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FULL PAPER

Functionalized $CoFe_2O_4$/lamellar mesopore silica anchored to melamine nanocomposite as a novel catalyst for synthesis of 4*H*-chromenes under mild conditions

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In this research, it was displayed an efficient method for the one-pot reaction of cyclohexanone, benzaldehyde and malononitrile for the synthesis of 4H-chromenes by using $CoFe_2O_4$/lamellar mesopore silica anchored to melamine as a magnetic nanocatalyst. This nanocatalyst was prepared in several steps and discriminated by XRD, FT-IR, SEM, VSM, TGA and BET techniques. The catalyst has a large active base site that has functionalized in both the surface and the pore of nanostructure. The advantages of magnetic nanocatalyst were simple accessible, heterogeneous nanocatalyst, easy work up and reusability. The various derivatives of 4H-chromenes were synthesized in the presence of $CoFe_2O_4$/lamellar mesopore silica/melamine magnetic nanocatalyst with the excellent yields and appropriate times. The products were identified by the melting point, FT-IR, ^{1}H NMR, ^{13}C NMR and C.H.N techniques.

KEYWORDS

4H-Chromene, cyclohexanone, lamellar, Malononitrile, Mesopore silica

1 | INTRODUCTION

The chromene compounds have the significant biological properties,[1] for example, anticancer,[2,3] anticonvulsant,[4] antibacterial,[5] antimicrobial,[6] antimalarial,[7] anti-influenza[8] and anti-virus[9] activities. One of the chromene derivatives is tetrahydro-4H-chromenes.[10] Also, tetrahydro-4H-chromenes can be applied as cognitive enhances, for the cure of neurodegenerative illnesses,[11] counting Huntington's disease,[12] amyotrophic lateral sclerosis[13] and Alzheimer's disease,[14] Parkinson's disease[15] and that also use for improving schizophrenia.[16] The typical process to synthesize the tetrahydro-4H-chromene derivatives is commonly a two-step reaction between a Michael acceptor and carbonyl compounds in the attendance of a catalyst.[17–20] Several multi-component reactions have been defined for the synthesis of different tetrahydro-4H-chromenes through condensation of an aldehyde, cyclic ketone and malononitrile in the attendance of various organic and inorganic catalysts.[21,22]

Surfactant-template mesoporous silicate obtains the wide application in catalysis,[23,24] drug delivery,[25,26] gas filtration,[27,28] sensors[29] and also as nano-sized quantum materials.[30] The large-area of mesoporous silicate caused applications in optical coatings and functionalization to catalytically processes.[31] The bulk mesophase managed with the silica-to-surfactant ratio and formation of cubic, lamellar, hexagonal, that this phase due to silica/surfactant self-assembly and so charge matching at the interface.[32] Recently, the heterogeneous[33–36] catalysts were used to synthesis of organic compounds because of high activity and recoverability.[37–41] Synthesis of tetrahydro-4H-chromenes was tested by using different catalysts, method and solvent. Though many of these techniques have drawbacks, for example, low yields of products,

toxic solvents, long reaction times and tedious work-ups so, different mesopore nanocatalyst was tested.

2 | EXPERIMENTAL

2.1 | Chemicals

All the reactants and solvents that used in the reaction contain the pure cyclohexanone, benzaldehyde, cetyltrimethyl ammonium bromide (CTAB), sodium hydroxide (NaOH), tetraethyl orthosilicate (TEOS), were obtain from Sigma, ferric (III) chloride ($FeCl_3$), cobalt (II) chloride ($CoCl_2$) and sodium bicarbonate were purchased from Sinopharm Chemical Company. The organic products were identified by ^{1}H NMR and FT-IR analyses. The ^{1}H NMR were recorded in $CDCl_3$ and DMSO-d_6 solvents using of Bruker DRX-400 spectrometer and the tetramethylsilane as internal reference. FT-IR spectra attained with KBr pellets with a Perkin-Elmer 550 spectrometer in the range of 400–4000 cm^{-1}. The TGA spectra recorded in an air atmosphere with a 10 °C/min rate and register via METLER-810 analyzer. The crystal structure of nanoparticle (XRD) recorded with (CuKa, radiation, $\lambda = 0.154056$ nm), and by the speed of 2° min^{-1} beginning 10° to 80° (2Θ). For determination of the composition and morphology of nanoparticles, it was used of Zeiss Scanning Electron Microscope (SEM) that worked with a 15 kV accelerating voltage. The surface areas and the size of pore in the nanostructure was displayed by BET analysis that assignment by nitrogen adsorption–desorption in −196 °C that recorded by Tristar 3020, Micromeritics Electron Microscope. The magnetic properties of nanostructure were measured by a vibrating sample magnetometer (VSM) with PPMS-9 T at 300 K.

2.2 | General procedure for preparation of nanocatalyst

2.2.1 | General procedure for preparation of $CoFe_2O_4$ nano magnetic

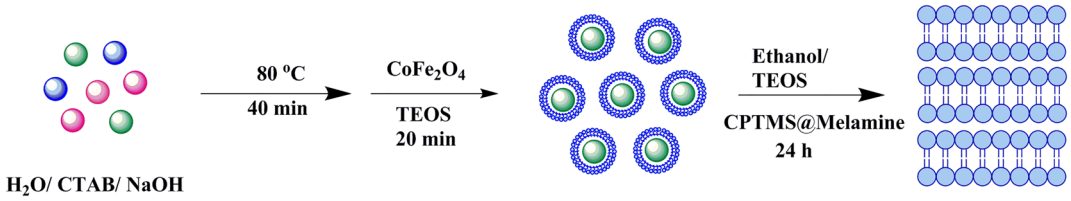
The cobalt ferrite nanoparticles prepared via sol–gel technique.[42] To achieve the chemical formula $CoFe_2O_4$, at the first 30 mL $FeCl_3$ 6 H_2O (4 M) was combined to 30 ml $CoCl_2$ 2H_2O (2 M), then added 1 g citric acid monohydrate ($C_6H_8O_7$ H_2O) as the surfactant to the reaction mixture. After that, the pH of the solution increased to 7.0 with a little ammonia-water (NH_3-H_2O). Then was heated the reaction mixture to evaporate the water at 85 °C and the brown colored gel was formed and at the end, the product burned at 800 °C for 3 hr.

