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Synthesis of chromene derivatives in the presence of mordenite zeolite/MIL-101 (Cr) metal-organic framework composite as catalyst

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Shabnam Sohrabnezhad, Department of Chemistry, Faculty of Science, University of Guilan, P.O. Box 1914, Rasht. Iran. Email: sohrabnezhad@guilan.ac.ir In the present study, the synthesis of mordenite zeolite/MIL-101(Cr) metalorganic framework (MOF) composite [MOR/MIL-101(Cr)] using the ship in a bottle method was suggested. The properties of prepared composite and individual MOF and MOR zeolite were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), nitrogen adsorption-desorption measurement, and thermogravimetric analysis (TGA). The XRD results indicated diffraction peaks for each compound (MOR and MOF) in composite. The SEM and TEM images showed the formation of plates MOR (with size of $2.5 \times 3 \,\mu m$) along with spherical particles MIL-101. The Brunauer-Emmett-Teller results showed that the surface area of the composite was smaller than individual MOF and MOR zeolite. Based on TGA plots, the hybrid zeolite/MOF composite was more thermally stable compared with the isolated MIL-101(Cr). The composite was functionalized by post-synthetic modification to obtain acid-base bifunctionality (H-MOR/MIL-101-ED) for the synthesis of chromene derivatives. The acidity from framework Al-O(H)-Si sites in MOR and basicity from amine groups in MIL-101 were obtained by post-synthetic modification.

KEYWORDS

chromene derivatives, metal-organic framework, metal-organic framework composite, mordenite zeolite

1 | INTRODUCTION

Zeolites and metal–organic frameworks (MOFs) with pore size smaller than 100 nm are two important examples of nanoporous materials being intensively studied for many applications.^[1–7] The structure of MOFs is constructed by metal ions or clusters that act as lattice nodes and are held in place by multidentate organic ligands. This new class of nanoporous materials was first discovered by Bernard Hoskins and Richard Robson in 1989.^[8] Until now, a number of conventional^[9] and novel synthesis methods have been developed for preparing of MOFs. Because a range of metal clusters and organic ligands can be built into MOFs, a wide structural diversity and highly designable pore sizes and shapes in MOFs are expected, which endow MOFs with tunable cavity architectures and properties.^[10] The diversity of MOF structures creates a variety of functionalities and potential applications for the as-synthesized MOFs. Additionally, the components in MOFs, either metal clusters or organic linkers, can be further modified to bring in new functionalities. The framework of MOFs can be functionalized through pre - or post-synthetic modification of metal clusters and/or organic ligands.^[11] As nanoporous materials, MOFs break the limitation of the

small pore sizes of zeolites. They can be used for a number of potential applications, including gas separation, storage and heterogeneous catalysis.^[12,13] MOFs as catalysts can be synthesized or functionalized with active sites, including unsaturated metal sites or functional groups on organic linkers.

Zeolites are crystalline microporous aluminosilicates, widely used as heterogeneous catalysts, adsorbents and ion-exchange materials in petrochemical and fine chemical industries. Hydrothermal synthesis is the conventional method used for generating zeolite materials. The required synthesis temperature and pressure depend on the zeolite type. Most commercial zeolites are synthesized at 90–100°C, but some dense zeolites need higher crystallization temperatures (up to 350°C). The optimal pH range for zeolite synthesis is 11–13,^[14] which can be modulated by the addition of OH⁻ guest molecules. The zeolite acidity in H ⁺-form zeolites originates from framework Al species.^[15]

