Preparation and Characterization of Hollow MgO/SiO₂ Nanocomposites and using as Reusable Catalyst for Synthesis of 1H-Isochromenes

Somaye Mohammadi

University of Kashan

Hossein Naeimi (✉ naeimi@kashanu.ac.ir)

University of Kashan <https://orcid.org/0000-0002-9627-596X>

Research Article

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Abstract

In the present study, hollow MgO/SiO₂ nanocatalyst with great base properties was made. This heterogeneous catalyst was a synthesis in several steps to create a great active area and decrease the density of the catalyst. The base hollow catalyst framework for the reaction of cyclohexanone, malononitrile and benzaldehyde to the synthesis of 1H-isochromene from Michael addition and aldol reaction at room temperature. All the reaction flowing was excellent in the yield of product and reaction times. At the end of the reaction, the nanocatalyst separated by simple filtration and reuse in several runs elsewhere.

1. Introduction

The 1H-isochromene derivatives are a special structural style commonly appearance in a numerous of naturally and non-naturally products (Butin et al., 2005; Hasan et al., 2015; Singh and Bodiwala, 2010; Tomás-Mendivil et al., 2015) which has represented as “advantaged structure” in various medicinally and related compounds due to its significant biological effects counting antitumor properties (Mondal et al., 2003; Morimoto et al., 2011; Shishido et al., 2008; Wang et al., 1998). Some natural compounds that include the isochromene were flaccidin separated of the orchids, *Dendrobium amoenum* also *Coelogyne flaccida* and also the numerous of compounds which separated from *Cannabis sativa*, can be observed as isochromene derivatives (Papadakis et al., 1983). Three derivatives of *Ulmus davidiana* which comes from Korea are utilized in oriental medicines for the usage of edema, inflammations, and stomach cancer. The enormous value of these compounds have inspired much effort to advance a vast number of influential and dependable procedures for their syntheses (Wang et al., 2017). Outdated 1H-isochromene synthesized with dimerization of benzopyrylium salts in acid conditional (Verin et al., 1991). The shortage of substrate range and the trouble in the supply of benzopyrylium salts was a disadvantage for this method. For solving this problem, direct and economical ways have been established to the synthesis of 1H-isochromenes via difference catalyst such as transition-metal-catalyzed and organic functional catalyzed.

The preparation of solid heterogeneous nanocatalyst with exact control the site of unique functionalities was commonly required in the organic reaction. In contrast, the solid catalysts attended with lacking clear morphology such as the hollow compound with small density and the great explicit surface area. Hollow catalyzed and nanoparticle wall, hollow spheres via nanometre or micrometre dimension often display singular chemical and physical properties dissimilar from dense particles.

Hollow spheres have used in many field, for example electrics, light-weight filler, optics selective adsorption, magnetics, drug delivery, medicine-release capsules, and catalysis (Budov, 1994; Cao et al., 2010; Chen et al., 2004; Fang et al., 2012; Ikeda et al., 2007; Russell et al., 2014). Consequently, there has been abundant interest in arranging hollow compound with altered arrangements in latest years. In earlier reports, the hollow structure with amorphous shells or nanocrystalline and hard template or soft template were ready in diversity courses. In the hard template structure, the first coating is formed on the core and

then the hard template (core) is eliminated by chemical or thermal method to form hollow structure. To fabricate hollow spheres variability of solid particles have been utilized as hard templates like polystyrene spheres, silica particles, carbon spheres (Caruso et al., 2001; Hentze et al., 2003; Imhof, 2001; Titirici et al., 2006; Wang et al., 2006). The hard template technique is the great method for the construction of hollow spheres: hollow spheres with altered dimensions can be attained by the usage of colloid particles with a particular size, and the thickness wall of hard template hollow particles is due to reaction restrictions. In the soft template method, regularly usage of emulsions, vesicles, and micelles molecules which formed via self-assembly to template (Lai et al., 2012; Li et al., 2005; Liu et al., 2013; Sasidharan and Nakashima, 2014; Wang et al., 2008).

In this research, it was prepared the hollow MgO/SiO_2 nanoparticles with the great surface active base area and used in the reaction of cyclohexanone, malononitrile and benzaldehyde for synthesis of 1H-isochromene under mild condition.