2.2.2 | Synthesis of $CoFe_2O_4$/lamellar mesopore silica/melamine

In order to prepare nitrogen containing base nanocatalysts, initially, 2,4,6-triamino-1,3,5-triazine (10 mmol) mixed with 3-chloropropyltrimethoxysilane (10 mmol) and sodium bicarbonate (5 mmol) in 30 ml dry toluene solvent and the mixture refluxed for 32 hr. The reaction product was assembled by centrifuge and washed three times with water and ethanol, respectively and then the product dried at 70 °C under nitrogen atmosphere.[42] In a distinguishing synthesis, 10 mL NaOH 2 M, and 0.5 g of CTAB dissolved in 100 ml distilled water and heated at 100 °C for 30 min. After that 0.1 g of $CoFe_2O_4$ nanoparticles were dispersed in 60 ml ethanol with sonication and added to the reaction mixture. After 10 min, 2 ml TEOS and 10 ml ethanol and so after 40 min, 2 ml TEOS, 0.5 g SiO_2@melamine and 10 ml ethanol added with strong stirring. NaOH has two roles in this process, one of them was presentations as a catalyst for the sol–gel technique and the other etchant role for structural progress. The reaction stirred at room temperature for 12 hr, the corresponding product was collected by centrifuge and washed with water and ethanol. Then, the product was dried at 70 °C for 24 hr. At the end to remove the surfactant from the nanostructure, the prepared compound dispersed in the ethanol (150 ml) and ammonium nitrate (72 mg) and the reaction followed at 70 °C for 4 hr. The final product separated with the centrifuge and dried at 80 °C for overnight (Scheme 1).

2.3 | General multicomponent procedure for synthesis of 4H-chromene

4H-chromene synthesized from the multi-component reaction. In this process, 0.104 ml (1 mmol) of cyclohexanone and 0.102 mL (1 mmol) of the benzaldehyde mixed in an ethanol solvent, then 10 mg of nanocatalyst added to the reaction mixture and stirred at room temperature for 10–15 min. When completed the first step of the reaction, 0.066 g (1 mmol) of the malononitrile added to the flask of reaction and the process monitored with thin layer chromatography. For separation and purification of the product, 5 ml water added to the mixture, the final product washed with cold ethanol. Then, the resulting solid product was resolved in the minimum of ethanol solvent and recrystallized to give 2-amino-4-phenyl-



SCHEME 1 preparation of $CoFe_2O_4$/lamellar mesopore silica/melamine nanocatalyst

5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile as the pure product. The final product recognized by the melting point, FT-IR and ^{1}H NMR spectra.

2-amino-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile **(4a)**; White solid; m.p.: 233–235 °C (Lit. m. p 240–241 °C)[43]; IR (KBr) ν = 3453, 3317, 3177, 2954, 2828, 2183, 1668, 1629 1483, 1411, 1382, 1253, 1132, 1069, 819, 514 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.37 (m, 4H), 6.88 (s, 1H), 4.52 (s, 1H), 3.97 (s. 2H, NH_2), 2.68–2.77 (m, 1H), 2.54–2.64 (m, 1H), 1.93–2.05 (m, 2H), 1.46–1.72 (m, 4H).

2-amino-4-(4-bromophenyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile **(4b)**; White solid; m.p.: 220–222 °C; IR (KBr) ν = 3446, 3335, 3235, 2935, 2863, 2214, 1667, 1663 1595, 1484, 1413, 1258, 1128, 1008, 822, 512 cm^{-1}, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (m, 1H), 7.13–7.17 (m, 2H), 6.79 (s, 1H), 4.54 (s, 2H, NH_2), 3.95 (s, 1H), 2.66 (s, 1H), 2.54 (s, 1H), 1.94–1.98 (d, J = 17.5 Hz, 2H), 1.57–1.63 (d, J = 24.8 Hz, 4H); ^{13}C NMR (100 MHz, Chloroform-d) δ 157.29, 146.81, 142.81, 128.64, 117.69, 116.60, 114.98, 55.17, 40.20, 36.31, 29.44, 25.02; Anal. calcd (%) for $C_{16}H_{15}$ Br N_2O: C 57.90, H 4.54, N 8.45. Found (%): C 57.92, H 4.53, N 8.45.

2-amino-4-(3-nitrophenyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile **(4c)**; Yellow solid; m.p.: 120–122 °C; IR (KBr) ν = 3460, 3363, 3085, 2931, 2863, 2189, 1669, 1633 1527, 1410, 1349, 1130, 809, 735, 680 cm^{-1}, ^{1}H NMR (400 MHz, Chloroform-d) δ 8.11–8-17 (d, J = 22.4 Hz, 1H), 7.63–7.65 (m, 2H), 6.95 (s, 1H), 4.68 (s, 2H, NH_2), 4.16 (s, 1H), 2.66–2.79 (m, 1H), 2.59–2.62 (d, J = 11.7 Hz, 1H), 2.06–2.10 (d, J = 17.6 Hz, 1H), 1.83–1.99 (m, 1H), 1.45–1.77 (m, 4H), ^{13}C NMR (400 MHz, Chloroform-d) δ22.14, 27.12, 39.39, 59.29, 119.67, 120.03, 126.26, 127.67, 128.32, 128.61, 129.52, 130.68, 159.43,Anal.calcd (%) for $C_{16}H_{15}N_3O_3$: C 64.57, H 5.13, N 14.40. Found (%): C 64.56, H 5.11, N 14.42.

2-amino-4-(4-fluorophenyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile **(4d)**; White solid; m.p.: 223–225 °C; IR (KBr) ν = 3448, 3346, 3057, 2955, 2863, 2187, 1671, 1635 1592, 1412, 1254, 1139, 700, 515 cm^{-1}, ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.33–7.37 (d, J = 8.2 Hz, 1H), 7.20 (s, 2H, NH_2), 6.93 (s, 1H), 6.81 (s, 2H), 4.00 (s, 1H), 3.34 (s, 1H), 2.59–2.62 (d, J = 15.3 Hz, 1H), 2.43–2.46 (d, J = 10.4 Hz, 1H), 2.01–2.05 (d, J = 17.1 Hz, 1H), 1.76–1.77 (d, J = 6.5 Hz, 2H), 1.39–1.61 (m, 2H), ^{13}C NMR (400 MHz, Chloroform-d) δ 22.20, 26.999, 27.39, 42.90, 60.46, 115.07, 115.33, 115.81, 119.81, 121.76, 129.49, 130.89, 138.62, 158.82, 160.90, Anal. calcd (%) for $C_{16}H_{15}$ F N_2O: C 71.11, H 5.55, N 10.37. Found (%): C 71.12, H 5.55, N 10.36.

