



## Short Communication

# Synthesis and characterization of poly(4-vinylpyridine)/MCM-48 catalyst for one-pot synthesis of substituted 4*H*-chromenes

Roozbeh Javad Kalbasi\*, Neda Mosaddegh

Department of Chemistry, Islamic Azad University, Shahreza Branch, 311-86145, Shahreza, Isfahan, Iran

## ARTICLE INFO

## Article history:

Received 11 February 2011

Received in revised form 3 April 2011

Accepted 5 April 2011

Available online 13 April 2011

## Keywords:

MCM-48

Poly(4-vinylpyridine)

Polymer-inorganic hybrid material

Multi-component reaction

4*H*-chromene

H<sub>2</sub>O

## ABSTRACT

In this paper, we wish to report the synthesis and characterization of poly(4-vinylpyridine) supported on MCM-48 by in situ polymerization of 4-vinylpyridine in the presence of MCM-48. This catalyst was effectively employed as a novel heterogeneous basic catalyst for the one-pot synthesis of 4*H*-chromenes in aqueous medium. This catalyst was easily prepared, and showed considerable level of reusability.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

Multi-component reactions (MCRs), in which multiple reactions are combined into a single synthetic operation, have been used extensively to form carbon–carbon bonds in synthetic chemistry [1]. Recently, the synthesis of 4*H*-chromene and quinoline derivatives has attracted great interest due to its useful biological and pharmacological properties [2,3]. The known procedure for the synthesis of 4*H*-chromene derivatives employs a three-component reaction of cyclic 1,3-diketones, aryl aldehydes, and malononitrile; and is performed under various reaction conditions. The process represents a typical cascade reaction [4].

Mesoporous molecular sieves have attracted much research interest because of their potential application in catalysis, sorption and synthesis of fine chemicals [5,6] since their pores are larger than those of microporous molecular sieves, allowing a faster diffusion and processing of bulky molecules. Mesoporous molecular sieve, MCM-48, has attracted considerable attention because of its high surface area, ordered pore structure array, and narrow pore size distribution. The cubic MCM-48 contains two independent three-dimensional pore systems interwoven and suited in a mirror-plane position to each other. This special pore system of MCM-48 provides more favorable mass transfer kinetics in catalytic and separation applications than MCM-41 in a one-dimensional hexagonal bisectional pore system [7].

Hybrid organic–inorganic polymers have received increasing interest from research groups because of their unique properties [8].

Nevertheless, among the different researches on these materials, there are relatively a few reports on the application of organic–inorganic hybrid polymer as a heterogeneous catalyst [9–11]. The hybrid materials could be obtained by combining organic polymers with inorganic materials [12]. These organic–inorganic hybrid materials could be prepared by various methods, depending on what kind of interaction is employed between organic polymers and inorganic elements, or on how organic moieties are introduced to inorganic phases. An in situ polymerization, which is the simultaneous polymerization of organic monomer in the presence of mesoporous materials, is an important method for the preparation of composite materials without chemical interaction.

In this paper, poly(4-vinylpyridine)/MCM-48 (P4VP/MCM-48) composite was prepared as a highly efficient heterogeneous basic catalyst by in situ polymerization method. The main goal of this catalytic synthesis was to introduce a novel and efficient organic–inorganic composite to expand the use of these types of composites for organic reactions. In order to investigate the catalytic activity of this catalyst, one-pot synthesis of substituted 4*H*-chromene derivative via three-component reaction was chosen as important synthetic compounds.

## 2. Experimental method

### 2.1. Catalyst characterization

The samples were analyzed using FT-IR spectroscopy (using a Perkin Elmer 65 in KBr matrix in the range of 4000–400 cm<sup>-1</sup>). The X-ray powder diffraction (XRD) of the catalysts was carried out on a

\* Corresponding author. Tel.: +98 321 3213211; fax: +98 321 3213103.  
E-mail address: [rkalbasi@iaush.ac.ir](mailto:rkalbasi@iaush.ac.ir) (R.J. Kalbasi).

