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Article

Fe₃O₄@MCM-48-SO₃H: An efficient magnetically separable nanocatalyst for the synthesis of benzo[*f*]chromeno[2,3-*d*]pyrimidinones

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ABSTRACT

Sulfonic acid groups were grafted onto three different types of synthesized magnetic nanoparticles, namely Fe₃O₄, Fe₃O₄@SiO₂, and Fe₃O₄@MCM-48. The sulfonic acid-functionalized nanoparticles were evaluated as catalysts for the synthesis of 5-aryl-1*H*-benzo[*f*]chromeno[2,3-*d*]pyrimidine-2,4(3*H*,5*H*)-dione derivatives in terms of activity and recyclability. Their catalytic activities were compared with that of the homogeneous acid catalyst 1-methylimidazolium hydrogen sulfate ([HMIIm][HSO₄]). The activity of Fe₃O₄@MCM-48-SO₃H was comparable to those of the other heterogeneous and homogeneous catalysts.

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1. Introduction

Benzochromenopyrimidines are an important class of naturally occurring organic compounds. They have various uses, e.g., as dyes, fluorescent materials for visualization of biomolecules, and in laser techniques, because of their spectroscopic properties [1]. Recently, more attention has been focused on the synthesis of benzochromenopyrimidines, because of their interesting biological and pharmaceutical activities such as antiviral [2], antibacterial [3–6], and anticonvulsant [7] properties.

The development of functionalized magnetic nanoparticles (MNPs), which have large specific surface areas and good textural properties, is currently being extensively researched, and they have potential uses as catalysts, sorbents, and drug carriers [8–10].

The use of magnetic nanocomposites as heterogeneous catalysts is an interesting research area. Various types of transition metal-catalyzed reactions have been performed using catalytic sites grafted on MNPs, including C–C cross-coupling reactions [11–16], hydroformylation [17,18], hydrogenation [19–21], and polymerization [22] reactions. Other reports of MNP-supported catalysts include enzymes for carboxylate resolution [23], amino acids for ester hydrolysis [24], and organic amine catalysts that promote Knoevenagel and related reactions [25,26].

In this study, in a continuation of our previous work [8–10], we investigated 1-methylimidazolium hydrogen sulfate ([HMIIm][HSO₄]) as a homogeneous catalyst, and Fe₃O₄-SO₃H, Fe₃O₄@SiO₂-SO₃H, and Fe₃O₄@MCM-48-SO₃H magnetic nanocomposites with high densities of sulfonic acid (SO₃H) groups

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as heterogeneous catalysts. We synthesized functionalized magnetite nanoparticles, and then investigated their performances as novel strong, recoverable, and stable catalysts for synthesis of benzochromenopyrimidines.

2. Experimental

2.1. Preparation of catalysts

All chemicals, i.e., $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, tetraethyl orthosilicate (TEOS), NaOH, NaF, and $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$, were high purity and purchased from Fluka (Buchs, Switzerland) and Merck (Darmstadt, Germany).

Fe_3O_4 and $\text{Fe}_3\text{O}_4\text{-SO}_3\text{H}$ MNPs were synthesized using the methods described in the literature [9,27].

The $\text{Fe}_3\text{O}_4@\text{SiO}_2$ MNPs were synthesized using a modified version of the method described in the literature [28]. $\text{Fe}_3\text{O}_4@\text{SiO}_2$ was functionalized with SO_3H groups by adding $\text{Fe}_3\text{O}_4@\text{SiO}_2$ (2.0 g) to an aqueous solution of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ (20 mL, 0.7 g, 5 mmol) and sonicating at 25 °C for 1 min. The mixture was stirred for 30 min to allow the NaHSO_4 to adsorb onto the MNPs. Finally, the water was removed and the powder was dried in an oven at 90 °C for 2.0 h, to give solid sulfonic acid-functionalized silica MNPs ($\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$).

$\text{Fe}_3\text{O}_4@\text{MCM-48}$ was synthesized by mixing Fe_3O_4 MNPs (1.5 g) and ammonia solution (5 mL) with distilled water (50 mL) in a glass reactor and sonicating for 2 min at 40 °C. After mixing, TEOS (10 mL), NaOH (0.9 g), and NaF (0.19 g) were added and the mixture was stirred for 2 h. Cetyltrimmonium bromide (7.0 g) was added to the mixture. The mixture was stirred at 40 °C for 2 h. The magnetic composite was then hydrothermally treated at 120 °C for 48 h in an autoclave. After 2 d, the resultant solid was filtered, washed with distilled water and dried at 60 °C. Finally, the template was removed by calcination of the synthesized particles for 3 h at 300 °C.