2-amino-4-(4-(dimethylamino)phenyl)-5,-6,7,8-tetrahydro-4H-chromene-3-carbonitrile **(4e)**; Yellow solid; m.p.: 223–225 °C; IR (KBr) ν = 3445, 3325, 3021, 2892, 2835, 2192, 1668, 1635 1595, 1417, 1247, 1133, 754, 699, 561 cm^{-1}, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18–7.19 (d, J = 7.0 Hz, 1H), 7.14 (s, 2H), 6.84 (s, 1H), 4.49 (s, 2H, NH_2), 3.93 (s, 1H), 2.69–2.72 (d, J = 9.0 Hz, 1H), 2.58 (m, 1H), 2.36 (s, 3H), 2.34 (s, 3H), 1.97–1.99 (d, J = 5.1 Hz, 2H), 1.62 (m, 4H).).^{13}C NMR (400 MHz, Chloroform-d) δ22.49,24.64, 25.02, 40.15, 41.14, 59.99, 11.61, 114.98, 119.29, 133.84, 154.23, 158.15, Anal. calcd (%) for $C_{18}H_{21}$ N_3O: C 73.12, H 7.15, N 14.21. Found (%): C 73.13, H 7.16, N 14.23.

2-amino-4-(2,4-dichlorophenyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile **(4f)**; White solid; m.p.: 130–132 °C; IR (KBr) ν = 3466, 3319, 3180, 2942, 2836, 2186, 1669, 1631 1596, 1486, 1410, 1259, 1090, 824, 512 cm^{-1},^{1}H NMR (400 MHz, Chloroform-d) δ 7.38–7.45 (m, 1H), 7.20–7.24 (dd, J = 18.6, 10.7 Hz, 1H), 6.85 (s, 1H), 4.64–4.67 (s, 2H, NH_2), 3.70–3.74 (q, J = 7.0 Hz, 1H), 2.34–2.65 (m, 2H), 2.18–2.01 (m, 1H), 1.87 (m, 1H), 1.59–1.62 (d, J = 12.2 Hz, 2H), 1.37–1.52 (m, 1H), 1.23–1.26 (t, J = 7.0 Hz, 1H).); ^{13}C NMR (100 MHz, Chloroform-d) δ 164.54, 145.69, 141.70, 138.39, 135.55, 131.86, 127.14, 124.27, 119.29, 114.98, 56.17, 44.24, 34.07, 27.97, 22.89; Anal. calcd (%) for $C_{16}H_{15}Cl_2N_2O$: C 59.77, H 4.35, N 8.71. Found (%): C 59.79, H 4.5636, N 8.72.

2-amino-4-(4-nitrophenyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile **(4 g)**; Yellow solid; m.p.: 180–183 °C; IR (KBr) ν = 3466, 3378, 2934, 2191, 1640, 1517, 1443, 1343 11032, 855, 705 cm$^{-1,}$ ^{1}HNMR (400 MHz, DMSO-d_6) δ 8.23 (s, 2H, NH_2) 7.57–7.59 (d, J = 8.5 Hz, 1H), 7.49–7.50 (d, J = 8.3 Hz, 1H), 7.07(s, 1H), 7.02(s, 1H), 4.27 (s, 1H), 2.62–2.77 (m, 1H), 2.54–2.56 (d, J = 7.1 Hz, 1H), 2.03–2.19 (m,2H), 1.71–1.88 (m, 2H),

1.56–1.57 (d, J = 4.6 Hz, 2H); ^{13}C NMR (100 MHz, Chloroform-d) δ 158.15, 145.32, 140.19, 129. 95, 124.96, 121.48, 117.69, 56.23, 42.24, 29.40, 25.02, 19.94 Anal. calcd (%) for $C_{16}H_{15}N_3O_3$: C 64.57, H 5.13, N 14.40. Found (%): C 64.58, H 5.14, N 14.43.

2-amino-4-(4-chlorophenyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile **(4 h);** White solid; m.p.: 274–277 °C; IR (KBr) v = 3421, 3343, 3252, 2944, 2212, 1645, 1606, 1492, 1389, 1212, 1095, 805, 514 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.34 (m, 2H), 7.18–7.23 (dd, J = 18.6, 10.7 Hz, 2H), 4.55 (s, 2H, NH2), 3.96 (s, 1H), 2.65–2.68 (m, 1H), 2.55(s, 1H), 1.93–2 (m, 2H), 1.62–1.67 (m, 3H), 1.25 (s,1H). Anal. calcd (%) for $C_{16}H_{15}ClN_2O$ C, 67.02; H, 5.27; N, 9.77;Found (%): C 67.92, H 5.64, N 9.50.

2-amino-6-methyl-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile **(4i)**; White solid; m.p.: 202–203 °C; IR (KBr) ν = 3417, 3338, 3252, 2935, 2211, 1649, 1602 1453, 1391, 1275, 1080, 712, 580 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d6) δ 7.38 (s, 1H), 7.33 (s, 1H), 7.25–7.27 (d, J = 7.1 Hz, 1H), 7.17–7.19 (d, J = 7.7 Hz, 1H), 6.96 (s, 1H), 6.78 (s, 2H, NH_2), 3.93 (s, 1H), 2.70 (d, J = 13.1 Hz, 1H), 2.33–1.94 (m, 2H), 1.83–1.85 (m, 2H), 1.62–1.44 (m, 1H), 0.83 (t, J = 7.2 Hz, 4H); Anal. calcd (%) $C_{17}H_{18}N_2O$: C, 76.66; H, 6.81; N, 10.52 Found (%): C, 76.84.; H 6.53, N, 10.45.

