]</sup>
4j	$4-CH_3OC_6H_4$	6	CH <sub>3</sub>	198-200	92	198–199 <sup>[47]</sup>
<b>4</b> k	$2-HOC_6H_4$	10	CH <sub>3</sub>	179–181	85	178-180 <sup>[53]</sup>
41	$4-HOC_6H_4$	6	CH <sub>3</sub>	209–211	90	210-212 <sup>[47]</sup>
4m	2-Furfural	6	CH <sub>3</sub>	200-202	88	201-203 <sup>[49]</sup>
4n	$C_6H_5$	5	Н	211-213	94	213-215 <sup>[49]</sup>
40	$2\text{-ClC}_6\text{H}_4$	4	Η	212–214	96	212-214 <sup>[49]</sup>
4p	$4-ClC_6H_4$	4	Н	222-225	96	224-226 <sup>[46]</sup>
4q	$2-O_2NC_6H_4$	4	Н	196–197	97	196–198 <sup>[49]</sup>
4r	$4-O_2NC_6H_4$	3	Н	230-232	98	230-232 <sup>[46]</sup>
4s	$4-H_3CC_6H_4$	6	Н	234–236	89	234-236 <sup>[54]</sup>
4t	$4-CH_3OC_6H_4$	6	Н	189–191	90	190–192 <sup>[49]</sup>
4u	$4-(CH_3)_2NC_6H_4$	5	Н	170–172	90	171-174 <sup>[52]</sup>
4v	$4-HOC_6H_4$	6	Н	232-235	88	234-236 <sup>[49]</sup>
4w	2-Furfural	6	Н	198–200	89	199-200 <sup>[49]</sup>

**TABLE 3** Synthesis of pyrano [2,3-d] pyrimidinones catalysed by MGO-D-NH-(CH2)4-SO3H

Entry	Ar	R <sup>1</sup>	Time (min)	X	M.p. (found) (°C)	Yield (%)	M.p. (lit.) (°C)
6a	$4-NCC_6H_4$	Н	4	0	254-256	96	254-256 <sup>[55]</sup>
6b	$4-O_2NC_6H_4$	Н	3	0	236-238	98	237-238 <sup>[55]</sup>
6c	$4-O_2NC_6H_4$	Н	5	S	234–236	92	235-236 <sup>[55]</sup>
6d	$4\text{-BrC}_6\text{H}_4$	Н	5	0	226-228	90	226-227 <sup>[56]</sup>
6e	$4\text{-BrC}_6\text{H}_4$	Н	6	S	234–236	89	236 <sup>[55]</sup>
6f	$4-F_3CC_6H_4$	Н	6	0	250-252	92	250-251 <sup>[55]</sup>
6g	$4-F_3CC_6H_4$	Н	6	S	239–241	88	239-240 <sup>[55]</sup>
6h	$C_6H_5$	Н	5	0	209–211	94	210-211 <sup>[56]</sup>
6i	$4\text{-}\mathrm{ClC}_6\mathrm{H}_4$	Н	5	0	214–216	92	214-215 <sup>[57]</sup>

(Continues)

#### **TABLE 3** (Continued)

Entry	Ar	R <sup>1</sup>	Time (min)	х	M.p. (found) (°C)	Yield (%)	M.p. (lit.) (°C)
6j	3-ClC <sub>6</sub> H <sub>4</sub>	Н	6	0	238-240	90	240-241 <sup>[55]</sup>
6k	$3-ClC_6H_4$	Н	6	S	235-236	89	237-238 <sup>[55]</sup>
61	$2\text{-}ClC_6H_4$	Н	5	0	214–216	93	214-215 <sup>[56]</sup>
6m	$C_6H_5$	$CH_3$	5	0	209–211	92	210 <sup>[58]</sup>
6n	$4-O_2NC_6H_4$	$CH_3$	4	0	211-213	96	212 <sup>[59]</sup>
60	$2\text{-}ClC_6H_4$	$CH_3$	6	0	238-240	92	238-239 <sup>[60]</sup>
6p	$4-ClC_6H_4$	$CH_3$	5	0	206–208	94	206-208 <sup>[61]</sup>
6q	$4-H_3CC_6H_4$	$CH_3$	6	0	220-222	90	221-223 <sup>[62]</sup>
6r	2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	$\mathrm{CH}_3$	7	0	209–211	91	209-210 <sup>[63]</sup>
6s	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub>	6	0	224–227	92	225-227 <sup>[64]</sup>