$\text{Fe}_3\text{O}_4@\text{MCM-48}$ was functionalized with SO_3H groups by adding the prepared mesoporous $\text{Fe}_3\text{O}_4@\text{MCM-48}$ nanoparticles (1.5 g) to an aqueous solution of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ (20 mL, 0.7 g, 5 mmol) and sonicating at 25 °C for 1 min. The mixture was stirred for 30 min to allow the NaHSO_4 to adsorb onto the mesoporous MNPs. Finally, the water was removed and the powder was dried in an oven at 90 °C for 2 h. A brown solid, i.e., sulfonic acid-functionalized MCM-48 mesoporous MNPs ($\text{Fe}_3\text{O}_4@\text{MCM-48-SO}_3\text{H}$), was obtained.

[Hmim][HSO_4] was synthesized according to procedure described in the literature [10].

2.2. Characterization

The crystal phases and crystallinities of the synthesized MNPs were determined by X-ray diffraction (XRD; X-PERTPRO X-ray diffractometer, PANalytical), using $\text{Cu-K}\alpha$ radiation, in the 2θ range 1.5°–70°. The qualities and compositions of the synthesized nanoparticles were determined using Fourier-transform infrared (FT-IR) spectroscopy (Shimadzu FT-IR-470) in the range of 400–4000 cm^{-1} . The sizes and morphologies of the particles were studied using transmission

electron microscopy (TEM; CM10 HT, Philips, 100 kV). The ultraviolet-visible (UV-Vis) absorption behavior of the synthesized MNPs was characterized using diffuse reflectance spectroscopy (DRS; S-4100, Sinco). Melting points (m.p.) were measured in open capillary tubes using an Electro-thermal IA 9100 melting-point apparatus. FT-IR spectra of the synthesized compounds were obtained with an FT-IR 8600 spectrometer, using KBr pellets. ^1H and ^{13}C NMR spectra were obtained at 500 and 100 MHz, using a Bruker 400 DRX Avance instrument. Elemental analysis were carried out using a Thermo Finnigan Flash EA 1112 series instrument. Separation of the magnetite nanoparticles from the reaction mixture was performed using an Nd-Fe-B super-magnet ($10 \times 5 \times 4 \text{ cm}^3$, 1.4 T).

2.3. General procedure for synthesis of 5-aryl-1H-benzo[f]chromeno[2,3-d]pyrimidine-2,4(3H,5H)-diones **4a–4j**

Method A. A mixture of an aryl aldehyde (1 mmol), β -naphthol (1 mmol), barbituric acid (1.2 mmol), and $\text{Fe}_3\text{O}_4@\text{MCM-48-SO}_3\text{H}$ was stirred at room temperature under solvent-free conditions. The reaction products were monitored using thin-layer chromatography (TLC). After completion of the reaction, the mixture was triturated with ethanol. The magnetic nanocomposites were then separated in the presence of a magnetic stirring bar; the reaction mixture became clear. The crude products were recrystallized from ethanol to give pure products.

Method B. A mixture of an aryl aldehyde (1 mmol), β -naphthol (1 mmol), barbituric acid (1.2 mmol), and [Hmim][HSO_4] (50 mol%) was heated at 120 °C for a certain time. After completion of the reaction, indicated by TLC, the reaction mixture was cooled to room temperature. Distilled water (5 mL) was added to the beaker and the mixture was stirred. The obtained precipitate was filtered off. The crude product was recrystallized from ethanol and dried to afford powders.

The structures of all products were confirmed using IR, ^1H NMR, and ^{13}C NMR spectroscopies.

2.4. Spectroscopic data for **4a–4j**

5-Phenyl-1H-benzo[f]chromeno[2,3-d]pyrimidine-2,4(3H,5H)-dione (**4a**). m.p.: 355–357 °C; IR (KBr, cm^{-1}): 1265, 1645, 1718, 3026, 3174; ^1H NMR (400 MHz, DMSO): δ 5.58 (s, 1H), 7.08 (t, J = 7.2 Hz, 1H), 7.19 (t, J = 7.6 Hz, 2H), 7.30 (d, J = 7.6 Hz, 2H), 7.43 (d, J = 8.8 Hz, 1H), 7.46–7.51 (m, 2H), 7.92–8.01 (m, 3H), 11.06 (s, 1H, NH), 12.09 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO): δ 35.0, 90.2, 117.1, 117.5, 124.1, 125.7, 126.8, 127.8, 128.5, 128.6, 129.0, 130.0, 130.8, 131.6, 145.0, 147.1, 150.0, 153.8, 163.5; Anal. Calcd. for $\text{C}_{21}\text{H}_{14}\text{N}_2\text{O}_3$: C 73.68, H 4.12, N 8.18; Found: C 73.95, H 4.05, N 8.34.