2-amino-4-phenyl-6-propyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile **(4j)**; White solid; m.p.: 230–232 °C; IR (KBr) ν = 3446, 3356, 3204, 2943, 2215, 1625, 1593, 1476, 1339, 1270, 1189, 1052, 880, 563 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d6) δ 7.36 (s, 1H), 7.32 (s, 1H), 7.21–7.26 (d, J = 7.0 Hz, 1H), 7.19 (s, 1H), 6.95 (s, 1H), 6.79 (s, 2H, NH_2), 3.95 (d, J = 10.0 Hz, 1H), 2.70–2.73 (d, J = 13.5 Hz, 1H), 2.30 (s, 1H), 2.08 (s, 1H), 1.83–1.85 (d, J = 7.6 Hz, 2H), 1.44–1.47 (d, J = 44.1 Hz, 2H), 1.13–1.16 (d, J = 12.8 Hz, 4H), 0.72 (s, 3H), Anal. calcd (%) for $C_{19}H_{22}N_2O$: C, 77.52; H, 7.53; N, 9.52; O, 5.43 Found (%): C, 77.92; H 7.59; N, 9.87.

2-amino-4,6-diphenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile **(4 k)**; White solid; m.p.: 250–252 °C; IR (KBr) ν = 3422, 3327, 3224, 2914, 2212, 1644, 1599, 1494, 1390, 1265, 754, 569 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.62–7.61 (d, J = 7.9 Hz, 1H), 7.46 (s, 2H, NH_2), 7.43 (s, 4H), 7.23–7.19 (t, J = 7.4 Hz, 2H), 7.14–7.10 (m, 3H), 4.34 (s, 1H), 3.63–3.60 (d, J = 12.4 Hz, 1H), 3.12–3.07 (m, 1H), 2.29–2.90 (m, 1H), 2.44–2.40 (m, 1H), 2.22–2.15 (m, 1H), 1.51–1.48 (d, J = 12.4 Hz, 1H), 1.25–119 (q, J = 12.1 Hz, 1H), Anal. calcd (%) for $C_{17}H_{17}BrN_2O$ C, 59.14; H, 4.96; N, 8.11; Found (%): C, 59.69; H 5.21; N, 8.57.

2-amino-4-(4-bromophenyl)-6-methyl-5,-6,7,8-tetrahydro-4H-chromene-3-carbonitrile **(4 l)**; White solid; m.p.: 280–283 °C; IR (KBr) ν = 3423, 3344, 3251, 2929, 2211, 1644, 1601, 1489, 1391, 1275, 1076, 835, 510 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.57 (s, 2H), 7.53 (s, 1H), 7.13–7.25 (m, 1H) 6.91 (s, 2H, NH_2), 3.99 (s, 1H), 2.64–2.67 (d, J = 14.9 Hz, 1H), 2.23–2.27 (d, J = 12.6 Hz, 1H), 2.15–1.91 (m, 2H), 1.91–1.61 (m, 2H), 1.53 (d, J = 19.2 Hz, 1H), 0.84 (s, 3H) Anal. calcd (%) for $C_{22}H_{20}N_2O$: C, 80.46; H, 6.14; N, 8.53; Found (%): C, 80.89; H 6.31; N, 8.58.

3 | RESULTS AND DISCUSSION

3.1 | Preparation and chracterization of catalyst

$CoFe_2O_4$/lamellar mesopore silica/melamine nanocatalyst prepared in two-step. At the first, the $CoFe_2O_4$ nanoparticles were synthesized through sol–gel method and then, the TEOS, SiO_2/Melamine, surfactant and NaOH added to the mixture. The role of surfactant and NaOH can be the creation the pore in the nanocatalyst and design the morphology of nanostructure **(**Scheme 1**)**.

After preparation of magnetic $CoFe_2O_4$/lamellar mesopore silica/melamine nanocatalyst, it was identified with different analyses such as; XRD, FT-IR, SEM, VSM and TGA. The X-ray diffraction patterns of magnetic $CoFe_2O_4$ and $CoFe_2O_4$/lamellar mesopore silica/melamine nanocatalyst were displayed in Figure 1. The situation of all peaks in the both the curves confirmed with regular XRD pattern[44] of JCPDS card. The XRD pattern of $CoFe_2O_4$ displays the crystal structure and the XRD of $CoFe_2O_4$/lamellar mesopore silica/melamine displays the crystal and amorphous structure **(**Figure 1**)**.

The pattern of the $CoFe_2O_4$ nanoparticles was indexed as a face-centered cubic structure, which is very close to the values in the literature (JCPDS No. card no 22–1086). The crystallite size for nanoparticles were calculated and reported in Table 1.

In the FT-IR spectra of the $CoFe_2O_4$, SiO_2/melamine and $CoFe_2O_4$/SiO_2/Melamine were investigated and the results were shown in Figure 2. The FT-IR spectra of the $CoFe_2O_4$the peaks appeared about 440 and 549 cm^{-1} due to the stretching vibrations of Co-Fe bonding. The peak that place about 1631 cm^{-1} due to bending vibration and the peak of 3414 cm^{-1} due to the stretching vibration of O-H bonding. In the FT-IR spectra of SiO_2/melamine the peaks of 3468, 3418, 3339 cm^{-1} related to stretching vibrations of N-H bond, the peak around of 3132 cm^{-1} related to stretching vibration of C-H, sp^2 bonding, the peaks of 1653 and 1438 cm^{-1} due to aromatic ring and the peak of 1553 cm^{-1} related to C=N stretching