As porous materials, zeolite and MOF share common characteristics of high surface areas and uniform micropores, but they differ in thermal/mechanical stability and structural flexibility.^[16] The integration of MOF and zeolites into composite particles is expected to produce useful hybrid nanoporous materials where inorganic zeolite and organic MOF components impart the advantages of high thermal, mechanical and structural stability of zeolites and specific functionality and high flexibility of MOFs. MOF-based composites are generally formed by physical or chemical mixing of MOFs with inorganic and/or organic substrates. MOF-based composite membranes such as ZIF-8/Matrimid have been synthesized for direct uses in gas and liquid separations.^[17] Silica@MOF core-shell composite spheres were prepared by the seeded growth method and were used as stationary phases for chromatographic separation.^[18] Zhu et al. reported synthesis of ZSM-5 zeolite@ UiO-66 MOF coreshell composites by solvothermal growth of MOF on the surface of zeolite support, and demonstrated an application of this material as a bifunctional acid-base catalyst in two-step cascade reactions.^[19] MOF [MIL (Fe)]-graphite oxide composites were used for ammonia adsorption.^[20] The loaded metal oxides or insolubilized materials into the MOFs pores are other composites that were prepared using post-synthesis methods, such as the impregnation method.^[21]

In this article, we will consider the ship in a bottle (SIB) method for the synthesis of mordenite zeolite (MOR)/MIL-101(Cr) MOF composite. The synthesized composite was modified by post-synthetic modification to obtain acid-base bifunctionality (H-MOR/MIL-101-ED) for the synthesis of chromene derivatives. On the basis of the structure of (H-MOR/MIL-101-ED), we anticipated that this reagent can be used as an efficient catalyst

for the promotion of the reactions that need the use of an acidic or basic catalyst to speed up. Here in, we wish to extend the application of this catalyst for the synthesis of chromene derivatives via one-pot condensation of aldehydes with resorcinol and malononitrile. MOR has special importance over other 12-membered ring zeolites because of its one-dimensional pore structure and high activity. These properties make MOR important in many industrial applications.^[22] MIL-101(Cr)^[2] is a threedimensional chromium terephthalate-based porous material with the empirical formula $[Cr_3(O)-X (bdc)_3(H_2O)_2]$ (bdc = benzene-1,4-dicarboxylate, X = OH or F). MIL-101(Cr) has two types of inner cages with diameters of 29 Å and 34 Å, and pore aperture window diameters of up to 16 Å with a high surface area [Brunauer-Emmett-Teller (BET) surface area of 4000 m² g⁻¹].^[2]

2 | EXPERIMENTAL

2.1 | Materials

Ditopic terephthalic acid (H₂BDC), chromium nitrate [Cr $(NO_3)_3 \cdot 9H_2O$] and dimethylformamide (DMF) were purchased from Fluka and Merck (Darmstadt, Germany). Silica gel (Fisher, 28–200 mesh) and sodium aluminate were used in the synthesis of MOR. Hydrochloric acid and sodium hydroxide were applied for a variation of the pH of sample solutions. 4-Nitrobenzaldehyde, resorcinol and malononitrile were used for catalytic reaction. All materials were from Merck.

2.2 | Synthesis of MIL-101(Cr) and MOR zeolite

The synthesis procedure for MOR zeolite was as reported in our previous paper.^[23] The chemical composition of the MOR gel was 6Na₂O:5Al₂O₃:30SiO₂:780H₂O. Crbased MOF (MIL-101) was synthesized by the hydrothermal method based on the published recipe with a slight modification.^[24] A small-scale synthesis of MIL-101 (Cr) includes a solution containing Cr (NO₃)₃·9H₂O (1.6 mg, 1.0 mmol), nitric acid 67% (0.65 mL, 1.0 mmol) and ditopic terephthalic acid (H₂BDC; 0.65 mg, 1.0 mmol) in 20 mL H₂O. The mixture was stirred for 90 min, and after that was transferred to a stainless-steel autoclave that was heated for 8 hr at 200°C and cooled afterwards slowly to room temperature. The content of the autoclave was turquoise-colored. The solid product was centrifuged, after that DMF (5 mL) was added to the solid product, which was then placed in a hot (80°C) ultrasonic bath and sonicated for 45 min. Centrifugation was again performed to separate MIL-101 and DMF. The precipitate

was transferred to a beaker, and it was stirred with 10 mL of water at 80°C for 2 hr. After separation by centrifugation, the washing procedure using ethanol was repeated. The final product was obtained by centrifugation and dried in an oven $(95^{\circ}C)$ for 2 hr.