5-(2-Chlorophenyl)-1H-benzo[f]chromeno[2,3-d]pyrimidine-2,4(3H,5H)-dione (**4b**). m.p.: 375–377 °C; IR (KBr, cm^{-1}): 1236, 1647, 1706, 2927, 3035, 3164, 3454; ^1H NMR (400 MHz, DMSO): δ 5.85 (s, 1H), 7.12 (t, J = 7.6 Hz, 1H), 7.18 (t, J = 7.4 Hz, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.39 (d, J = 8.8 Hz, 1H), 7.44 (t, J = 7.5 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.93

(d, $J = 8.4$ Hz, 1H), 7.96 (d, $J = 9.2$ Hz, 1H), 8.06 (d, $J = 8.4$ Hz, 1H), 11.01 (s, 1H, NH), 12.09 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO): δ 33.6, 89.0, 116.5, 117.1, 123.7, 125.7, 127.8, 128.7, 129.2, 130.1, 130.4, 131.1, 131.5, 132.5, 132.6, 141.7, 147.2, 150.0, 154.0, 163.2; Anal. Calcd. for $\text{C}_{21}\text{H}_{13}\text{ClN}_2\text{O}_3$: C 66.94, H 3.48, N 7.43; Found: C 66.73, H 3.39, N 7.30.

5-(4-Chlorophenyl)-1*H*-benzo[*f*]chromeno[2,3-*d*]pyrimidine-2,4(3*H*,5*H*)-dione (**4c**). m.p.: 362–364 °C; IR (KBr, cm^{-1}): 1226, 1647, 1706, 2970, 3074, 3157, 3371; ^1H NMR (400 MHz, DMSO): δ 5.60 (s, 1H), 7.25 (d, $J = 7.6$ Hz, 2H), 7.32 (d, $J = 7.6$ Hz, 2H), 7.42 (d, $J = 6.8$ Hz, 1H), 7.43–7.52 (m, 2H), 7.93–7.99 (m, 3H), 11.09 (s, 1H, NH), 12.12 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO): δ 34.5, 89.7, 116.9, 117.1, 124.0, 125.8, 127.9, 128.6, 129.1, 130.0, 130.4, 130.7, 131.4, 131.7, 143.9, 147.1, 150.0, 153.8, 163.5; Anal. Calcd. for $\text{C}_{21}\text{H}_{13}\text{ClN}_2\text{O}_3$: C 66.94, H 3.48, N 7.43; Found: C 67.13, H 3.75, N 7.37.

5-(4-Bromophenyl)-1*H*-benzo[*f*]chromeno[2,3-*d*]pyrimidine-2,4(3*H*,5*H*)-dione (**4d**). m.p.: 297–299 °C; IR (KBr, cm^{-1}): 1271, 1643, 1706, 2997, 3124; ^1H NMR (400 MHz, DMSO): δ 5.58 (s, 1H), 7.26 (d, $J = 8.4$ Hz, 2H), 7.37 (d, $J = 8.4$ Hz, 2H), 7.41–7.51 (m, 3H), 7.93–7.98 (m, 3H), 11.10 (s, 1H, NH), 12.12 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO): δ 34.6, 89.6, 116.8, 117.1, 120.0, 124.0, 125.8, 127.9, 129.1, 130.3, 130.5, 130.7, 130.8, 131.7, 144.3, 147.0, 150.0, 153.8, 163.5; Anal. Calcd. for $\text{C}_{21}\text{H}_{13}\text{BrN}_2\text{O}_3$: C 59.88, H 3.11, N 6.65; Found: C 59.61, H 2.86, N 6.69.

5-(4-Methylphenyl)-1*H*-benzo[*f*]chromeno[2,3-*d*]pyrimidine-2,4(3*H*,5*H*)-dione (**4e**). m.p.: 353–355 °C; IR (KBr, cm^{-1}): 1265, 1645, 1712, 3176, 3444; ^1H NMR (400 MHz, DMSO): δ 2.15 (s, 3H), 5.53 (s, 1H), 6.99 (d, $J = 7.8$ Hz, 2H), 7.18 (d, $J = 7.8$ Hz, 2H), 7.40 (d, $J = 8.8$ Hz, 1H), 7.42–7.51 (m, 2H), 7.95 (t, $J = 9.6$ Hz, 2H), 7.99 (d, $J = 8.4$ Hz, 1H), 11.06 (s, 1H, NH), 12.05 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO): δ 20.9, 34.6, 90.3, 117.1, 117.6, 124.1, 125.7, 127.7, 128.4, 129.0, 129.2, 130.0, 130.8, 131.6, 135.9, 142.1, 147.0, 150.0, 153.7, 163.5; Anal. Calcd. for $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_3$: C, 74.15; H, 4.53; N, 7.86. Found: C 74.44, H 4.78, N 7.69.