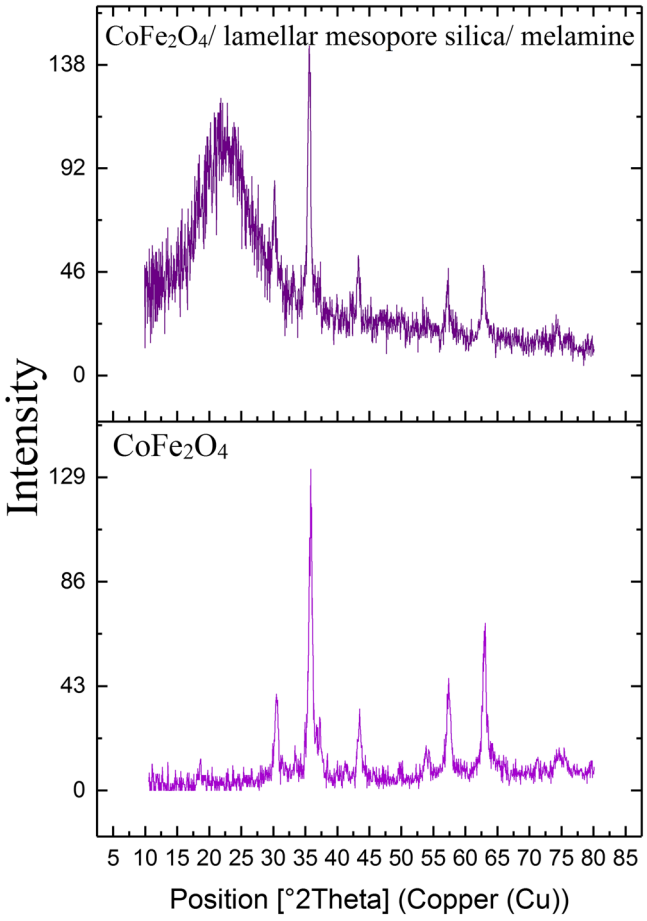


FIGURE 1 XRD spectra of $CoFe_2O_4$, $CoFe_2O_4$/lamellar mesopore silica/melamine

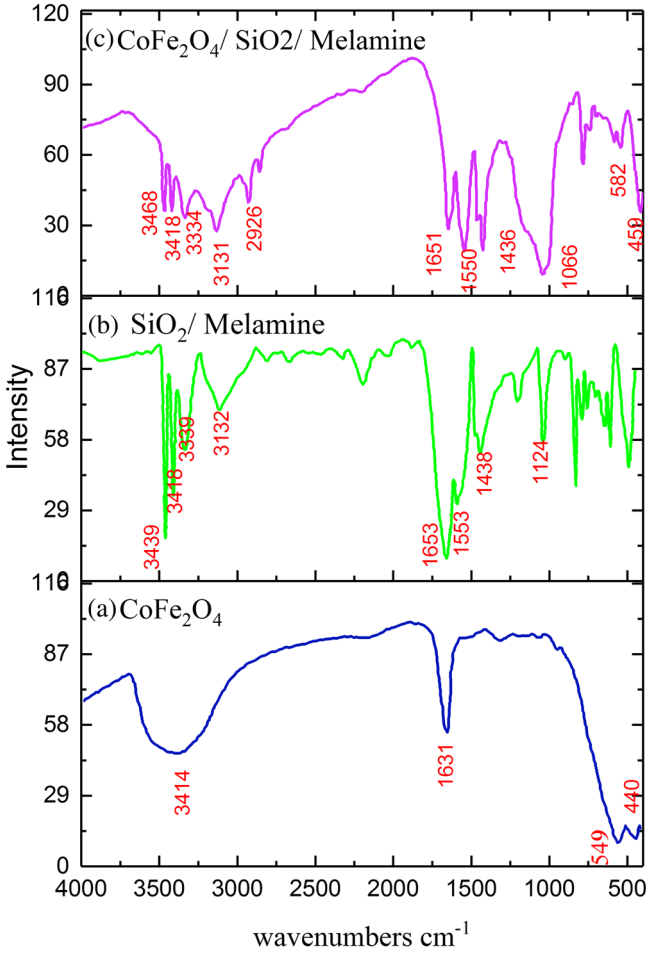


FIGURE 2 The spectra of FT-IR $CoFe_2O_4$, SiO_2/Melamine, $CoFe_2O_4/SiO_2$/Melamine

TABLE 1 The peak position, full width at half maximum (β ½) and calculated crystal size for nanoparticles

	$CoFe_2O_4$/lamellar mesopore silica/melamine ʎ = 0.154 nm, K = 0.94, Pos. [°2Th.]FWHM Left [°2Th.][1]							
Element	**(111)**	**(220)**	**(222)**	**(400)**	**(422)**	**(511)**	**(440)**	**(533)**
2Θ position(°)	18.12	30.27	37.28	43.47	53.88	57.16	62.28	73.99
β ½	0.94	0.47	0.41	0.47	1.41	0.70	0.47	1.41
Size (nm)	8.93	18.27	21.34	18.99	6.60	13.49	20.61	7.36

vibration, the peak of around 1124 cm^{-1} due to C-O, and the peak of 1030 cm^{-1} related to Si-O stretching vibration.[44]

SEM images of $CoFe_2O_4$/lamellar mesopore silica/melamine were displayed in Figure 3. The several layers of these plates next to each other formed the lamellar mesopore silica. The average size of the nanoparticles is 26 nm. The obtained nanoparticles size from the SEM was very close with the calculated size from XRD techniques (Table 1).

Furthermore, the mesoporous structure of synthetic compound has been demonstrated by BET analysis (Figure 4**)**. Displaying the N_2 adsorption–desorption isotherms and hysteresis loop, along with BET plot, was provided better confirmation of the mesoporous structure. The BET analysis of the nanoparticles shows a surface area about 619 m^2g^{-1}, the pore size of the mesopore compound equal to 2.11 nm, and the p/p^o of the nanoparticle reported 0.327 cm^3g^{-1}.

To investigate the magnetic properties of $CoFe_2O_4$/lamellar mesopore silica/melamine nanoparticles examined the vibrating sample magnetometry (VSM) spectrum of the compound with Ms 80 emu/g **(**Figure 5).