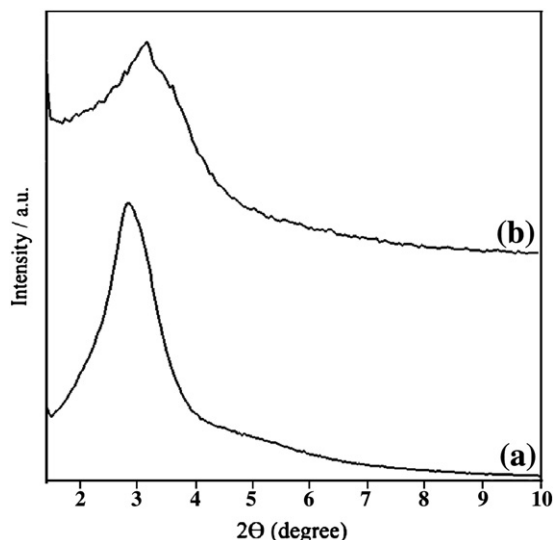


Fig. 1. The powder XRD pattern of (a) mesoporous silica MCM-48 and (b) P4VP/MCM-48.

Bruker D8Advance X-ray diffractometer using nickel filtered Cu K $\alpha$  radiation at 40 kV and 20 mA. Moreover, the thermal gravimetric analysis (TGA) data were obtained by a Setaram Labsys TG (STA) in a temperature range of 30–650 °C and heating rate of 10 °C/min in N<sub>2</sub> atmosphere. The BET specific surface areas and BJH pore size distribution of the samples were determined by adsorption–desorption of nitrogen at liquid nitrogen temperature, using Series BEL SORP 18. Scanning electron microscope (SEM) studies were performed on Philips, XL30, SE detector.

## 2.2. Catalyst preparation

### 2.2.1. Preparation of MCM-48

Cetyltrimethylammonium bromide (CTAB) (2.4 g, 6.6 mmol) was dissolved in 50 mL deionized water. To this, 50 mL technical grade ethanol (0.87 mol) and 12 mL of aqueous ammonia (32 wt.%, 0.20 mmol) were added. The solution was stirred for 10 min, after which tetraethylorthosilicate (TEOS) (3.4 g, 16 mmol) was added. After stirring for 2 h at room temperature, the resulting solid was recovered by filtration, washed with deionized water and dried in air at ambient temperature. The template was removed by calcination at 550 °C for 6 h.

### 2.2.2. Preparation of P4VP/MCM-48

4-Vinyl pyridine (4VP) (0.5 mL, 4.6 mmol), and MCM-48 (0.5 g) in 7 mL tetrahydrofuran (THF) were placed in a round bottom flask. Benzoyl peroxide (3% mol, 0.034 g) was added and the mixture was heated to 65–70 °C for 5 h while being stirred. The resulting white fine powder composite was collected by filtration, washed several times with THF, and finally dried at 60 °C under reduced pressure.

Basic content of P4VP/MCM-48 composite (Pyridine content) was estimated by back titration using NaOH. 5 mL of HCl (0.2 N) was added to 0.05 g of this composite and the mixture was stirred for 30 min. The catalyst was removed and washed successively with deionized water. The excess amount of HCl was titrated with NaOH (0.1 N) in the presence of phenolphthalein as an indicator. The pyridine content of catalyst was 4.45 mmol g<sup>-1</sup>.

## 2.3. General procedure for synthesis of 4H-chromenes

In the typical procedure for the one-pot synthesis of 4H-chromenes, in a round bottom flask was placed a mixture of a benzaldehyde (1 mmol), malononitrile (1 mmol), 1,3-cyclohexadione (1 mmol) and