5-(3-Nitrophenyl)-1*H*-benzo[*f*]chromeno[2,3-*d*]pyrimidine-2,4(3*H*,5*H*)-dione (**4f**). m.p.: 371–373 °C; IR (KBr, cm^{-1}): 1232, 1641, 1710, 3224, 3398; ^1H NMR (400 MHz, DMSO): δ 5.81 (s, 1H), 7.44–7.52 (m, 4H), 7.75 (d, $J = 8.4$ Hz, 1H), 7.95–8.01 (m, 3H), 8.03 (d, $J = 9.2$ Hz, 1H), 8.19 (t, $J = 2.0$ Hz, 1H), 11.11 (s, 1H, NH), 12.18 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO): δ 34.8, 89.2, 116.1, 117.2, 122.1, 123.1, 124.1, 125.9, 128.1, 129.1, 130.2, 130.6, 130.7, 131.7, 135.2, 147.2, 148.0, 149.9, 154.0, 163.5; Anal. Calcd. for $\text{C}_{21}\text{H}_{13}\text{N}_3\text{O}_5$: C 65.12, H 3.38, N 10.85; Found: C 65.04, H 3.63, N 10.26.

5-(4-Nitrophenyl)-1*H*-benzo[*f*]chromeno[2,3-*d*]pyrimidine-2,4(3*H*,5*H*)-dione (**4g**). m.p.: 371–373 °C; IR (KBr, cm^{-1}): 1236, 1668, 1708, 2945, 3064, 3276; ^1H NMR (400 MHz, DMSO): δ 5.75 (s, 1H), 7.42–7.50 (m, 3H), 7.60 (d, $J = 8.4$ Hz, 2H), 7.94 (t, $J = 7.2$ Hz, 2H), 7.99 (d, $J = 9.2$ Hz, 1H), 8.04 (d, $J = 8.4$ Hz, 2H), 11.24 (s, 1H, NH), 12.14 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO): δ 35.1, 89.0, 116.1, 117.2, 123.8, 123.9, 125.9, 128.0, 129.1, 129.9, 130.6, 131.7, 146.4, 147.1, 150.0, 152.2, 154.1, 163.5; Anal. Calcd. for $\text{C}_{21}\text{H}_{13}\text{N}_3\text{O}_5$: C 65.12, H 3.38, N 10.85; Found: C 64.83, H 3.64, N 10.50.

5-(2-Methoxyphenyl)-1*H*-benzo[*f*]chromeno[2,3-*d*]pyrimidine-

2,4(3*H*,5*H*)-dione (**4h**). m.p.: 357–359 °C; IR (KBr, cm^{-1}): 1249, 1649, 1708, 3396; ^1H NMR (400 MHz, DMSO): δ 3.74 (s, 3H), 5.75 (s, 1H), 6.82 (t, $J = 7.4$ Hz, 1H), 6.89 (d, $J = 7.6$ Hz, 1H), 7.08 (t, $J = 7.8$ Hz, 1H), 7.32 (d, $J = 7.0$ Hz, 1H), 7.37 (d, $J = 9.2$ Hz, 1H), 7.42 (t, $J = 7.5$ Hz, 1H), 7.49 (t, $J = 7.7$ Hz, 1H), 7.90 (d, $J = 8.8$ Hz, 2H), 8.17 (d, $J = 8.4$ Hz, 1H), 10.94 (s, 1H, NH), 11.98 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO): δ 30.8, 56.4, 89.1, 112.7, 116.9, 117.5, 120.9, 123.9, 125.4, 127.5, 128.3, 128.9, 129.5, 131.0, 131.2, 131.4, 132.7, 147.3, 150.1, 154.4, 157.1, 163.3; Anal. Calcd. for $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_4$: C 70.96, H 4.33, N 7.52; Found: C 70.78, H 4.79, N 7.75.

