Journal of Magnetism and Magnetic Materials 398 (2016) 205–214

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Fe_3O_4@B-MCM-41: A new magnetically recoverable nanostructured catalyst for the synthesis of polyhydroquinolines

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ARTICLE INFO

Article history:
Received 9 June 2015
Received in revised form
5 September 2015
Accepted 10 September 2015
Available online 12 September 2015

Keywords:
B-MCM-41
Magnetite
Nanostructured
Mesoporous silica
Polyhydroquinoline
Fe_3O_4

ABSTRACT

Boron modified MCM-41 with magnetite core (Fe_3O_4@B-MCM-41) as a new magnetically recoverable heterogeneous catalyst was prepared and characterized by SEM, TEM, BET, XRD, VSM and FT-IR techniques. The catalytic activity of Fe_3O_4@B-MCM-41 was investigated in the four-component reaction of aldehyde, dimedone, active methylene compounds and ammonium acetate for the synthesis of polyhydroquinolines. According to optimization and characterization results the catalyst with Si:B:Fe_3O_4 mole composition of 40:4:1 has the best activity. The catalyst could be recovered easily by external magnet and has excellent reusability many times without significant decrease of activity.

1. Introduction

Recently, magnetite nanoparticles have been attracted considerable attentions due to their various fields of applications such as electronic [1], biotechnology [2], biomedicine [3], medicine [4], metal ion extraction [5], optical imaging [6], catalyst [7] and magneto resistance [8]. This material has been prepared by precipitation [9], co-precipitation [10] and hydrothermal [11] methods. Due to simple recovery and coupling with organic ligands [12] and inorganic compounds such as silica [7], magnetite nanoparticles have been widely used as core of the catalyst support in organic transformation [13]. On the other hand, silica based mesoporous materials such as Al-MCM-41 [14], TPA/MCM-41 [15], BF_3/MCM-41 [16], Cu-MCM-41 [17], Ti-MCM-41 [18], $RhCl_3$/MCM-41 [19] and Mn-MCM-41 [20] have been used as both catalyst and catalyst support in organic reactions, duo to high surface area (up to 1000 m^2/g) and thermal stability (up to 800 °C) [21]. In recent years, immobilizing MCM-41 on the magnetite nanoparticles has been improved as a powerful tool for the recovery of MCM-41 based catalyst from the reaction media [13,22–25]. However, due to importance of recovery and reusability of solid catalysts, improvement of new magnetically recoverable catalytic system is also desirable.

Polyhydroquinoline derivatives (PHQs) have been attracted considerable attentions due to their biological applications [26]. Many synthetic methodologies have been improved for the synthesis of these compounds. General methods for the synthesis of PHQs is multi-component reaction of aldehyde, β-dicarbonyl compounds, active methylene compound and ammonium acetate in the presence of acid catalyst such as $HClO_4/SiO_2$ [27], Sulfonated cellulose [28], Ni(0) nanoparticles [29], Palladium(0) nanoparticles [30] and $Yb(OTf)_3$ [31].

In this research, we aim to report preparation, characterization and catalytic application of Fe_3O_4@B-MCM-41 as a new magnetically recoverable solid acid catalyst for the synthesis of polyhydroquinolines by four-component reaction of aldehyde, dimedone, active methylene compounds and ammonium acetate (Scheme 1). A modified method for the preparation of mesoporous silica under mild condition was also improved. A variety of new polyhydroquinolines were also synthesized by this method.

2. Experimental

2.1. Materials and methods

All chemicals were commercial reagents and the reactions were monitored by TLC and all yields refer to isolated products. Melting points were obtained by Buchi B-540 apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a

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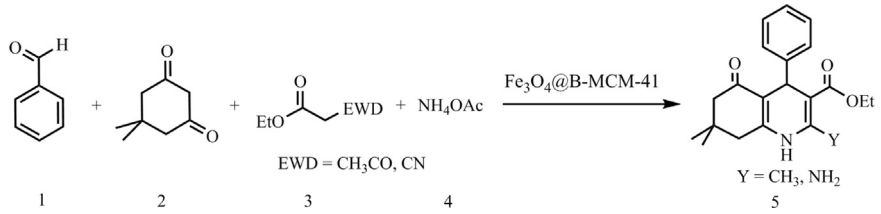
http://dx.doi.org/10.1016/j.jmmm.2015.09.048
0304-8853/