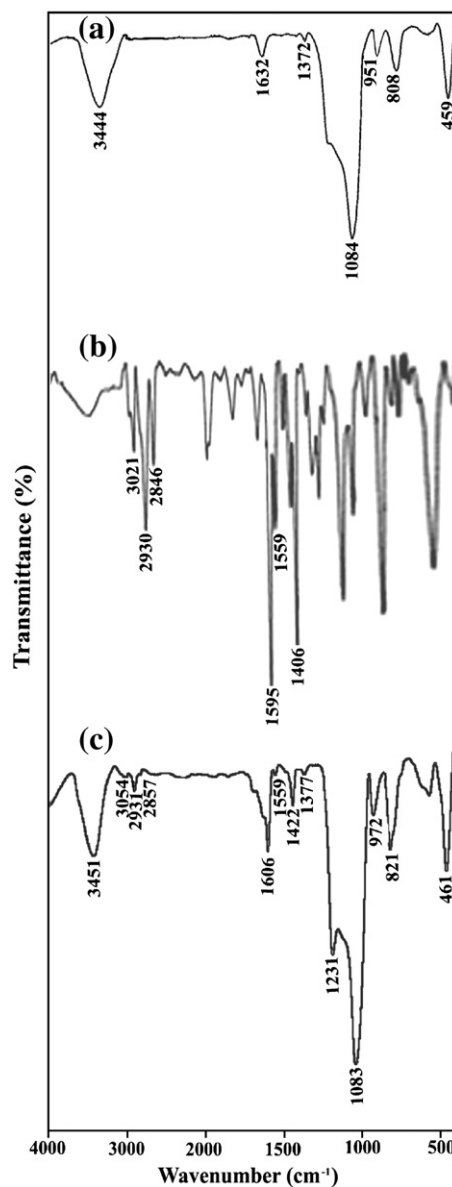


Fig. 2. FT-IR spectra of (a) mesoporous silica MCM-48, (b) P4VP and (c) P4VP/MCM-48.

catalyst (0.14 g, P4VP/MCM-48) in H<sub>2</sub>O (5 mL). The suspension was stirred at 95 °C for 2 h. The progress of reaction was monitored by Thin Layer Chromatography (TLC) using n-hexane/ethylacetate (16:4) as eluent. After completion of the reaction (monitored by TLC), for the reaction work-up, the catalyst was removed from the reaction mixture by filtration. Then, the filtrate was cooled to room temperature so that the product would solidify. The water was removed and the precipitated product recrystallized from methanol to afford pure product (98% isolated yield). The product was identified with <sup>1</sup>H NMR, <sup>13</sup>C NMR and FT-IR spectroscopy techniques.

Table 1

Porosity data of mesoporous silica MCM-48 and P4VP/MCM-48 samples.

Sample	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	V <sub>p</sub> (cm <sup>3</sup> g <sup>-1</sup> )	D <sub>p</sub> (nm)
Mesoporous silica MCM-48	1673	0.89	2.14
P4VP/MCM-48	1174	0.72	1.60

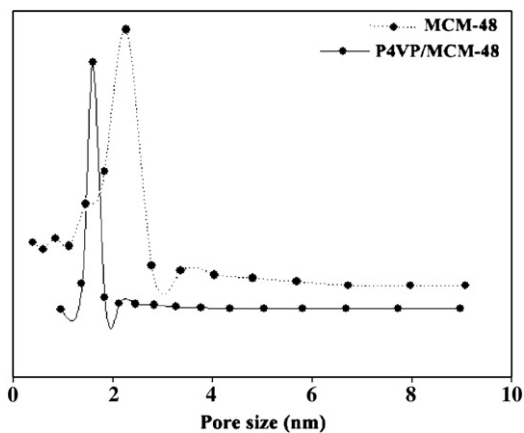


Fig. 3. Pore size distribution of MCM-48 and P4VP/MCM-48 calculated from  $N_2$  adsorption data using the BJH (Barrett–Joyner–Halender) method.

#### 2.4. General procedure for Knoevenagel condensation

In the typical procedure for Knoevenagel condensation, a mixture of a benzaldehyde (1 mmol), malononitrile (1 mmol, 0.066 g), and catalyst (0.12 g, P4VP/MCM-48) was ground at room temperature (25 °C) in a glass mortar and pestle. The progress of reaction was monitored by Thin Layer Chromatography (TLC) using n-hexane/ethylacetate (16:4) as eluent. After completion of the reaction (monitored by TLC), for the reaction work-up, 5 mL of hot ethanol was added to the mixture and the catalyst was removed from the mixture by filtration. The filtrate was cooled to  $-10$  °C, the precipitated product was separated and recrystallized from ethanol to afford pure product. The products were identified with  $^1H$  NMR,  $^{13}C$  NMR, GC–Mass and FT-IR spectroscopy techniques. Additionally, by using the reused catalyst, the selectivity (100% to  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds) and yield (100%) were not changed.