2.3 | Synthesis of MOR/MIL-101 (Cr) composite via the ship in a bottle method

The synthesis of MOR/MIL-101 (Cr) composite via the SIB method was performed by the addition of MIL-



SCHEME 1 (H-MOR/MIL-101-ED) catalyzed synthesis of chromene derivatives



101(Cr) MOF to the synthesis mixture of MOR zeolite. The starting materials required for preparing MOR gel with composition of 6Na₂O:Al₂O₃:30SiO₂:780H₂O were added in the following order: double-deionized water, sodium hydroxide, sodium aluminate and silica gel. The resulting mixture was stirred for 1 hr in the presence of 0.15 g MIL-101(Cr) MOF, and then transferred to Teflon-lined stainless-steel autoclaves. Crystallization was carried out under hydrothermal conditions at 170°C for 24 hr. After the autoclave was quenched in cold water, the solid products were filtered, washed with water and dried at 110°C overnight. The prepared sample was called MOR/MIL-101SIB.

2.4 | Incorporation of amine (-NH₂) groups and acid exchange activation into MOR/MIL-101 composite

Modification of composite by $-NH_2$ and acid groups was performed based on the published recipe with a slight



FIGURE 1 Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) Images of MIL-101 and MOR zeolite

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modification.^[19] The incorporation of amine groups in the composites was performed in a 50-mL flask equipped with a reflux condenser and heated in a temperaturecontrolled oil bath under atmospheric pressure and magnetic stirring conditions; 50 μ L ethylenediamine was added to 30 mL anhydrous toluene in the flask, and 0.5 g MOR/MIL-101 composites was added to the solution sequentially. The mixture was refluxed at 110°C for 12 hr. The particles were collected by centrifugation and washed with ethanol three times. The particles were then dried in conventional oven at 70°C.

The acid exchange was performed in a 50-mL flask equipped with a reflux condenser and heated in a temperature-controlled oil bath under atmospheric pressure and magnetic stirring; 0.5 g -NH₂-modified MOR/MIL-101 composites was added to 50 mL 0.1 mol L⁻¹ HCl ethanol solution. The mixture was refluxed at 90°C for a total of 6 hr. The acid-exchanged particles were washed with water and ethanol repeatedly. The sample was then dried at 100°C in a vacuum oven. The sample was denoted as H-MOR/MIL-101-ED after this step.

2.5 | Catalytic reaction for the synthesis of chromene derivatives

A mixture of aldehyde (1.0 mmol), malononitrile (1.2 mmol), resorcinol (1.0 mmol) and H-MOR/MIL-101-ED (5 mg) in H₂O was stirred at 80°C. The progress of the reaction was monitored by thin-layer chromatography. After completion of the reaction, evaporation of water and ethanol (5 mL) was added to the mixture. Then the solid catalyst was obtained through simple filtering. After evaporation of solvent, the solid product was recrystal-lized from ethanol to afford pure product in good to high yields (Scheme 1).

2.6 | Characterizations

The powder X-ray diffraction (XRD) patterns of the samples were recorded using an X-ray diffractometer (XRD Philips, Model PW 1730) with Cu K α radiation ($\lambda = 1.545$ Å) under conditions of 45 kV and 30 mA, at a step size of $2\theta = 0.05^{\circ}$. The XRD patterns were recorded between 2° and 70° 2θ at a scanning speed of 0.5° per min. All samples were analyzed in random orientation. The transmission electron microscopies (TEM) were recorded with a Zeiss-EM10C, working at a 100 kV accelerating voltage. Samples for TEM were prepared by dispersing the powdered sample in acetone by sonication, and then drip-drying on a copper grid coated with carbon film. Samples were sonicated for 15 min. The scanning electron microscopy (SEM) was conducted with a FESEM

Analyzer, Model TESCAN MIRA II. The SEM operated at 30 kV. Chemical analysis of the samples was performed by energy-dispersive X-ray analysis (EDX) joined with a Philips XL30 SEM. The specific surface area and pore diameter were measured using a BET Analyzer, Model BEL SORP mini II. The thermogravimetric analysis (TGA) was conducted using a TGA/DSC Instruments LINSIES STP PT-1000 with a heating rate of 5°C per min under air atmosphere.