Scheme 1

Bruker DRX-500 AVANCE (500 MHz for ^{1}H and 125.72 MHz for ^{13}C) and Bruker DRX-400 AVANCE (400 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometers. Infrared spectra of the catalysts and products were recorded on a Bruker FT-IR Equinox-55 spectrophotometer in KBr pellets. XRD patterns were recorded on a Bruker D8 ADVANCE X-ray diffractometer using nickel filtered Cu Kα radiation (λ=1.5406 Å). The morphology was studied using a Philips XL30 scanning electron microscopy. The magnetic measurements were performed using Vibrating Sample Magnetometer Model VSM-4 inh, Daghigh Meghnatis Kashan Co. The BET surface area was measured using a PHS-1020(PHSCHINA) from the nitrogen adsorption–desorption isotherms at 77 K. All samples were degassed at 120 °C under flowing nitrogen for 2 h. The specific surface area (S_{BET}) was calculated from the adsorption data using the BET equation. The pore size distribution was calculated by the Barret–Joyner–Halenda (BJH) method. Transmitance electron microscopy (TEM) was performed with Zeiss-EM10C at 80 kV. Analyticjena spectrophotometer model SPECORD 250 was used for spectrophotometric study in order to boron determination. Analyticjena spectrometer model noAA 300 was used for atomic absorption spectrometric study in order to Fe determination.

2.2. Preparation of magnetite nanoparticles

Magnetite was prepared by co-precipitation technique. In a typical procedure, $FeCl_2 \cdot 4H_2O$ (1.99 g, 10 mmol) and $FeCl_3 \cdot 6H_2O$ (5.41 g, 20 mmol) were dissolved in distillated water (30 mL). The solution was heated to 60 °C under nitrogen while being stirred by a mechanical stirrer about 30 min, followed by the slow addition of 25% ammonia solution (35 mL). The precipitate was stirred for 30 min and then precipitate was separated by external magnet and washed with deionized water (3 × 100 mL). The gel was dried at 80 °C in an oven for 2 h.

2.3. Preparation of Fe_3O_4@B-MCM-41 nanoparticles

Fe_3O_4@B-MCM-41 was prepared by sol–gel technique with the gel composition of SiO_2:CTAB:NH_4OH:H_2O:B:Fe_3O_4=1:0.127:1.26:480:0.1:x (x=0.025 and 0.05). In a typical procedure for the synthesis of Fe_3O_4@B-MCM-41 with Si:B:Fe_3O_4 mole composition of 40:4:1, Fe_3O_4 nanoparticles (0.131 g, 0.565 mmol) was dispersed in deionized water (200 mL) by ultrasound and cetyltrimethylammonium bromide (1.00 g) was added to the obtained suspension along with smoothly increasing of temperature to 70 °C. To this suspension, H_3BO_3 (0.139g, 2.26 mmol) was added and then tetra ethylorthosilicate (5 mL, 22.6 mmol) was added dropwise for 1 h. The final mixture was allowed to cool to room temperature. The pH of the suspension was adjusted to 10 with aqueous ammonia (25 wt%) and then was stirred for 10 h at room temperature. The gel was separated by centrifuge and washed with distilled water (2 × 100 mL) and EtOH (2 × 100 mL), respectively. The gel was dried in an oven at 120 °C for 1 h and then calcined at 350, 450 and 550 °C for 4 h. The obtained samples were denoted as MBM-120, MBM-350, MBM-450 and MBM-550.

2.4. General procedure for the synthesis of polyhydroquinolines in the presence of MBM-450

A mixture of dimedone (1.0 mmol), aromatic aldehyde (1.0 mmol), β-ketoester (1.1 mmol), ammonium acetate (1.2 mmol) and MBM-450 (50 mg) was refluxed in EtOH (2 mL). After completion of the reaction (monitored by TLC, eluent; *n*-hexane:EtOAc, 8:2), the catalyst was separated by external magnet and washed with hot EtOH (2 × 5 mL). After evaporation of the solvent, the pure products were achieved by recrystallization in EtOH.