### 3. Results and discussion

#### 3.1. Catalyst characterization

Fig. 1 shows the powder X-ray diffraction patterns of silica MCM-48 (a) and P4VP/MCM-48 composite (b). All samples exhibit a strong (211) diffraction peak at  $\sim 2.35^\circ$  [13,14]. The characteristic reflections

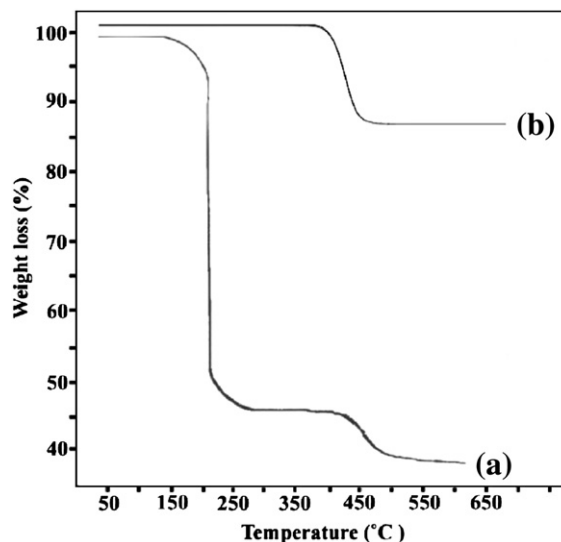


Fig. 5. TGA curves of (a) P4VP and (b) P4VP/MCM-48.

Table 2

Effect of temperature and catalyst amount on the synthesis of 4*H*-chromene <sup>a</sup>.

Entry	Amount of catalyst (g)	Temperature (°C)	Yield (%) <sup>b</sup>	Time (h)
1	–	95	–	12
2	0.10	95	70	3
3	0.12	95	88	2
4	0.14	95	98	2
6	0.14	25	60	6
5	0.16	95	98.7	2

<sup>a</sup> Reaction conditions: catalyst (P4VP/MCM-48), benzaldehyde (1 mmol), malononitrile (1 mmol), 1,3-cyclohexadione (1 mmol),  $H_2O$  (5 mL).

<sup>b</sup> Isolated yield.

Table 3

Effect of MCM-48 on the catalytic activity of P4VP/MCM-48 catalyzed three-component reaction of benzaldehyde and malononitrile with 1,3-cyclohexadione <sup>a</sup>.

Catalyst	Time (h)	Yield (%) <sup>b</sup>	TOF ( $h^{-1}$ ) <sup>c</sup>
P4VP	5	50	0.08
MCM-48	6	0	0
P4VP/MCM-48	2	98	0.80

<sup>a</sup> Reaction conditions: P4VP/MCM-48 (0.14 g), benzaldehyde (1 mmol), malononitrile (1 mmol), 1,3-cyclohexadione (1 mmol),  $H_2O$  (5 mL), 95 °C.

<sup>b</sup> Isolated yield.

<sup>c</sup> Moles of product per mol of catalyst per hour.