3 | **RESULTS AND DISCUSSION**

3.1 | Characterization of composite

The morphological characteristics of MOR, MIL-101 and synthesized composite can be shown by SEM and TEM images (Figure 1). The SEM image of MOR zeolite revealed the presence of aggregates of thin plate-shaped crystals with varying geometry. The thickness of the plates is less than 100 nm. The SEM image of MIL-101 (Cr) indicated clearly small crystal particles. The crystal size is less than 500 nm, and MIL-101(Cr) MOF exhibited regularly octahedral shape. The TEM images of MOR and



FIGURE 2 X-ray diffraction (XRD) patterns of samples

MIL-101 were in agreement with their SEM images. Based on the TEM image of MOR, the size of the smooth plate was $\sim 1.2 \times 3 \mu m$.

The XRD profiles of the MOR/MIL-101 composite, MOR and MIL-101 samples are shown in Figure 2. The composite showed all the peaks that had been ascribed to individual MIL-101(Cr) MOF and MOR zeolite, in its XRD pattern. The XRD pattern of composite was matched quite well with patterns that were given in articles,^[25,26] which allowed identifying the product as MOR zeolite and MIL-101 MOF, respectively.

The SEM image of MOR/MIL-101SIB indicated smooth plates MOR with overall size of $2.5 \times 3 \,\mu$ m (Figure 3a and b), and spherical particles MIL-101 that diffused in mordenite plates. In this method, formation of plates MOR is observed in the presence of MIL-101. The octahedral MIL-101 is not observed in the SEM image of the MOR/MIL-101SIB sample. Probably, the morphology of pre-synthesized MIL-101 MOF changes during the hydrothermal treatment in a basic aqueous solution, because mordenite and MIL-101(Cr) are hydrothermally synthesized in basic and acidic aqueous

solution, respectively.^[23,24] These kinds of SEM images were observed by Liu *et al.*^[27]

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The TEM image and EDX results of the composite are exhibited in Figure 3c and d, respectively. The TEM image of MOR/MIL-101SIB indicated aggregation of MIL-101 MOF that was located over the surface area of MOR zeolite. This image was in agreement with SEM images. The EDX result of the composite (Figure 3d) indicated all elements (Al, Si, O, Cr, C and Si) in the composite and elemental analysis were in agreement with SEM images.

The nitrogen sorption isotherms of the synthesized materials [MOR, MIL-101 (Cr)] and composites at 77 K and 1 bar are observed in Figure 4. The MIL-101(Cr) and MOR samples showed a Type I isotherm with uptake at $P/P_0 \sim 0.2$ that is characteristic of microporous materials.^[24] The pore volumes and surface areas of the MOR zeolite according to the Si/Al value (Si/Al = 6) and MIL-101 (Cr) are listed in Table 1. MIL-101(Cr) and MOR had BET surface areas of 2583 and 450 m² g⁻¹, respectively. The total pore volumes of MIL-101 and MOR zeolite were obtained as 3.45 and 0.16 cm³ g⁻¹,



FIGURE 3 (a), (b) Scanning electron microscopy (SEM) images of MOR/MIL-101 composite with different magnification. (c) Transmission electron microscopy (TEM) image and (d) energy-dispersive X-ray analysis (EDX) result of MOR/MIL-101(Cr) composite