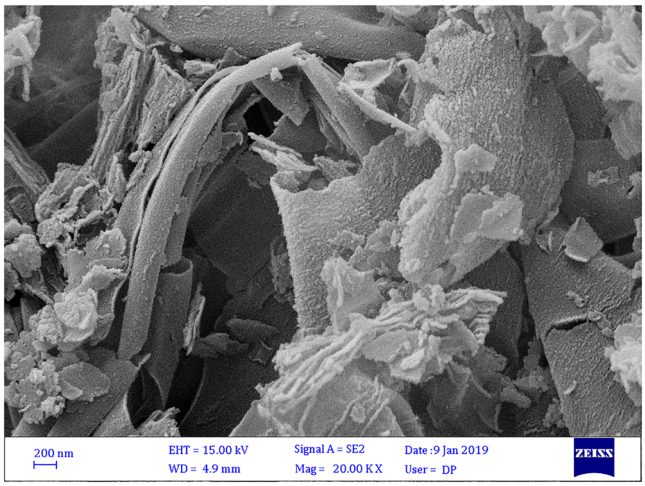


FIGURE 3 FE-SEM image of $CoFe_2O_4$/lamellar mesopore silica/melamine

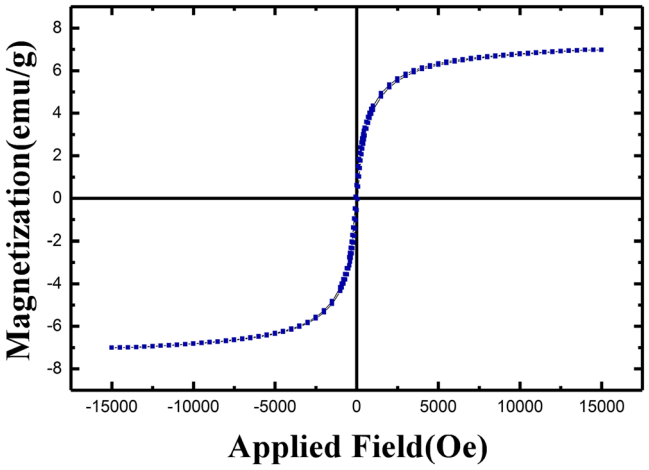


FIGURE 5 VSM curves for $CoFe_2O_4$/lamellar mesopore silica/melamine

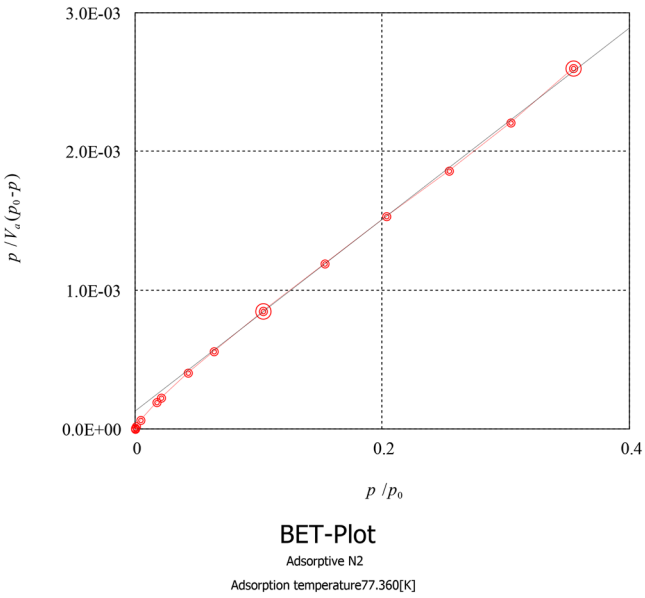


FIGURE 4 BET curves for $CoFe_2O_4$/lamellar mesopore silica/melamine

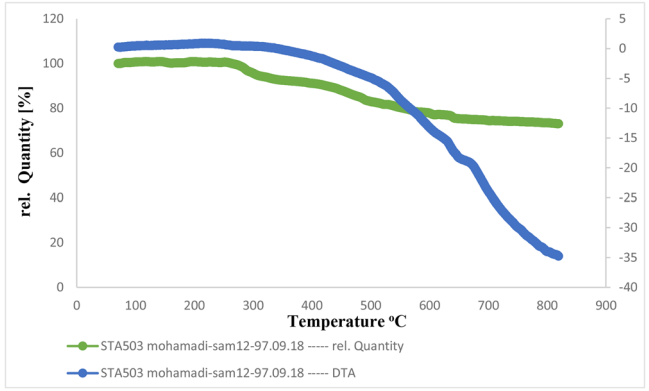


FIGURE 6 TGA curves for $CoFe_2O_4$/lamellar mesopore silica/melamine

Thermogravimetric analysis (TGA) curves of $CoFe_2O_4$/lamellar mesopore silica/melamine (Figure 6) show that the losses weight under 200 °C that in all models are endorsed to the freedom of adsorbed water. TGA analysis in 400–800 °C showed the losses melamine that displays the weight due to destroy the structure of nanocatalyst. Consequently, the weight % of the organic compound that anchored to the $CoFe_2O_4$/lamellar mesopore silica was calculated 23% due to loss the weight between 300–800 °C.

3.2 | Investigation of catalytic activity

In order to optimize the protocol, cyclohexanone, benzaldehyde and malononitrile for the synthesis of 4H-chromene, considered in the presence of various catalysts, solvents and temperatures (Scheme 2). At first, the reaction was carried out in the attendance of altered catalyst in a different amounts at ethanol solvent (Table 2). At the result, the best catalyst for the reaction was nanomagnetic $CoFe_2O_4$/lamellar mesopore silica/melamine with the large surface area and attended of the melamine function in the surface and pore. The reaction carried out in the attendance of 0.1 mg of nanocatalyst (Table 2, entry 2).

The different solvents examined to check the effect of them in the model reaction. At the results, the reaction in the ethanol solvent has an excellent yield in a short time (Table 3).

SCHEME 2 Synthesis of 4H-chromene in different condition

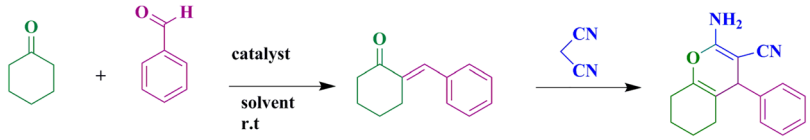


TABLE 2 Investigation of catalyst in multicomponent reaction for synthesis of 4H-chromene[a]

Entry	Catalyst	Catalyst amount (mg)	Time (min)	Yield [b] (%)
1	Guanidine	10 mg	90	70
2	Melamine	10 mg	80	75
3	$MgFe_2O_4$	10 mg	60	80
4	MgO	10 mg	60	82
5	$CoFe_2O_4/SiO_2$/ melamine	10 mg	45	85
6	$CoFe_2O_4$/lamellar mesopore silica/melamine	10 mg	20	93
7	$CoFe_2O_4$/lamellar mesopore silica/melamine	5 mg	30	82

[a]Reaction conditions: cyclohexanone (1 mmol), malononitrile (1 mmol), benzaldehyde (1 mmol), room temperature, ethanol solvent (5 ml).
[b]Isolated yield.