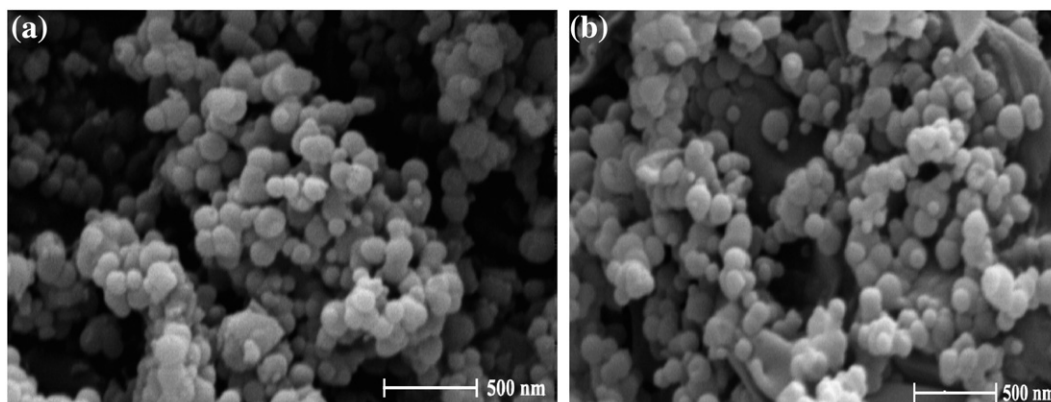
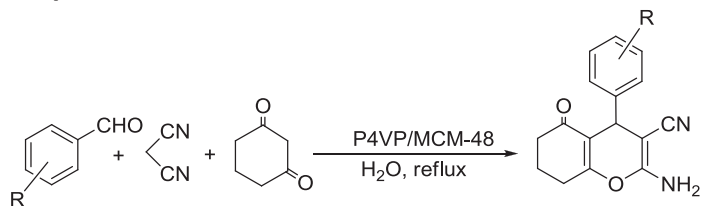
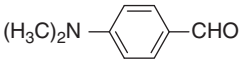
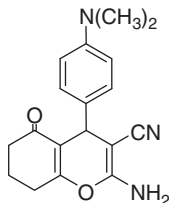


Fig. 4. Scanning electron microscopy (SEM) photographs of (a) MCM-48 and (b) P4VP/MCM-48.

**Table 4**One-pot synthesis of 4*H*-chromene derivatives in presence of P4VP/MCM-48<sup>a</sup>.

Entry	Substrate	Product	Time (h)	Yield (%) <sup>b</sup>	Mp (°C)	
					Found	Reported ref
1			2	98	221–223	218–220 [16]
2			1	98	201–203	202–204 [15]
3			0.5	98	235–237	234–236 [15]
4			1.5	98	210–212	210–212 [15]
5			1.5	98	220–222	224–226 [15]
6			2	98	216–218	214–216 [16]

Table 4 (continued)

Entry	Substrate	Product	Time (h)	Yield (%) <sup>b</sup>	Mp (°C)	
					Found	Reported ref
7			3	98	172–174	168–170 [16]

<sup>a</sup> Reaction conditions: P4VP/MCM-48 (0.14 g), aromatic aldehydes (1 mmol), malononitrile (1 mmol), 1,3-cyclohexadione (1 mmol), H<sub>2</sub>O (5 mL), 95 °C.

<sup>b</sup> Isolated yield.

of a well-ordered cubic structure are present in both cases indicating that polymerization has no adverse effects on the long-range structure.

Fig. 2 presents the FTIR spectra of MCM-48 (a), similarly prepared bulk P4VP (b), and P4VP/MCM-48 composite (c). Similar to mesoporous silica MCM-48 (Fig. 2a), P4VP/MCM-48 composite shows the typical vibrations of asymmetric and symmetric stretching, as well as the rocking of Si–O–Si at around 1083, 821, and 461 cm<sup>-1</sup> (Fig. 2c). The existence of P4VP in the composite is evidenced by the appearance of typical P4VP vibrations on the FTIR spectrum. In the FT-IR spectrum of P4VP/MCM-48 (Fig. 2c), the new bands at 1606, 1559 and 1422 cm<sup>-1</sup> are the characteristic absorptions of pyridine ring. Among them, the band which appeared at around 1606 cm<sup>-1</sup> (this band in the spectrum of P4VP is around 1595) is the stretching vibration absorption of C–N bond, and the bands at 1559 and 1422 cm<sup>-1</sup> are attributed to the stretching vibration absorption of aromatic C–C bonds. Moreover, the presence of peaks at around 2800–3100 cm<sup>-1</sup> corresponds to the aromatic and aliphatic C–H stretching in P4VP/MCM-48. These are in accordance with the spectrum of P4VP (Fig. 2b). The appearance of the above bands shows that P4VP has been attached to the surface of MCM-48 and the P4VP/MCM-48 has been obtained.