5-(3-Methoxyphenyl)-1*H*-benzo[*f*]chromeno[2,3-*d*]pyrimidine-2,4(3*H*,5*H*)-dione (**4i**). m.p.: 308–310 °C; IR (KBr, cm^{-1}): 1263, 1647, 1712, 3190; ^1H NMR (400 MHz, DMSO): δ 3.65 (s, 3H), 5.57 (s, 1H), 6.68 (dd, $J = 2.4, 6.4$ Hz, 1H), 6.77 (d, $J = 8.2$ Hz, 1H), 6.91 (t, $J = 2$ Hz, 1H), 7.09 (t, $J = 7.8$ Hz, 1H), 7.41 (d, $J = 8.8$ Hz, 1H), 7.43–7.53 (m, 2H), 7.94 (d, $J = 8.2$ Hz, 1H), 7.97 (d, $J = 9.2$ Hz, 1H), 8.02 (d, $J = 8.4$ Hz, 1H), 11.07 (s, 1H, NH), 12.08 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO): δ 34.9, 55.3, 90.1, 111.5, 115.1, 117.1, 117.4, 120.6, 124.1, 125.7, 127.8, 129.0, 129.7, 130.1, 130.8, 146.5, 147.1, 150.0, 153.8, 159.4, 163.5; Anal. Calcd. for $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_4$: C 70.96, H 4.33, N 7.52; Found: C 70.74, H 4.65, N 7.75.

5-(4-Methoxyphenyl)-1*H*-benzo[*f*]chromeno[2,3-*d*]pyrimidine-2,4(3*H*,5*H*)-dione (**4j**). m.p.: 313–315 °C; IR (KBr, cm^{-1}): 1249, 1660, 1710, 2925, 3008, 3425; ^1H NMR (400 MHz, DMSO): δ 3.62 (s, 3H), 5.53 (s, 1H), 6.74 (d, $J = 8.8$ Hz, 2H), 7.20 (d, $J = 8.8$ Hz, 2H), 7.40 (d, $J = 9.2$ Hz, 1H), 7.42–7.51 (m, 2H), 7.92 (t, $J = 8.8$ Hz, 2H), 7.99 (d, $J = 8.0$ Hz, 1H), 11.05 (s, 1H, NH), 12.05 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO): δ 34.2, 55.3, 90.4, 114.0, 117.1, 117.7, 124.1, 125.7, 127.7, 129.0, 129.5, 129.9, 130.8, 131.7, 137.2, 147.0, 150.0, 153.6, 158.1, 163.5; Anal. Calcd. for $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_4$: C 70.96, H 4.33, N 7.52; Found: C 70.17, H 4.52, N 7.65.

3. Results and discussion

3.1. Characterization of synthesized MNPs

Magnetite nanoparticles (Fe_3O_4) of average diameter 9.0 nm were prepared by chemical coprecipitation. MCM-48 MNPs and silica-coated MNPs were prepared in two steps: (1) preparation of colloidal Fe_3O_4 MNPs and (2) development of an MCM-48 mesoporous structure and silica layer on the MNP surfaces. NaHSO_4 was used as the sulfonating agent for the synthesis of $\text{Fe}_3\text{O}_4@\text{MCM-48-SO}_3\text{H}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2-\text{SO}_3\text{H}$ nanoparticles. In the preparation of $\text{Fe}_3\text{O}_4-\text{SO}_3\text{H}$ MNPs, the sulfonic groups were directly coated on the MNP backbones. The new synthesized nanoparticles and the solid acid catalysts were characterized using FT-IR spectroscopy, XRD, UV-Vis DRS, TEM, vibrating sample magnetometry, and titration.

XRD patterns of the bare MNPs, $\text{Fe}_3\text{O}_4@\text{MCM-48}$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2$ are shown in Fig. 1. The MNP patterns have peaks at $2\theta = 29.72^\circ$, 35.57° , 43.17° , 57.15° , and 62.77° , identical to those of pure magnetite, which XRD is consistent with that for spinal magnetite reported in the literature [29]. The XRD patterns of the mesoporous MNPs have (1) four peaks, at $2\theta =$

Fig. 1. XRD patterns of Fe_3O_4 MNPs, $\text{Fe}_3\text{O}_4@\text{MCM-48}$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2$.

Fig. 2. UV-Vis DR spectra of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{MCM-48-SO}_3\text{H}$.

1.5° – 10° , for (211), (220), (420), and (332) reflections, which are characteristic peaks of the MCM-48 siliceous mesoporous structure; and (2) peaks similar to those of MNPs, indicating the presence of magnetite in the caves of the synthesized composites.

The same peaks were observed in the bare and silica-coated magnetite nanoparticles, indicating retention of the crystalline spinel magnetite core structure during the silica-coating process. The broad peak at $2\theta = 20^\circ$ – 30° is consistent with an amorphous silica phase in the shell of the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ [30].

Figure 2 shows the UV-Vis DR spectra of the synthesized Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{MCM-48-SO}_3\text{H}$ MNPs. The MNPs have peaks

Fig. 4. Magnetic hysteresis curves of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{MCM-48}$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2$.

at 250 nm; this indicates that the synthesized Fe_3O_4 was pure. The same peaks were observed for all particles. The results indicate the presence of a magnetic core in all the MNP syntheses.