TABLE 3 Investigation of solvent in multicomponent reaction for synthesis of 4H-chromene [a]

Entry	Solvent	Yield [b] (%)	Time (mine)
1	Chloroform	85	45
2	Dichloromethane	80	40
3	Methanol	87	35
4	Ethanol	93	20

[a]Reaction conditions: cyclohexanone (1 mmol), malononitrile (1 mmol), benzaldehyde (1 mmol), room temperature, nanocatalyst (10 mg).
[b]Isolated yield.

To survey the influence of temperature on the yield of 4H-chromene product, the reaction was study in various temperatures (25 °C to 80 °C) (Table 4). At the result the best temperature for the reaction was the ambient temperature.

After optimization, it was selected as the best condition for the synthesis of 4H-chromene under the $CoFe_2O_4$/lamellar mesopore silica/melamine nanocatalyst. In this reaction, the variety derivatives of benzaldehyde (1 mmol), different derivatives of cyclohexanone (1 mmol) and nanocatalyst (10 mg) mixed and after 7–10 min malononitrile (1 mmol) added to the mixture (Scheme 3). The best solvent that selects for the reaction was ethanol (5 ml). The reaction stirred for 10–15 min at room temperature. In this condition, the 4-H-chromene derivatives with electron donating and electron withdrawing synthesized in excellent yields (Table 5).

3.3 | Proposed reaction mechanism

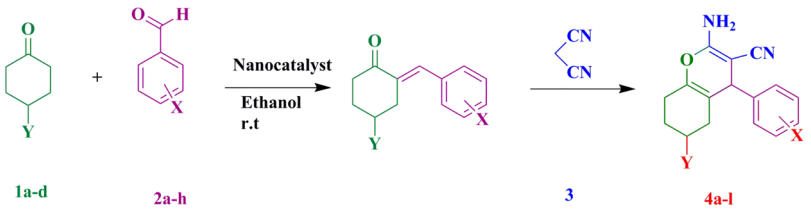
The mechanism of reaction for the synthesis of 4H-chromenes contained several steps, in the first step cyclohexanone and benzaldehyde reacted together with condensation reaction and synthesis of the α,β-unsaturated intermediate under the nanomagnetic base $CoFe_2O_4$/lamellar mesopore silica/melamine catalyst. This catalyst has the grate base activity because of the large active base site in both surface and pore. Then the malononitrile under Michael addition join to the C=C bond for the synthesis of intermediate G, then processes followed with cyclization by the formation of C–O bond. At the end of the reaction, 4H-chromene (4a) synthesized with the elimination of a hydrogen and rearrangement of double bonds (Scheme 4).

The $CoFe_2O_4$/lamellar mesopore silica/melamine simple separated with magnetic properties and recyclability for six runs (Figure 7). After each of the reaction, the catalyst separated and washed three times with acetone and used in the other reaction. The recycled catalyst could be reused for six times without considerable loss of its catalytic activity and gave the corresponding product in high yields.

TABLE 4 Investigation of various temperatures in multicomponent reaction for synthesis of 4H-chromene [a]

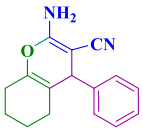
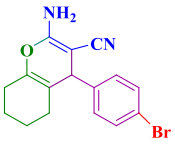
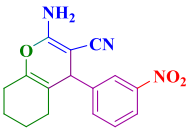
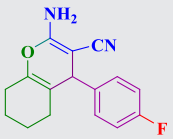
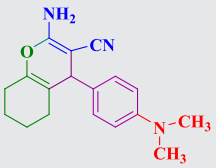
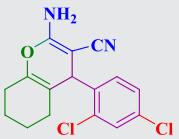
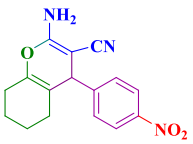
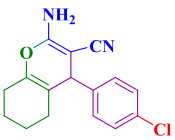
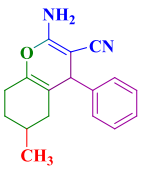
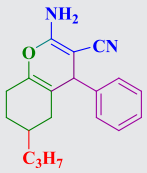
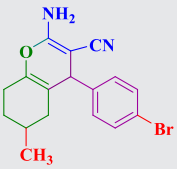
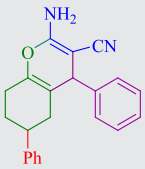
Entry	Temperature	Yield [b] (%)	Time (mine)
1	25	93	20
2	35	85	15
3	45	80	15
4	60	75	15

[a]Reaction conditions: cyclohexanone (1 mmol), malononitrile (1 mmol), benzaldehyde (1 mmol), ethanol solvent (5 ml), nanocatalyst (10 mg).
[b]Isolated yield.



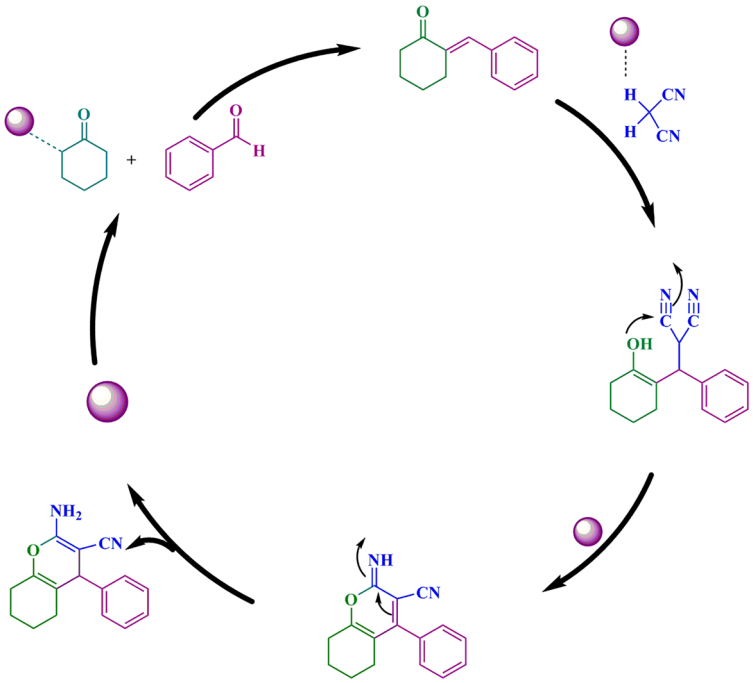
SCHEME 3 synthesis of 4H-cheromene from cyclohexanone, benzaldehyde and malononitrile