The BET specific surface areas and the pore size, the host MCM-48 and P4VP/MCM-48 had already been calculated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively (Table 1). Both samples show isotherms of type IV, according to the IUPAC nomenclature, which are the typical characteristics of mesoporous materials. The corresponding BJH pore size distribution curves for the MCM-48 and P4VP/MCM-48 materials are shown in Fig. 3. Compared to these two pore size distribution curves, it can be seen clearly that the pore size distribution is narrowed after the insertion of polymer, which indicates that the polymer is distributed uniformly on the surface of MCM-48. It is known that calcined MCM-48 has a high BET surface area (1673 m<sup>2</sup> g<sup>-1</sup>), a large pore volume (0.89 cm<sup>3</sup> g<sup>-1</sup>) and pore size (2.1 nm), indicative of its potential application as a host in organic materials. After hybridization with P4VP through in situ polymerization, P4VP/MCM-48 exhibits a smaller specific surface area, pore size and pore volume in comparison to those of pure MCM-48, which might be due to the presence of polymer on the surface of MCM-48. Although these textural properties are smaller than those found for mesoporous silica MCM-48, P4VP/MCM-48 still has a mesoporous form. So, it is suitable to act as a basic catalyst.

The morphologies of the MCM-48 host and P4VP/MCM-48 are shown in Fig. 4. MCM-48 host (Fig. 4a) and P4VP/MCM-48 (Fig. 4b) are agglomerations of small irregular particles. Virtually no difference in particle surface morphology between the MCM-48 host and the P4VP/MCM-48 composite is observed.

TGA curves of bulk P4VP and P4VP/MCM-48 composite are presented in Fig. 5 under N<sub>2</sub> atmosphere. The weight loss (around 62%, w/w) of P4VP begins at 210 °C because of thermo degradation of P4VP polymer chains, and the degradation ends at 500 °C (Fig. 5a). Whereas for P4VP/MCM-48, the weight loss (around 14%, w/w) begins at 360 °C that is related to the degradation of the polymer chains and the degradation ends at 460 °C (Fig. 5b). Obviously, the hybrid P4VP/MCM-48 shows higher thermal stability and a slower degradation rate than P4VP. Therefore, after hybridization, the thermal stability is enhanced greatly, which is very important for the catalyst application.

### 3.2. Catalytic activity

The effect of different parameters on the three-component reaction of benzaldehyde and malononitrile with 1,3-cyclohexadione over P4VP/MCM-48 as catalyst was investigated, and the results are as follows:

The effect of reaction temperature and catalyst amount on the reaction yield was studied and the values are shown in Table 2, for the reaction of benzaldehyde (1 mmol), malononitrile (1 mmol), 1,3-cyclohexadione (1 mmol) and catalyst (P4VP/MCM-48) in H<sub>2</sub>O (5 mL). When the catalyst amount increases from 0.10 to 0.14 g the yield increases from 70% to 98% in 95 °C. With excess amount of catalyst, the yield obviously increases because of the availability of more basic sites. As the amount of catalyst exceeds 0.14 g, the yield still increases but not so obviously as that below 0.14 g. So, the 0.14 g of the catalyst was chosen. In addition, it should be mentioned that in the absence of the catalyst, the product was not observed after 6 h.

The yield increases from 60% to 98% by increasing the temperature from 25 °C to 95 °C. Also, by increasing the temperature, the duration of reaction decreases from 6 h to 2 h. Thus, 95 °C (reflux) was considered as an optimum reaction temperature (Table 2).

The effect of MCM-48 on the catalytic activity of P4VP/MCM-48 composite was investigated for three-component reactions of benzaldehyde and malononitrile with 1,3-cyclohexadione, and the results are shown in Table 3. One of the greatest advantages of this catalyst is that it is used easily due to its powdery structure. P4VP is adhesive, and this characteristic makes it hard to separate it from the vessel; but after mixing with MCM-48 and making P4VP/MCM-48 composite, it becomes powdery which is easy to use and recycle. Also, comparative reaction by using P4VP and P4VP/MCM-48 shows that P4VP/MCM-48 is more efficient, by completing the reaction in a short time. On the other hand, the yield is decreased and the reaction is carried out in a long period of time using P4VP. On the basis of the turnover frequency (TOF) defined in Table 3, it is obvious that composite P4VP/MCM-48 system is advantageous. In fact, the activity of P4VP is much lower

**Table 5**

The catalyst reusability for the synthesis of 4*H*-chromene<sup>a</sup>.