The TEM images of the prepared sulfonated MNPs are shown in Fig. 3. The bare sulfonated MNPs show aggregation of MNPs, roughly 9.0 nm in diameter. The images of the sulfonic acid-functionalized silica and MCM-48-coated magnetite nanoparticles show dark MNP cores surrounded by lighter amorphous silica shells of particle diameter about 12 nm.

It is important that the synthesized nanocatalysts have sufficient magnetic and super-paramagnetic properties for use in magnetic carrier techniques. The magnetic hysteresis curves of the MNPs are shown in Fig. 4. The Fe_3O_4 MNPs and $\text{Fe}_3\text{O}_4@\text{MCM-48}$ MNPs showed typical super-paramagnetic behavior. The saturation magnetizations of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, and $\text{Fe}_3\text{O}_4@\text{MCM-48}$ MNPs were 82, 60, and 50 emu/g respectively; these are sufficiently high for magnetic separation using a conventional magnet.

The FT-IR spectra of Fe_3O_4 , $\text{Fe}_3\text{O}_4\text{-SO}_3\text{H}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$, $\text{Fe}_3\text{O}_4@\text{MCM-48}$, and $\text{Fe}_3\text{O}_4@\text{MCM-48-SO}_3\text{H}$ confirmed the structures of the synthesized nanoparticles (Fig. 5). For the bare MNPs, the peak at $\sim 575\text{ cm}^{-1}$ is attributed to the Fe–O band vibration of Fe_3O_4 . The band at 1085 cm^{-1} for the MCM-48-coated nanoporous particles, corresponding to Si–O–Si antisymmetric stretching vibrations, shows the presence of SiO_2 in the nanoparticles. The FT-IR spectra of the mesoporous-coated MNPs before and after calcination confirm the removal of the surfactant template. According to previous

Fig. 3. TEM images of $\text{Fe}_3\text{O}_4@\text{SO}_3\text{H}$ (a), $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$ (b), and $\text{Fe}_3\text{O}_4@\text{MCM-48-SO}_3\text{H}$ (c).

Fig. 5. FT-IR spectra of $\text{Fe}_3\text{O}_4\text{-SO}_3\text{H}$ (1), $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$ (2), and $\text{Fe}_3\text{O}_4@\text{MCM-48-SO}_3\text{H}$ (3).

studies, the stretching and bending vibrations of O–H bonds can be observed at ~ 3500 and 1647 cm^{-1} , respectively. Also, the external vibrations of SiO_4 chains can be observed at ~ 1222 and 789 cm^{-1} ; there are vibrations at 962 cm^{-1} from asymmetric Si–O vibrations adjacent to silanol groups, at 580 cm^{-1} from the presence of double-ring vibrations, and at 454 cm^{-1} from angular bending of Si–O units [31,32]. Fe_3O_4 usually shows bands at ~ 570 and 430 cm^{-1} , from Fe–O vibrations at tetrahedral and octahedral sites, respectively [33]. In the case of $\text{Fe}_3\text{O}_4@\text{MCM-48-SO}_3\text{H}$, the sulfonic acid bond vibrations can be observed at $\sim 1200\text{--}1250$, $1010\text{--}1100$, and 650 cm^{-1} , and are attributed to the O=S=O asymmetric and symmetric stretching vibrations and S–O stretching vibration of $\text{-SO}_3\text{H}$, respectively. The increase in the intensities of the bands at $3000\text{--}3500\text{ cm}^{-1}$ suggests that there are more OH groups under the surfaces of mesoporous MNPs after sulfonation. In contrast, the band at $\sim 3360\text{ cm}^{-1}$ became much broader (Fig. 5). All these observations confirm that the MNP surfaces were functionalized with sulfonic groups.

The amounts of sulfonic acid groups on the functionalized MNPs, determined by neutralization titrations, were $1.90\text{--}3.25\text{ mmol/g}$ (Table 1). This means an effective density of acid sites. These results confirm the synthesis of MNPs functionalized with $\text{-SO}_3\text{H}$ groups and functioning as strong solid acid catalysts.

3.2. Method development

The prepared $\text{-SO}_3\text{H}$ -functionalized MNPs, and 1-methylimidazolium hydrogen sulfate, which is a Brönsted acid

Table 1

Amounts of sulfonic acid groups on functionalized MNPs.

Catalyst	Amounts of sulfonic acid groups (mmol/g)
$\text{Fe}_3\text{O}_4\text{-SO}_3\text{H}$	1.90–1.95
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$	2.80–2.82
$\text{Fe}_3\text{O}_4@\text{MCM-48-SO}_3\text{H}$	3.20–3.25

ionic liquid, were tested as catalysts in the synthesis of benzochromenopyrimidine derivatives (Scheme 1). This reaction is important in organic synthesis because of the broad applications of these compounds in various fields [34–43].