2. Experimental

Chemicals

All material and solvents were used as the starting resources attained deprived of further purification cyclohexanone, malononitrile, benzaldehyde, cetyltrimethyl ammonium bromide (CTAB), tetraethyl orthosilicate (TEOS), ammonium, were acquired from Sigma. Magnesium oxide, sodium bicarbonate, ammonium peroxydisulfate and Hydrogen chloride, were purchased from Sinopharm Chemical. The products were recognized with melting point, FT-IR and ^1H NMR analysis, the spectra were recorded in DMSO-d_6 and CDCl_3 solvents and register on a Bruker DRX-400 spectrometer via tetramethylsilane as the inner reference. FT-IR spectra were attained via KBr pellets and record with Perkin-Elmer 781 spectrophotometer by an Impact 400 Nicolet FT-IR spectrophotometer. XRD analysis was recorded with (CuK α , radiation, $\lambda = 0.154056 \text{ nm}$), with the speed of 2° min^{-1} beginning 10° to 80° (2θ). The nanocatalyst size was determined with Zeiss Scanning Electron Microscope (SEM) worked at a 15 kV accelerating voltage. The surface areas (BET) were assignment via nitrogen adsorption-desorption in -196°C that record by analyser Tristar 3020, Micromeritics

2.1. Synthesis of compact SiO_2 spheres (s SiO_2)

For a synthesis of s SiO_2 from Stober procedure, 5 mL of tetraethylorthosilicate instantly was added to the mixture of deionized water (8 mL), ethanol (70 mL) and ammonium aqueous solution (28%, 4 mL). Then the mixture was stirred for 1.5h in ambient temperature. At the end of the reaction, the white silica suspension was formed, then the product separated with a centrifuge and washed three times by deionized water and ethanol.

2.2. Synthesis of hollow SiO_2

60 mg of the sSiO_2 that prepared at prior step was dispersed in 15 ml deionized water via the ultrasonic waves for 20 min. Then 1.5 mL of the CTAB aqueous solution (1 mg, 1.5 ml) was added and stirred the mixture at ambient temperature for 1 h. Then 212 mg of Na_2CO_3 added to the reaction mixture and followed the reaction at 35°C for 24 h. In the end, the product has separated and washed with deionized water and ethanol.

2.3. Synthesis of hollow SiO_2 /MgO by Self-Assembly

50.0 mg of hollow SiO_2 was dispersed in 5.0 mL toluene by ultrasonic water bath for 30 min. After that, 2.0 mL of the MgO NPs which dispersed in toluene was added to the mixture and sonicated for 1.5-2 h. Consequently, the product was washed by toluene and dried at 120°C overnight.

2.4. Preparation of hollow SiO_2 /MgO.

The product of previous steps was converted to hollow MgO/ SiO_2 with hydrothermal removal of CTAB phase in 450°C for 4h. As a result, the hollow MgO/ SiO_2 were prepared.

2.5. General multicomponent procedure for synthesis of 1H-isochromene

1H-isochromene was synthesized from the three-component reaction. In this reaction, 1 mmol of cyclohexanone (1a-d) with 1 mmol of malononitrile were mixed in an ethanol solvent. Then 10 mg of hollow MgO/ SiO_2 nanocatalyst was added to the mixture and stirred for 10–20 min at room temperature. After completed, the first step 1 mmol of benzaldehyde was added to the mixture and the reaction followed for 10–20 min at room temperature. In the end, the nanocatalyst was separated with simple filtration and added 5ml water to the mixture, for the formation of the pure product. The final product was characterized by melting points, IR and ^1H NMR spectra.

3-amino-1-phenyl-5,6,7,8-tetrahydro-1H-isochromene-4-carbonitrile (**4a**); White solid; m.p.: $255\text{--}258^\circ\text{C}$; IR (KBr) $\nu = 3419, 3338, 3252, 2934, 2211, 1647, 1602, 1452, 1393, 1277, 1081, 712, 582\text{ cm}^{-1}$, ^1H NMR (400 MHz, CDCl_3) δ 7.57–7.45 (m, 5H), 6.04 (s, 1H), 4.85 (s, 2H, NH_2), 3.11–3.08 (d, $J = 12.5\text{ Hz}$, 1H), 2.92–2.87 (m, 1H), 2.33–2.28 (m, 1H), 2.17–2.14 (m, 1H), 1.81–1.78 (m, 1H), 1.68–1.71 (m, 1H), 1.57–1.48 (m, 1H), 1.01–0.92 (m, 1H).