TABLE 5 Synthesis of various derivatives of 4H-cheromene in the presence of $CoFe_2O_4$/lamellar mesopore silica/melamine nanocatalyst

4a-l [a], Yield % [b], Time (min) TON, TOF (h^{-1})		
 **4a: X = H, Y = H, 90, 30 50, 100**	 **4b: X = Br, Y = H, 88, 30 48.8, 97.6**	 **4c: X = NO_2, Y = H, 90, 35 50, 86.2**
 **4d: X = F, Y = H, 89, 20 49.4, 149.6**	 **4e: X = N,N dimethyl, Y = H, 88, 45, 48.8, 65.1**	 **4f: X = 2,4 dichloro, Y = H, 86, 35, 47.7, 89.2**
 **4 g: X = NO_2, Y = H, 93, 25 51.7, 126.0**	 **4 h: X = Cl, Y = H, 93, 35, 51.7, 89.1**	 **4i: X = H, Y = CH_3, 92, 25, 51.1, 124.6**
 **4j: X = H, Y = C_3H_7, 91, 20, 50.6, 153.2**	 **4 k: X = Br, Y = CH_3, 90, 27, 50, 111.1**	 **4 l: X = H, Y = Ph, 94, 20, 52.2, 158.2**

[a]Reaction conditions: benzaldehyde (1 mmol), cyclohexanone (1 mmol), malononitrile (1 mmol), 0.1 mmol nanocatalyst (10 mg), ethanol solvent (5 ml), r.t.
[b]Isolated yield.

SCHEME 4 Proposed reaction mechanism for the synthesis of 1H-isochoromene



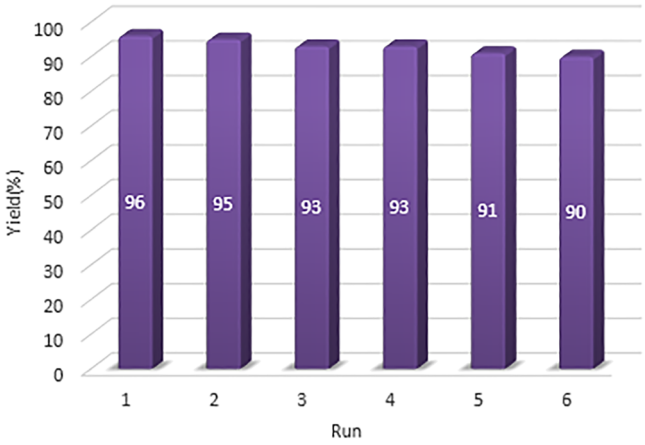


FIGURE 7 The recyclability of $CoFe_2O_4$/lamellar mesopore silica/melamine in six runs

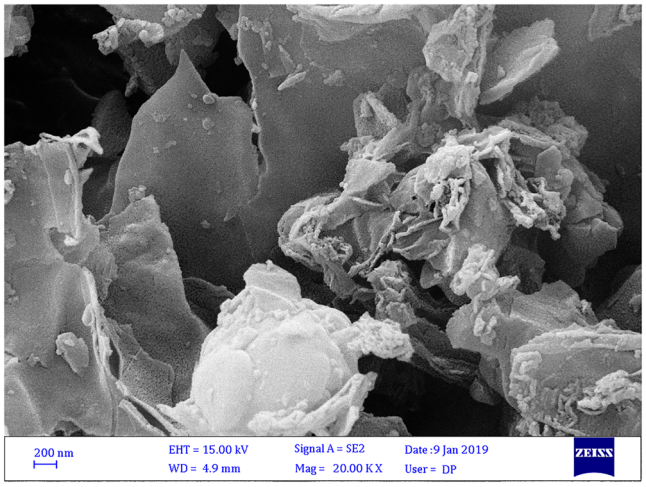


FIGURE 8 FE-SEM image of $CoFe_2O_4$/lamellar mesopore silica/melamine after recycling

Also, the leaching of the nanocatalyst was investigated with the hot filtration. The reaction of benzaldehyde, cyclohexanone, and malononitrile at the presence of nanocatalyst was stopped after 5 min and the nanocatalyst filtered from the reaction mixture. The filtrate was heated and the reaction followed and checked with thin layer chromatography. The reaction did not progress after filtration, so the negative consequences of hot filtration test show that the leaching of nanocatalyst is insignificant.

For investigating the properties of nanoparticles after recycling and reusing in 6 runs of reactions, it was examined the SEM analysis of recovered $CoFe_2O_4$/lamellar mesopore silica/melamine catalyst. The SEM image of this catalyst explored to determine the morphology of the nanocatalyst after recycling of the nanocatalyst. So, the result displayed the nanocatalyst retain the lamellar morphology (Figure 8).

4 | CONCLUSION

In this research, it was functionalized the $CoFe_2O_4$/lamellar mesopore silica magnetic nanoparticles with

the melamine compound. The mesopore silica with a large area has a great surface area to functionalization. So, the $CoFe_2O_4$/lamellar mesopore silica/melamine has a strong basic activity. In this protocol, for examination of the catalytic activity of nanoparticles, the synthesis of 4H-chromenes was studied. It was found that the reaction by using $CoFe_2O_4$/lamellar mesopore silica/melamine as a nanocatalyst has excellent yields and short reaction times in this reaction. The nanocatalyst was characterized by FT-IR, XRD, SEM, TGA, VSM techniques and the organic products identified with the melting point, FT-IR and ^{1}H NMR analyses (see Supporting information).

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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