In the preliminary stage of investigation, we focused on the systematic evaluation of different catalysts for the model reaction of β -naphthol (1), benzaldehyde (2a), and barbituric acid (3) under solvent-free conditions. The synthesized solid acid catalysts, i.e., $\text{Fe}_3\text{O}_4\text{-SO}_3\text{H}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$, and $\text{Fe}_3\text{O}_4@\text{MCM-48-SO}_3\text{H}$, and the homogeneous catalyst $[\text{HMI}][\text{HSO}_4]$, were used to synthesize 5-phenyl-1*H*-benzo[*f*]chromeno[2,3-*d*]pyrimidine-2,4(3*H*,5*H*)-dione (4a). The reaction with $[\text{HMI}][\text{HSO}_4]$ gave only low yields of the products, even with prolonged reaction times and high temperatures. The catalytic performances of $\text{Fe}_3\text{O}_4\text{-SO}_3\text{H}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$ were similar. The catalytic performance of the $\text{Fe}_3\text{O}_4@\text{MCM-48-SO}_3\text{H}$ MNPs was better than those of the other catalysts under the same conditions. This is probably because of the high surface area and the high density of sulfonic acid groups on the MNPs (Table 2).

The amount of catalyst had a major effect on the synthesis. The results achieved using various amounts of $\text{Fe}_3\text{O}_4@\text{MCM-48-SO}_3\text{H}$ (Table 2, entries 7–10) show that the product yield ranged from 70% to 95%; 0.05 g of

Table 2

Effect of various homogeneous and heterogeneous catalysts in synthesis of benzochromenopyrimidine 4a.

Entry	Catalyst	T (°C)	Time (min)	Isolated yield (%)
1	$[\text{HMI}][\text{HSO}_4]$ (25 mol%)	120	45	72
2	$[\text{HMI}][\text{HSO}_4]$ (50 mol%)	120	45	90
3	$[\text{HMI}][\text{HSO}_4]$ (75 mol%)	120	45	89
4	$[\text{HMI}][\text{HSO}_4]$ (50 mol%)	25	120	—
5	$\text{Fe}_3\text{O}_4\text{-SO}_3\text{H}$ (0.05 g)	25	40	80
6	$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$ (0.05 g)	25	33	82
7	$\text{Fe}_3\text{O}_4@\text{MCM-48-SO}_3\text{H}$ (0.05 g)	25	25	95
8	$\text{Fe}_3\text{O}_4@\text{MCM-48-SO}_3\text{H}$ (0.1 g)	25	25	88
9	$\text{Fe}_3\text{O}_4@\text{MCM-48-SO}_3\text{H}$ (0.025 g)	25	45	77
10	$\text{Fe}_3\text{O}_4@\text{MCM-48-SO}_3\text{H}$ (0.0125 g)	25	80	70

Reaction conditions: β -Naphthol (1mmol), barbituric acid (1.2 mmol) and benzaldehyde (1 mmol), solvent-free.

Scheme 1. Synthesis of benzochromenopyrimidines.

Table 3

Comparison of catalytic activities of $\text{Fe}_3\text{O}_4\text{@MCM-48-SO}_3\text{H}$ and $[\text{HMIIm}][\text{HSO}_4]$ in synthesis of benzochromenopyrimidines **4a–4j**.

Product	R	Method A ^a		Method B ^b		m.p. (°C)
		Time (min)	Yield (%)	Time (min)	Yield (%)	
4a	H	25	95	40	90	355–357
4b	2-Cl	18	87	50	81	375–377
4c	4-Cl	18	98	45	89	362–364
4d	4-Br	20	94	40	92	297–299
4e	4-Me	25	89	40	75	353–355
4f	3-NO ₂	18	92	50	79	371–373
4g	4-NO ₂	18	90	40	88	371–373
4h	2-OMe	22	85	60	75	357–359
4i	3-OMe	25	88	30	81	308–310
4j	4-OMe	25	86	50	79	313–315

Reaction conditions: β -Naphthol (1 mmol), barbituric acid (1.2 mmol) and aryl-aldehyde (1 mmol) in presence of ^a $\text{Fe}_3\text{O}_4\text{@MCM-48-SO}_3\text{H}$ (0.05 g) at room temperature or ^b $[\text{HMIIm}][\text{HSO}_4]$ (50 mol%) at 120 °C.

$\text{Fe}_3\text{O}_4\text{@MCM-48-SO}_3\text{H}$ were therefore used to catalyze the synthesis of benzochromenopyrimidine derivatives.