2.5. Physical and spectroscopic data of new compounds

5l: MP: 155–158 °C, FT-IR (KBr) υ_{max}: 3400, 3287, 2950, 1693, 1649, 1595, 1538, 1490, 1367, 1252, 1202, 1034, 865, 694 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)=1.02 (s, 3H), 1.21 (s, 3H), 1.21 (t, 3H, J=7.1 Hz), 2.21 (d, 1H, J=12.8 Hz), 2.28 (d, 1H, J=12.8 Hz), 2.45 (s, 2H), 3.8 (s, 3H, OMe), 4.1 (m, 2H), 4.73 (s, 1H), 6.23 (s, 2H, NH_2), 6.68 (d.d, 2H, J=7.7 Hz), 6.87 (s, 1H) 6.9 (d, 1H, J=7.5 Hz) 7.15 (t, 1H, J=7.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)=14.2, 28.2, 28.9, 32.1, 34.3, 41.1, 51.1, 55.2, 60.1, 81.1, 110.9, 114.2, 116.9, 121.1, 129.1, 147.0, 159.1, 160.2, 162.1, 169.1, 196.0. Anal. Calcd for $C_{21}H_{26}N_2O_4$: C, 68.09; H, 7.07; N, 7.56. Found: C, 68.37; H, 6.99; N, 7.64.

5m: MP: 140–143 °C, FT-IR (KBr) υ_{max}: 3435, 3305, 2951, 1695, 1521, 1350, 1202, 1196, 1038, 690 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)=1.02 (s, 3H), 1.13 (s, 3H), 1.2 (t, 3H, J=7.0 Hz), 2.18 (d, 1H, J=12.7 Hz), 2.27 (d, 1H, J=12.7 Hz), 2.46 (s, 2H), 4.08 (m, 2H), 4.7 (s, 1H), 6.28 (s, 2H, NH_2), 7.1 (t, 1H, J=7.6 Hz), 7.23 (d, 1H, J=7.7 Hz), 7.26 (d, 1H, J=7.8 Hz), 7.42 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)=14.2, 27.1, 29.0, 32.1, 34.2, 41.1, 50.9, 60.1, 80.2, 116.0, 122.1., 127.2, 129.0, 130.1, 131.1, 147.9, 149.2, 157.9, 162.0, 169.1, 197.1. Anal. Calcd for $C_{20}H_{23}BrN_2O_3$: C, 57.29; H, 5.52; N, 6.68. Found: C, 57.11; H, 5.40; N, 6.54.

5n: MP: 179–180 °C, FT-IR (KBr) υ_{max}: 3335, 3200, 2958, 1690, 1663, 1543, 1369, 1279, 1200, 1040, 707 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)=0.99 (s, 3H), 1.12 (s, 3H), 1.16 (t, 3H, J=7.0 Hz), 2.17 (d, 1H, J=16.2 Hz), 2.25 (d, 1H, J=16.2 Hz), 2.46 (s, 2H), 4.04 (m, 2H), 4.71 (s, 1H), 6.29 (s, 2H, NH_2), 7.15 (m, 1H), 7.61 (m, 1H), 8.37 (m, 1H), 8.53 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)=14.2, 27.5, 29.0, 39.9, 40.6, 50.6, 59.8, 79.7, 115.8, 122.8, 135.8, 141.3, 147.4, 150.0, 158.4, 161.7, 168.7, 196.2. Anal. Calcd for $C_{19}H_{23}N_3O_3$: C, 66.84; H, 6.79; N, 12.31. Found: C, 66.73; H, 6.61; N, 12.37.

5o: MP: 220–225 °C, FT-IR (KBr) υ_{max}: 3491, 3169, 2957, 1604, 1528, 1479, 1396, 1366, 1282, 1224, 758 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)=0.92 (s, 3H), 1.01 (s, 3H), 1.2 (t, 3H, J=7.2 Hz), 2.18 (d, 1H, J=13.2 Hz), 2.27 (d, 1H, J=13.2 Hz), 2.45 (m, 2H), 4.08 (m, 2H), 4.64 (s, 1H), 6.25 (s, 2H, NH_2) 6.37 (d, 1H, J=1.6 Hz), 6.4 (d, 1H, J=2.0 Hz), 6.5 (d, 1H, J=4.4 Hz), 8.43 (s, 1H, OH), 8.55 (s, 1H, OH), ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)=14.0, 26.9, 29.1, 32.0, 34.2, 41.0, 50.9, 60.1, 80.1, 116.0, 122.3, 127.1, 129.0, 130.1, 131.1, 148.0, 149.0, 158.1, 161.9, 169.2, 197.0. Anal. Calcd for $C_{20}H_{24}N_2O_5$: C, 64.50; H, 7.50; N, 7.52. Found: C, 64.38; H, 7.63; N, 7.56.

5p: MP: 183–185 °C, FT-IR (KBr) υ_{max}: 3420, 3307, 3217, 1692, 1652, 1613, 1530, 1395, 1285, 1038, 757 cm^{-1}. ^{1}H NMR (400 MHz,