3-amino-1-(2,4-dichlorophenyl)-5,6,7,8-tetrahydro-1H-isochromene-4-carbonitrile (**4b**); White solid; m.p.: $277\text{--}278^\circ\text{C}$; IR (KBr) $\nu = 3444, 3354, 3202, 2941, 2213, 1623, 1591, 1474, 1337, 1268, 1107, 1052, 878, 563\text{ cm}^{-1}$, ^1H NMR (400 MHz, CDCl_3) δ 7.67–7.53 (m, 2H), 7.44–7.42 (m, 1H), 6.12–6.08 (m, 1H), 4.88 (s, 2H, NH_2), 3.99–3.97 (d, $J = 8\text{ Hz}$, 1H), 2.80–2.98 (t, $J = 7\text{ Hz}$, 1H), 2.34–2.32 (m, 2H), 2.25–2.08 (m, 1H), 1.88–1.76 (m, 1H), 1.61–1.45 (m, 3H), 0.98–0.97 (m, 1H).

3-amino-1-(4-nitrophenyl)-5,6,7,8-tetrahydro-1H-isochromene-4-carbonitrile (**4c**); White solid; m.p.: $229\text{--}232^\circ\text{C}$; IR (KBr) $\nu = 3419, 3348, 3287, 2937, 2207, 1645, 1524, 1449, 1349, 1133, 1042, 858, 557\text{ cm}^{-1}$, ^1H

NMR (400 MHz, DMSO- d_6) δ 8.55–8.27 (m, 2H), 8.23–8.19 (t, J = 7.9 Hz, 1H), 8.06–7.80 (m, 1H), 7.78–7.33 (m, 1H), 6.66 (s, 2H, NH_2), 5.63 (s, 1H), 3.52 (d, J = 8.5 Hz, 1H), 3.43 (s, 1H), 2.87–3.85 (d, J = 12.5 Hz, 1H), 2.15–2.11 (m, 1H), 1.71–1.61 (m, 1H), 1.45–1.42 (t, J = 7.5 Hz, 1H), 0.89 (m, 1H).

3-amino-1-(4-bromophenyl)-5,6,7,8-tetrahydro-1H-isochromene-4-carbonitrile (**4d**); White solid; m.p.: 260–263°C; IR (KBr) ν = 3423, 3344, 3251, 2929, 2211, 1644, 1601, 1489, 1391, 1275, 1076, 835, 508 cm^{-1} , 1H NMR (400 MHz, $CDCl_3$) δ 7.77–7.43 (m, 3H), 7.19 (d, J = 8.5 Hz, 1H), 6.11–6.06 (m, 1H), 4.86 (s, 2H, NH_2), 3.10–3.06 (d, J = 8.6 Hz, 1H), 2.89–2.86 (d, J = 8.5 Hz, 1H), 2.34–2.28 (m, 1H), 2.27–2.04 (m, 1H), 1.84 (m, 2H), 1.74–1.40 (m, 2H), 1.08–0.74 (m, 1H).

3-amino-1-(4-chlorophenyl)-5,6,7,8-tetrahydro-1H-isochromene-4-carbonitrile (**4e**); White solid; m.p.: 274–277°C; IR (KBr) ν = 3421, 3343, 3252, 2944, 2212, 1645, 1602, 1492, 1388, 1212, 1095, 805, 514 cm^{-1} , 1HNMR (400 MHz, DMSO- d_6) δ 7.58 (d, J = 8.5 Hz, 1H), 7.52 (d, J = 7.8 Hz, 1H), 7.46 (d, J = 7.2 Hz, 2H), 5.75 (s, 1H), 3.65 (s, 2H, NH_2), 2.77, 2.48 (m, 1H), 2.15–2.18 (m, 3H), 1.66 (s, 1H), 1.42–1.51 (m, 2H), 0.79–0.88 (m, 1H)

3-amino-1-(4-(dimethyl amino) phenyl)-5,6,7,8-tetrahydro-1H-isochromene-4-carbonitrile; White solid (**4f**); m.p.: 248–250°C; IR (KBr) ν = 3448, 3356, 3207, 2917, 2212, 1618, 1526, 1447, 1358, 1272, 1115, 948, 525 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 7.52–7.35 (m, 1H), 7.15 (d, J = 7.5 Hz, 1H), 6.89–6.61 (m, 2H), 6.06–6.02 (m, 1H), 4.88 (s, 2H, NH_2), 3.01 (s, 6H), 2.92–2.76 (m, 1H), 2.34–2.24 (m, 1H), 2.15 (m, 1H), 1.81–1.75 (m, 2H), 1.64–1.41 (m, 2H), 1.04–0.85 (m, 1H).