**TABLE 4** Comparison of MGO-D-NH- $(CH_2)_4$ -SO<sub>3</sub>H with some reported catalysts in the synthesis of tetrahydrobenzo[*b*]pyran and pyrano[2,3-*d*]pyrimidinone

Entry	Product	Conditions	Time (min)	Yield (%)
4a	CN CN O NH <sub>2</sub>	$\begin{split} NH_{4}H_{2}PO_{4}/Al_{2}O_{3}/EtOH/reflux^{[46]} \\ [PVPH]HSO_{4}/H_{2}O:EtOH (7:3), 80^{\circ}C^{[67]} \\ [DABCO-PDO][CH_{3}COO]/H_{2}O, 80^{\circ}C^{[68]} \\ [Ch][OH]/H_{2}O/reflux^{[69]} \\ H_{2}PO_{4}\text{-}SCMNPs/solvent-free, 80^{\circ}C^{[70]} \\ Fe_{3}O_{4}@Ph\text{-}SO_{3}H/H_{2}O/r.t./ultrasonic condition^{[71]} \\ MGO-D-NH-(CH_{2})_{4}\text{-}SO_{3}H/H_{2}O\text{-}EtOH (4:1), r.t. (this work) \end{split}$	15 10 15 120 20 25 5	86 96 95 96 92 95 95
6h		Diammonium hydrogen phosphate (10 mol %)/EtOH, r.t. <sup>[72]</sup> Na <sub>2</sub> SeO <sub>4</sub> (5 mol%)/EtOH, 120°C <sup>[73]</sup> Nano SiO <sub>2</sub> (20 mol%)/H <sub>2</sub> O, 90°C <sup>[74]</sup> MGO-D-NH-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H/H <sub>2</sub> O–EtOH (4:1), r.t. (this work)	120 180 20 5	81 85 94 94

MGO-D-NH- $(CH_2)_4$ -SO<sub>3</sub>H is highly efficient in minimizing the reaction time, performing at room temperature, increasing the product yield and elimination of hazardous solvent.

A plausible mechanism for the synthesis of tetrahydrobenzo[*b*]pyran and pyrano[2,3-*d*]pyrimidinone derivatives is outlined in Scheme 5. According to the reaction procedure, initially the MGO-D-NH-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H catalyst activates the carbonyl group of the aromatic aldehyde by H<sup>+</sup> of catalyst. Then, the Knoevenagel condensation of activated aromatic aldehyde with malononitrile is completed by the elimination of one H<sub>2</sub>O molecule forming arylidenemalononitrile. In the second step, the nucleophilic (Michael) addition of the enolizable 1,3-dicarbonyl compounds (**A** or **B**) to

arylidenemalononitrile creates intermediates C or D. Finally, tautomerization affords the corresponding products (tetrahydrobenzo[*b*]pyrans and pyrano[2,3-*d*] pyrimidinones).

#### 3.3 | Recycling of catalyst

One of the most significant advantages of a heterogeneous catalyst for industrial applications is reusability. A modest decrease in the catalytic activity as shown in Figure 5 after six runs was evident by the percentage yields of each recycle. These results indicate the reusability of MGO-D-NH-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H.





**FIGURE 5** Recyclability of MGO-D-NH- $(CH_2)_4$ -SO<sub>3</sub>H for synthesis of **4a** 

## 4 | CONCLUSIONS

With the aim of obtaining an efficient and low-cost hybrid catalyst, we have successfully synthesized MGO-

D-NH-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H nanoparticles by doublefunctionalization of MGO with PAMAM dendrimer and 1,4-butanesultone. The obtained heterogeneous catalyst shows some excellent properties such as very strong activity towards the synthesis of tetrahydrobenzo[b]pyrans and pyrano[2,3-d]pyrimidinones and sufficient durability in at least six consecutive reaction cycles without any notable activity loss, which indicate its promising potential for industrial applications.

#### ACKNOWLEDGEMENTS

The authors thank the Research Council of the University of Mazandaran and Hakim Sabzevari University for support of this work.

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How to cite this article: Alinezhad H, Tarahomi M, Maleki B, Amiri A. SO<sub>3</sub>H-functionalized nano-MGO-D-NH<sub>2</sub>: Synthesis, characterization and application for one-pot synthesis of pyrano[2,3-d] pyrimidinone and tetrahydrobenzo[b]pyran derivatives in aqueous media. *Appl Organometal Chem.* 2019;e4661. https://doi.org/10.1002/aoc.4661