Cycle	Yield (%) <sup>b</sup>
fresh	98
1	98
2	98
3	98
4	97
5	97
6	97
7	96
8	96
9	95

<sup>a</sup> Reaction conditions: P4VP/MCM-48 (0.14 g), benzaldehydes (1 mmol), malononitrile (1 mmol), 1,3-cyclohexadione (1 mmol), H<sub>2</sub>O (5 mL), 95 °C.

<sup>b</sup> Isolated yield.

than that of P4VP/MCM-48. These results are due to the large surface area of P4VP/MCM-48 in comparison to P4VP. MCM-48 has very high surface area on whose surface polymer chains can be distributed uniformly. In this condition, the pyridine rings, that are the original centers for doing the reaction, are free; and it is possible for reactant to reach the active sites of the catalyst (nitrogen atoms of pyridine

rings). Therefore, we can conclude that the yield of the reaction was high on the surface of P4VP/MCM-48. On the other hand, in the P4VP there are many interactions between the chains of the polymers and some of the pyridine ring trapped in the chains of the polymer. Hence, we have hindrance around the pyridine rings that can prevent the reactant from reaching the active sites of the catalyst (nitrogen atoms of pyridine rings). This can reduce the activity of the P4VP.

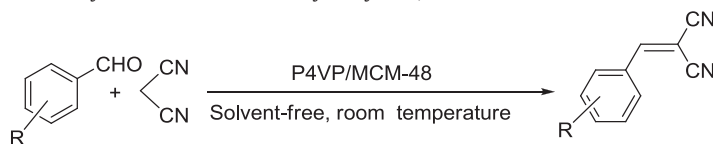
The study was then extended to the application of P4VP/MCM-48 in synthesis of substituted 4*H*-chromenes of various aldehydes and malononitrile with 1,3-cyclohexadione. These reactions produced 4*H*-chromene derivatives in high yield with 100% selectivity [15,16]. Reactions were carried out in water at reflux condition. The results are listed in Table 4.

The recovered catalyst from the experiment was washed with water (10 mL) and acetone (3 × 5 mL). Then, it was dried in an oven at 60 °C and used in the synthesis of 4*H*-chromene. The results show that this catalyst can be reused without any modification 9 times, and no significant loss of activity/selectivity performance was observed (Table 5).

In addition, the catalytic activity of P4VP/MCM-48 was investigated for the Knoevenagel condensation by employing various aromatic and hetero aromatic aldehydes with malononitrile as an active methylene compound. All reactions were almost completed at room temperature (Table 6) [17–22]. These reactions produced the corresponding electrophilic alkenes in high yield with 100% selectivity

**Table 6**

Knoevenagel condensation reaction of aromatic aldehydes and malononitrile catalyzed by P4VP/MCM-48.



Entry	Substrate	Product	Time (min)	Yield (%) <sup>b</sup>	Mp (°C)	
					Found	Reported ref
1			3	100	81–83	82–84 [17,19,22]
2			18	60	182–183	180–182 [20]
3			6	100	160–162	159–161 [17,19,22]
4			8	100	97–100	102–103 [17,21]
5			18	98	167–168	168–169 [17,19,20]
6			27	98	132–134	133–135 [17,18]
7			8	98	102–104	103–104 [17,22]

<sup>a</sup> Reaction conditions: benzaldehyde (1 mmol), malononitrile (1 mmol), catalyst (0.12 g, P4VP/MCM-48), solvent-free, room temperature.

<sup>b</sup> Isolated yield.



to the condensation products. In addition, it should be mentioned that in the absence of the catalyst, the product was not observed after 1 h.