3-amino-1-(3-nitrophenyl)-5,6,7,8-tetrahydro-1H-isochromene-4-carbonitrile (**4g**); White solid; m.p.: 248–250°C; IR (KBr) ν = 3441, 3357, 3248, 2947, 2208, 1639, 1531, 1442, 1352, 907, 829, 547 cm^{-1} , 1H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.3 Hz, 2H), 7.36–7.22 (m, 2H), 6.07–6.02 (m, 1H), 4.88 (s, 2H, NH_2), 3.08–3.05 (d, J = 8.5 Hz, 1H), 2.94–2.78 (m, 1H), 2.18–2.16 (m, 1H), 1.84–1.82 (m, 1H), 1.74–1.71 (m, 1H), 1.66–1.48 (m, 3H), 1.03–0.88 (m, 1H).

3-amino-1-(4-fluorophenyl)-5,6,7,8-tetrahydro-1H-isochromene-4-carbonitrile (**4h**); White solid; m.p.: 262–265°C; IR (KBr) ν = 3422, 3337, 3251, 2949, 2213, 1649, 1598, 1455, 1391, 1273, 828, 516 cm^{-1} , 1H NMR (400 MHz, DMSO- d_6) δ 7.65–7.28 (m, 4H, 2H, NH_2), 5.72 (s, 1H), 3.63–3.61 (d, J = 12.2 Hz, 1H), 2.78–2.78 (d, J = 8.5 Hz, 1H), 2.21–2.19 (d, J = 8.9 Hz, 1H), 2.07 (s, 1H), 1.66 (s, 1H), 1.59–1.37 (m, 2H), 0.85 (q, J = 7.5, 1H).

3-amino-1,7-diphenyl-5,6,7,8-tetrahydro-1H-isochromene-4-carbonitrile (**4i**); White solid; m.p.: 250–252°C; IR (KBr) ν = 3423, 3328, 3225, 2915, 2213, 1645, 1598, 1495, 1391, 1264, 755, 568 cm^{-1} , 1H NMR (400 MHz, DMSO- d_6) δ 7.63–7.62 (d, J = 7.8 Hz, 1H), 7.45 (s, 2H, NH_2), 7.42 (s, 4H), 7.22–7.18 (t, J = 7.4 Hz, 2H), 7.15–7.11 (m, 3H), 5.81 (s, 1H), 3.64–3.61 (d, J = 8.4 Hz, 1H), 3.13–3.08 (m, 1H), 2.28–2.91 (m, 1H), 2.45–2.41 (m, 1H), 2.23–2.16 (m, 1H), 1.52–1.49 (d, J = 7.8 Hz, 1H), 1.24–1.18 (q, J = 7.6 Hz, 1H).

3-amino-7-methyl-1-phenyl-5,6,7,8-tetrahydro-1H-isochromene-4-carbonitrile (**4j**); White solid; m.p.: 218–220°C; IR (KBr) ν = 3425, 3332, 3235, 2957, 2215, 1652, 1602, 1453, 1392, 1267, 711, 597 cm^{-1} , ^1H NMR (400 MHz, DMSO- d_6) δ 7.68–7.38 (m, 6H), 7.37 (s, 2H, NH_2), 5.98 (s, 1H), 3.58 (d, J = 8.6 Hz, 1H), 2.91–2.88 (d, J = 7.4 Hz, 1H), 2.32–2.24 (m, 1H), 1.67–1.67 (d, J = 8.2 Hz, 1H), 1.37–1.34 (m, 1H), 0.93–0.88 (d, J = 7.2 Hz, 1H), 0.81–0.79 (d, J = 5.4 Hz, 3H), 0.66–0.63 (q, J = 8.7 Hz, 1H).