In this study, we used sulfonic acid-functionalized MNPs, i.e., $\text{Fe}_3\text{O}_4\text{@MCM-48-SO}_3\text{H}$, as a heterogeneous solid acid catalyst, and $[\text{HMIIm}][\text{HSO}_4]$ as a homogeneous acid catalyst, for the synthesis of new benzochromenopyrimidines from the reactions of various aromatic aldehydes with β -naphthol and barbituric acid. A comparison of their catalytic performances is shown in Table 3. It shows that when the reactions were carried out in the presence of $\text{Fe}_3\text{O}_4\text{@MCM-48-SO}_3\text{H}$, the desired products **4a–4j** were obtained at room temperature, with better yields, and considerably shorter reaction times.

Under the optimum conditions, the electronic nature of the substituent on the aromatic ring had no significant effect on the conversion. However, as indicated in Table 3, aromatic aldehydes with electron-withdrawing groups reacted faster than did aromatic aldehydes with electron-releasing groups. The reaction with aliphatic aldehydes did not give significant amounts of products, even with prolonged reaction times.

The following mechanism for this condensation is proposed based on the above results. The catalyst $\text{Fe}_3\text{O}_4\text{@MCM-48-SO}_3\text{H}$ activates the carbonyl of the aromatic aldehyde via bonding between the carbonyl group and the sulfonic acid group of the nanocatalyst, and this decreases the energy of the transition state. The reaction proceeds via a cascade of condensation reactions involving the formation of intermediate **7**, which is formed in situ by reaction of β -naphthol (**1**) with the activated carbonyl group of the aromatic aldehyde. Intermediate **7** reacts with barbituric acid to give intermediate **8**. This intermediate undergoes cyclocondensation and dehydration to afford the corresponding products **4** (Scheme 2).

It is important to note that because of its super-paramagnetic properties, $\text{Fe}_3\text{O}_4\text{@MCM-SO}_3\text{H}$ can be easily separated from reaction mixture and reused. After completion of the reaction, the catalyst was separated using a permanent magnet. After washing and drying in air, the $\text{Fe}_3\text{O}_4\text{@MCM-48-SO}_3\text{H}$ can be reused directly, without deactivation, even after five cycles. Under the same conditions, the reusability of the $\text{Fe}_3\text{O}_4\text{@MCM-48-SO}_3\text{H}$ MNPs was better than those of the other catalysts (Table 4).

Scheme 2. Proposed mechanism for synthesis of 5-aryl-1H-benzo[f]chromeno[2,3-d]pyrimidine-2,4(3H,5H)-diones.

Table 4

Isolated yield of **4c** over reuse of magnetic catalysts.

Run	Isolated yield of 4c (%)		
	$\text{Fe}_3\text{O}_4\text{-SO}_3\text{H}$	$\text{Fe}_3\text{O}_4\text{@SiO}_2\text{-SO}_3\text{H}$	$\text{Fe}_3\text{O}_4\text{@MCM-48-SO}_3\text{H}$
1	95	98	98
2	90	98	98
3	70	90	97
4	60	90	97
5	55	88	96

Reaction conditions: β -Naphthol (1mmol), barbituric acid (1.2 mmol) and 4-chloro-benzaldehyde (1 mmol) solvent-free, room temperature.

4. Conclusions

$\text{Fe}_3\text{O}_4\text{@MCM-48-SO}_3\text{H}$ efficiently catalyzed the one-pot, three-component condensation of β -naphthol, barbituric acid, and an aromatic aldehyde for the synthesis of new derivatives of 5-aryl-1H-benzo[f]chromeno[2,3-d]pyrimidine-2,4(3H,5H)-dione. This catalyst is thermally stable, green, recyclable, inexpensive, and easy to prepare. In addition, it can be easily separated from the reaction mixture and recycled up to five times without any significant impact on its activity or the reaction yield. The operational simplicity, high yields, and facile work-up procedures associated with this catalytic process give it advantages over other methods.

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Graphical Abstract

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Fe₃O₄@MCM-48-SO₃H: An efficient magnetically separable nanocatalyst for the synthesis of benzo[*j*]chromeno[2,3-*d*]pyrimidinones

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Three types of magnetite nanoparticles, i.e., Fe₃O₄-SO₃H, Fe₃O₄@SiO₂-SO₃H, and Fe₃O₄@MCM-48-SO₃H, were synthesized and evaluated as catalysts in the synthesis of 5-aryl-1*H*-benzo[*j*]chromeno[2,3-*d*]pyrimidine-2,4(3*H*,5*H*)-dione derivatives in terms of activity and recyclability. Their catalytic activities were compared with that of 1-methylimidazolium hydrogen sulfate.

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