FIGURE 4 N2-sorption isotherms plots of MIL-101(Cr), MOR and hybrid composite

TABLE 1 Physical properties of MIL-101(Cr), MOR and MOR/MIL-101 composite

Sample	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore diameter (nm)
MOR	450	0.16	0.65
MIL-101 (Cr)	2583	3.45	5.3
MOR/MIL- 101SIB	440	0.99	1.11

BET, Brunauer-Emmett-Teller.

respectively. These results were in agreement with other articles.^[24,28] The presence of a hysteresis over the higher P/P_0 region of the composite (MOR/MIL-101SIB) is an indication that some mesoporosity had been developed, indicating structural modifications that were induced by the presence of the MIL-101. Additionally, the surface area of MOR/MII-101SIB (440 m² g⁻¹) was similar to pure MOR (450 m² g⁻¹), but the pore volume (0.99 cm³ g⁻¹) of the MOR/MIL-101SIB composite was greater than that of the pure MOR sample (0.16 cm³ g⁻¹; Table 1). This observation can be ascribed to the formation of additional mesoporous in the resulting hybrid composite.

Further, it can be observed from the TGA that MIL-101(Cr) showed two weight losses (Figure 5): the first one before 150°C could be attributed to the removal of the solvent water or methanol trapped within the pores



FIGURE 5 Thermogravimetric analysis (TGA) plots of MIL-101(Cr) and MOR/MIL-101(Cr) composite

and the MIL-101(Cr) can be stable up to 400°C; The second one from 400°C to 600°C should result from the decomposition of the framework (87.7%) due to the presence of the nitro-group. This means that there are more degradable species in MIL-101(Cr) that could be mainly attributed to the existence of the nitro-group in MIL-101. The TGA plots in Figure 5 showed that MOR/MIL-101 composite became more thermally stable compared with the isolated MIL-101(Cr). This enhancement can be attributed to the incorporation of the MOR, which is a crystalline aluminosilicate material with high thermal stability and only starts to decompose at relatively higher temperatures.^[22] Based on SEM and TEM images, MOR/MIL-101SIB composite consists of a strong interaction between MIL-101 and MOR zeolite, and this interaction was visible in SEM images. On the one hand, one of the disadvantages of mesoporous materials such as MIL-101 MOF is low thermal stability,^[23] then, MIL-101 MOF as a mesoporous material with inner cages diameters of 29 Å and 34 Å has lower thermal stability than MOR zeolite.

3.2 | Study of the preparation of chromene derivatives by modified composite

In order to confirm the crystallinity of the MOR/MIL-101 composite after treatment with ethylenediamine (ED) and HCl, XRD were employed. The XRD pattern of H-MOR/MIL-101-ED composite is shown in Figure 2. The composite consists of diffraction peaks from both MIL-101 and MOR, indicating the presence of both phases in the composite material. In addition, the crystalline phases were well preserved after the addition of ED and HCl.On the basis of the information obtained from the abovementioned studies and the structure of (H-MOR/MIL-101-ED), we anticipated that this reagent can be used as

TABLE 2Preparation of chromene derivatives using (H-MOR/MIL-101-ED) as the catalyst

				m. p. (°C)	
Entry	Aldehyde	Time (min)	Yield (%)	Found	Reported [Ref.]
1	4-ClC ₆ H ₄ CHO	16	90	156-159	161–162 ^[29]
2	4-MeC ₆ H ₄ CHO	12	85	178–180	184–186 ^[29]
3	4-MeOC ₆ H ₄ CHO	12	87	106-108	112-114 ^[29]
4	4-NO ₂ C ₆ H ₄ CHO	8	90	205-207	210-212 ^[30]
5	3-NO ₂ C ₆ H ₄ CHO	10	83	163-165	169–170 ^[29]
6	2-NO ₂ C ₆ H ₄ CHO	10	85	156-158	160-162 ^[31]
7	4-HOC ₆ H ₄ CHO	20	80	248-250	252-254 ^[30]