#### 4. Conclusions

A novel polymer-inorganic hybrid material (poly(4-vinylpyridine/MCM-48)) was prepared by a very simple and inexpensive method. This new heterogeneous basic catalyst can practically replace soluble bases in view of the following advantages: a) high catalytic activity under mild reaction conditions; b) easy separation of the catalyst after reaction; c) organic and inorganic phases in this composite with critical effects on the catalyst activity; d) reusability of the catalyst for several times without any loss in the yield of the reaction. We have developed a facile, convenient and environmentally benign one-pot synthesis of 4*H*-chromenes under reflux conditions using P4VP/MCM-48 in very good yields. Most importantly, water has been chosen as a green solvent for these reactions. Finally, we believe that the new synthetic method reported here would greatly contribute to an environment-friendly process.

#### Acknowledgement

The support by the Islamic Azad University, Shahreza Branch (IAUSH) Research Council and Center of Excellence in Chemistry is gratefully acknowledged.

#### References

- [1] J.M. Khurana, B. Nand, P. Saluja, *Tetrahedron* 66 (2010) 5637–5641.
- [2] S. Gao, C.H. Tsai, C. Tseng, C. Yao, *Tetrahedron* 64 (2008) 9143–9149.
- [3] S. Makarem, A.A. Mohammadi, A.R. Fakhari, *Tetrahedron Lett.* 49 (2008) 7194–7196.
- [4] M.N. Elinson, A.I. Ilovaisky, V.M. Merkulova, P.A. Belyakov, A.O. Chizhov, G.I. Nikishin, *Tetrahedron* 66 (2010) 4043–4048.
- [5] A. Taguchi, F. Schuth, *Micropor. Mesopor. Mater.* 77 (2005) 1–45.
- [6] B.J. Scott, G. Wirnsberger, G.D. Stucky, *Chem. Mater.* 13 (2001) 3140–3150.
- [7] F. Wei, J. Yang, F.N. Gu, L. Gao, J.H. Zhu, *Micropor. Mesopor. Mater.* 130 (2010) 266–273.
- [8] J.E. Mark, *Acc. Chem. Res.* 39 (2006) 881–888.
- [9] R.J. Kalbasi, M. Kolahdoozan, A.R. Massah, K. Shahabian, *Bull. Korean Chem. Soc.* 31 (2010) 2618–2626.
- [10] R.J. Kalbasi, M. Kolahdoozan, M. Rezaei, *Mater. Chem. Phys.* 125 (2011) 784–790.
- [11] R.J. Kalbasi, M. Kolahdoozan, K. Shahabian, F. Zamani, *Catal. Commun.* 11 (2010) 1109–1115.
- [12] M.T. Run, S.Z. Wu, D.Y. Zhang, G. Wu, *Mater. Chem. Phys.* 105 (2007) 341–347.
- [13] M. Pedernera, O.D. Iglesias, R. Mallada, Z. Lin, J. Rocha, J. Coronas, J. Santamaría, *J. Membr. Sci.* 326 (2009) 137–144.
- [14] M. Bandyopadhyay, H. Gies, C. R. Chimie 8 (2005) 621–626.
- [15] T.-S. Jin, A.-Q. Wang, F. Shi, L.-S. Han, L.-B. Liu, T.-S. Li, *ARKIVOC* (14) (2006) 78–86.
- [16] K. Gong, H.-L. Wang, J. Luo, Z.-L. Liu, *J. Heterocycl. Chem.* 46 (2009) 1145–1150.
- [17] M. Hosseini-Sarvari, H. Sharghi, S. Etemad, *Chin. J. Chem.* 25 (2007) 1563–1567.
- [18] B.M. Reddy, M.K. Patil, K.N. Rao, G.K. Reddy, *J. Mol. Catal. A Chem.* 258 (2006) 302–307.
- [19] G. Postole, B. Chowdhury, B. Karmakar, K. Pinki, J. Banerji, A. Auroux, *J. Catal.* 269 (2010) 110–121.
- [20] S.D. Sharma, P. Gogoi, D. Konwar, *Indian J. Chem.* 46 (2007) 1672–1678.
- [21] M. Gupta, R. Gupta, M. Anand, *Beilstein J. Org. Chem.* 5 (2009) 68.
- [22] A. Kumar, M. Dewan, A. Saxena, A. De, S. Mozumdar, *Catal. Commun.* 11 (2010) 679–683.