3-amino-1-(4-bromophenyl)-7-methyl-5,6,7,8-tetrahydro-1H-isochromene-4-carbonitrile (**4k**); White solid; m.p.: 246–248°C; IR (KBr) ν = 3424, 3347, 3252, 2952, 2213, 1646, 1601, 1488, 1391, 1268, 827, 508 cm^{-1} , ^1H NMR (400 MHz, DMSO- d_6) δ 7.81–7.47 (m, 4H), 7.38 (s, 2H, NH_2), 5.68 (s, 1H), 3.68–3.63 (d, J = 7.7 Hz, 1H), 2.87 (s, 1H), 2.27–2.22 (d, J = 8.8 Hz, 1H), 1.69 (s, 1H), 1.36–1.32 (d, J = 8.5 Hz, 1H), 0.81 (s, 3H), 0.74–0.54 (m, 1H).

3-amino-1-phenyl-7-propyl-5,6,7,8-tetrahydro-1H-isochromene-4-carbonitrile (**4l**); White solid; m.p.: 194–198°C; IR (KBr) ν = 3428, 3343, 3255, 2952, 2211, 1648, 1597, 1456, 1393, 1274, 708, 579 cm^{-1} , ^1H NMR (400 MHz, DMSO- d_6) δ 7.61–7.42 (m, 4H), 7.39 (s, 2H, NH_2), 5.71 (s, 1H), 3.58–3.51 (m, 1H), 2.88–2.85 (d, J = 8.9 Hz, 1H), 2.32–2.26 (d, J = 7.6 Hz, 1H), 1.74–1.55 (m, 2H), 1.49–1.34 (m, 1H), 1.28–1.13 (m, 2H), 1.08–1.06 (q, J = 8.5, 2H), 0.79–0.76 (t, J = 7.4 Hz, 3H), 0.62 (q, J = 8.7 Hz, 1H).

3. Results And Discussion

3.1 Preparation and chracterization of catalyst

In this research, the hollow MgO/SiO₂ nanoparticles were prepared in three-steps that show in Scheme 1 (Fang et al., 2011; Wang and Zeng, 2009). At the first step, compact SiO₂ sphere (sSiO) was prepared and decreased density and increased of the active area space via converted to hollow SiO₂. The hollow SiO₂ was functionalized with MgO nanoparticles then the nanostructure calcinated and converted to hollow MgO/SiO₂ nanocatalyst.

After preparation, the nanocatalyst was characterized by various analysis such as FT-IR, XRD, BET, SEM and TEM. For the determined the crystal structure of nanoparticles, the X-ray diffraction patterns of nanostructure were investigated with the XRD spectrum (Fig 1). In the graph (a), the structure of hollow SiO₂ considered by X-ray diffraction (XRD) (tetragonal, JCPDS card N 34-0425). The spectra were showed a wide peak in 20-30 that assignment an amorphous structure of SiO₂ (Fig 2a). The graph (b) that due to hollow SiO₂@MgO furthermore the wide peak in 20-30, it has two peaks in 43, 62 that due to MgO (Fig 2b).

The hollow catalyst was considered by FT-IR spectrum (Fig 2). Fig 2a described the hollow SiO₂, the peak of around 1066 cm^{-1} determined stretching vibration from Si-O bonding. The peaks of 2924, 2853 cm^{-1} were showed C-H bonding from the CTAB and the peak of 3410 cm^{-1} due to the stretching vibration of the O-H bond. The spectrum 2b was related to hollow MgO/SiO₂ and displayed Mg-O bonding in 3697 cm^{-1} .

The hollow structure of synthetic compound has been demonstrated. The N₂ adsorption-desorption isotherms and hysteresis loop, provide better confirmation of the mesoporous structure. The Brunauer–Emmett–Teller (BET) was demonstrate 619 m² g⁻¹ surface area and the mean pore diameter is 2.11 nm. (Fig 3).

Hollow spheres morphology was achieved after calcination and considered by FE-SEM. The SEM images was displayed the formation of hollow MgO/SiO₂ nanoparticles with smooth and regular morphology (Fig 4). The average crystal size of nanocatalyst was170 nm.

3.2. Investigation of catalytic activity

1H-isochromene was synthesized from cyclic ketones, malononitrile and benzaldehyde in varies conditions. The model reaction was investigated with different catalysts, the amount of catalyst and solvents moreover the result displayed in **Table 1**.