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an efficient catalyst for the promotion of the reactions that need the use of an acidic or basic catalyst to speed up.^[29–31] Herein, we wish to extend the application of this catalyst for the synthesis of chromene derivatives via onepot condensation of aldehydes with resorcinol and malononitrile. In order to optimize the reaction conditions, we carried out the reaction of 4-nitrobenzaldehyde (1 mmol), resorcinol (1 mmol) and malononitrile (1.2 mmol) in H₂O as green solvent in the presence of the new catalyst (Scheme 1). The obtained result showed that the reaction using 5 mg of the catalyst in water at 80°C proceeded with the highest yield in the shortest reaction time (Table 2, entry 4). Then, to assess the efficiency of (H-MOR/MIL-101-ED) in the synthesis of chromene



SCHEME 2 Proposed mechanism for the synthesis of chromene derivatives in the presence of (H-MOR/MIL-101-ED) as a catalyst

TABLE 3 Compared performance of various catalysts in synthesis of 2-amino-3-cyano-7-hydroxy-4-(4-chlorophenyl)-4H-chromene

Entry	Catalyst/condition	Catalyst loading (mol%)	Time (min)	Yield (%)	Ref.
1	L-Proline/EtOH, reflux	10	5 hr	98	[3]
2	Na ₂ CO ₃ /Grinding, 50°C	10 (10.5 mg)	30	88	[4]
3	MIL-101(Cr)-SO ₃ H/H ₂ O, 100°C	0.37	7 hr	76	[5]
4	Saccharose/EtOH:H ₂ O, reflux	20 (60 mg)	50	88	[1]
5	Tungstic acid functionalized SBA-15/H ₂ O, 100°C	1.11 (30 mg)	15 hr	80	[6]
6	Potassium hydrogen phthalate/H ₂ O, 50°C	25	2.5 hr	95	[2]
7	Amino-appended β -cyclodextrin/H ₂ O, r.t.	0.5	5 hr	90	[7]
8	(H-MOR/MIL-101-ED) /H ₂ O, 80°C	5 mg	16	90	This work

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derivatives, a wide range of aromatic aldehydes containing electron-withdrawing groups as well as electrondonating groups were easily subjected to the same reaction under the optimal conditions. It has been observed that this method is quite general, and all these reactions occurred with good to excellent yields in very short times (Table 2, entries 1–7).

In Scheme 2, a mechanism has been suggested based on the available literature for this reaction.^[29] It seems that (H-MOR/MIL-101-ED) catalyzes the reaction by the activation of the aldehyde and malononitrile. Firstly, Knoevenagel product (I) was obtained from the condensation of these activated compounds. Then the Michael addition (II) occurred between the Knoevenagel product and resorcinol, which is followed by intra-molecular cyclization to yield 2-amino-4*H*-chromene derivatives (Scheme 2).

In order to show the efficiency of the present method, we have compared our result obtained from the reaction of 4-chlorobenzaldehyde, resorcinol and malononitrile in the presence of (H-MOR/MIL-101-ED) with other results reported in the literature.^[32–35] As can be seen in Table 3, this method avoids the disadvantages of other procedures, such as difficult work-up procedures, use of organic solvents, long reaction times and large amounts of catalysts.

4 | CONCLUSIONS

The MOR/MIL-101 composite was prepared using the SIB method. In the SIB method, the octahedral shape of MII-101 was converted to spherical particles, and a strong interaction was observed between them. The MOR/MOF composite was more thermally stable compared with the isolated MIL-101(Cr). The BET results showed that the surface area of the new composite was smaller than individual MOF and MOR zeolite. The composite was functionalized by post-synthetic modification to obtain acid-base bifunctionality (H-MOR/MIL-101-ED) as an efficient solid catalyst for the simple synthesis of 2-amino-3-cyano-4H-chromene derivatives. This procedure has several advantages, such as ease of preparation and handling of the catalyst, simple experimental procedure, high reaction rates and good yields of the products.

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