Table 1. Several condition in multicomponent reaction for synthesis of 1H-isochromene ^a

Entry	Catalyst	Amount of catalyst (mg)	Solvent	Time (h)	Yield (%) ^b
1	p-TSA	10	Ethanol	12	10
2	Nano NiFe ₂ O ₄	10	Ethanol	12	15
3	Nano CoFe ₂ O ₄	10	Ethanol	12	15
4	pyridine	10	Ethanol	2.5	50
5	Et ₃ N	10	Ethanol	1.5	65
6	morpholine	10	Ethanol	1	75
7	CaO	10	Ethanol	1.5	70
8	nano MgFe ₂ O ₄	10	Ethanol	2	65
9	MgO	10	Ethanol	1	75
10	Hollow MgO/SiO ₂	10	Ethanol	0.25	97
11	Hollow MgO/SiO ₂	10	Methanol	1	85
	MgO/SiO ₂				
12	Hollow MgO/SiO ₂	10	Chloroform	1.5	75
13	Hollow MgO/SiO ₂	10	Acetonitrile	1	80
14	Hollow MgO/SiO ₂	10	Dichloromethane	1.5	75

^a Reaction conditions: cyclohexanone (1 mmol), malononitrile (1 mmol), benzaldehyde (1 mmol), room temperature

^b Isolated yield

After optimization of the reaction conditions with different catalysts and solvents, the situation of a reaction was determined (**Scheme 2**). The hollow MgO/SiO₂ with strong base properties selected as the

catalyst for the synthesis of 1H-isochromene from cyclohexanone (1 mmol), malononitrile (1 mmol) and benzaldehyde (1mmol) in the ethanol solvent. Therefore, the different derivatives of 1H-isochromene (**Table 2**) were synthesized at room temperature in 20-30 min.

Table 2. The reaction of cyclohexanone 1a-d, malononitrile and benzaldehyde 3a-h for synthesis of 1H-isochromenes 4a-l^a

Entry	Product	Time (min)	Yield (%) ^b
1		15	97
2		17	95
3		18	96
4		17	95
5		17	96
6		20	94
7		18	96
8		16	94
9		20	93
10		15	94
11		20	95
12		18	93

^a Reaction conditions: cyclohexanone (1 mmol), malononitrile (1 mmol), benzaldehyde (1 mmol), ethanol solvent, room temperature

^b Isolated yield

3.3. Proposed reaction mechanism

Synthesis of 1H-isochromene was done in the two-step, the first step, including the mixed of cyclohexanone with malononitrile in ethanol under the base condition. The reaction was followed by vinylogous Michael addition for the synthesis of vinylmalononitriles. In the second step, benzaldehyde was added to the mixture and during the aldol reaction vinyl malononitrile reacted with benzaldehyde. The vinyl malononitrile was adsorbed hydrogen, and the processes followed by cycle creation of C–C and C–O bonds. In the end, 1H-isochromene was synthesized with loss of the hydrogen via the base catalyst (Scheme 3).

3.4. Reusability

At the end of reaction, the hollow catalyst separated with simple filtration and washed with acetone and ethyl acetate solvent. The heterogeneous nanostructure can catalyze the reaction in six consecutive runs without loss of activity. (Fig 5).

4. Conclusions

In this research, it was prepared a novel heterogeneous hollow catalyst for the synthesis of 1H-isochromene from cyclohexanone, malononitrile, and benzaldehyde. The reaction was followed in the ethanol solvent at room temperature and hollow MgO/SiO₂ nanostructure used as the base catalyst. The product was synthesized with excellent yield and short reaction time, the catalyst easily recovered and reused for several runs of the reactions.

Declarations

Authors' contributions: Article publication approved by co-authors, as well as by the responsible authorities at the institute where the work has been carried out.

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Consent for publication: In accordance to the copyright transfer or open access rules.

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Supplementary data: Supplementary material related to this article can be found in the online version at doi//:

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Figures

Figure 1

XRD spectra of a: sSiO₂ b: hollow SiO₂/MgO

Figure 2

The spectrume of FT-IR a) SiO_2 b) Hollow MgO/SiO_2

Figure 3

BET curves of hollow MgO/SiO₂

Figure 4

SEM image of hollow MgO/SiO₂

Figure 5

Catalyst recyclability in model reaction

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