Chem. Pap. (2018) 72:289–299
https://doi.org/10.1007/s11696-017-0279-4

ORIGINAL PAPER

Key factor affecting the basicity of mesoporous silicas MCM-41: effect of surfactant extraction time and Si/Al ratio

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Received: 7 April 2017 / Accepted: 20 August 2017 / Published online: 29 August 2017

Abstract Mesoporous silica Si-MCM-41 was prepared by hydrothermal method using TEOS and CTAB as the source of silica and structuring agent, respectively. The surface of the as-synthesized material was treated using HCl/ETOH solvent to remove the CTA surfactant instead of using the calcination. Characterization of the catalysts was performed using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), nitrogen sorption at 77 K, scanning and transmission electronic microscopy (SEM, TEM), and thermogravimetric analysis TGA. The catalytic properties of the prepared materials in the condensation of acetophenone with ethyl cyanoacetate were studied. The effects of the catalyst type, Si/Al ratio, reaction kinetics, and reaction temperature were also investigated to find an optimal parameter. The results show that an interesting yield was obtained (about 96%) in a short reaction time; it is found that the yields of products depend not only on the amount of surfactant inside the mesopores but also on the Si/Al ratio. The catalyst reuse shows that this catalyst can be used up to five cycles, and at temperatures higher than 50 °C, the yield of products decreases due to the slight destruction of the catalyst as confirmed by the XRD analysis. Based on the results obtained, a possible mechanism of the condensation reaction of acetophenone was proposed.

Keywords Mesoporous silica · As-synthesized Si-MCM-41 · Surfactant removal · Condensation of acetophenone · Catalyst reuse

Introduction

The discovery of mesoporous silicates materials by Mobile Oil has attracted intense interest of several laboratories (Beck et al. 1992; Kresge et al. 1992), these materials are characterized by higher pore sizes (≈20 nm), specific surface area significantly larger than the zeolites, inert framework, nontoxicity, biocompatibility, and high hydrothermal stability (Davis 2002; Izquierdo-Barba et al. 2011; Wu et al. 2011), which allow them to be used as effective catalysts and adsorbents (Lixin et al. 2011; Semsarzadeh et al. 2012; Terrab et al. 2017; Ouargli-Saker et al. 2017; Boukoussa et al. 2015a; Chikh et al. 2015; Talha et al. 2017). Among these mesoporous materials, there is MCM-41 which has known wider applications due to its uniform pore diameter, high surface area (>1000 m^2/g), and regular pore structure. All these properties expand the field application of this material in adsorption (Morsli et al. 2015; Boukoussa et al. 2017; Sekkiou et al. 2016), separation (Sunghwan et al. 2014), and catalysis

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Electronic supplementary material The online version of this article (doi:10.1007/s11696-017-0279-4) contains supplementary material, which is available to authorized users.

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(Boukoussa et al. 2015a, b, c; Parangi et al. 2014; Brahmi et al. 2016).

To date, several reactions have been tested using MCM-41 as basic catalyst for transesterification reaction (Pirouzmand et al. 2015; Ranucci et al. 2015): Claisen–Schmidt and Knoevenagel condensations (Martins et al. 2006, 2010), cycloaddition of 4-nitrophenyl azide with activated alkenes (Boukoussa et al. 2015b), Michael additions (Kubota et al. 2006), and cycloaddition reactions of CO_2 with epoxides (Srivastava et al. 2006). in order to improve the properties of this catalyst (increasing the basicity and improving the reusability), several methods have been developed using surface modification by cation exchange (e.g., Na^+, K^+, Cu^{+2},…) (Venkatesan et al. 2005; Jlalia et al. 2014), functionalization by organic molecules (e.g., $–NH_2$,…) (Deepak et al. 2014; Parida and Dharitri 2009), and deposition of oxides on the surface (Cs_2O, K_2O, or calcium–lanthanum oxide…) (Martins et al. 2010; Lu et al. 2014; Gholami et al. 2014). However, these methods lead to the structural degradation of the catalyst during the preparation process or treatment reuse, whereas the exchanged catalysts incur a major problem due to the leaching of cations in the reaction medium.

Recently, particular attention was focused on the use of the as-synthesized Si-MCM-41 as the basic catalyst without any modification of surface, with the presence of CTA^+ inside the pores showing interesting and remarkable basic properties (Boukoussa et al. 2015c; Martins et al. 2006, 2010). The catalytic properties of this material were also compared with different materials containing Si-MCM-41 such as NH_2-Si-MCM-41, Cs_2O/Si-MCM-41, or Na^+/Si-MCM-41, and the best catalytic proprieties were obtained by the as-synthesized Si-MCM-41 due to the higher basicity of siloxy ions which are linked to the cationic surfactant CTA^+ (Martins et al. 2006, 2010). In fact, its reusability revealed it is stable for several successive cycles (Martins et al. 2006, 2010).

The Knoevenagel condensation reaction is known for its wide range of applications in organic chemistry due to carbon–carbon bond formation (Knoevenagel 1898); generally, this reaction is catalyzed by weak bases such as ethylenediamine, piperidine, or corresponding piperidinium salts, potassium fluroiodide, and alkali metal hydroxides (e.g., NaOH and KOH) (Rao and Venkataratnam 1991; Prajpati et al. 1996). Due to poor product recovery and environmental problems generated by these catalysts, many efforts have been made to prepare olefinic compounds via the Knoevenagel reaction by an environmental-friendly method employing solid catalysts such as ZIF-8/NaA composite (Guangcai et al. 2015), KOH/SnO_2 (Jun et al. 2015), polyvinylamine/SBA-15 (Wach et al. 2015), NH_2-MSNS mesoporous silica (Zhu et al. 2015), NH_2-Graphene Oxide (Huang et al. 2015), MOF (Burgoyne and Meijboom 2013), and Ca-FSM-16 (Ikeue et al. 2011). However, all these previously cited catalysts are costly or less efficient to be considered as catalysts for Knoevenagel condensation; this is the reason why researchers are still trying to find less costly and more efficient catalysts.

The works of Martins et al. (2006, 2010) showed that the as-synthesized Si-MCM-41 is an efficient and reusable catalyst for the condensation of different aldehydes, knowing that the condensation of aldehydes provided good yields under mild conditions. However, the condensation of ketones suffers from the consumption of a longer reaction time, elevated temperature, and low-to-moderate yields of the obtained products. In order to take benefit from the textural proprieties of mesoporous materials (i.e., facile diffusion), we have tried to modify the amount of surfactant inside the pores so as to have a good compromise between basicity of siloxy ions and porosity of the catalysts.

By examining the literature, we find that the use of the as-synthesized Si-MCM-41 as catalyst for condensation of acetophenone with ethyl cyanoacetate is practically nonexistent. We also show a detailed study on the correlation between the surface basicity, extraction of organic template, and the reaction yield. Another parameter is discussed which consists on the relationship between Si/Al ratios and the basicity of the as-synthesized mesoporous catalysts.

Experimental

Synthesis of Si-MCM-41

The as-synthesized Si-MCM-41 catalyst was prepared using cetyltrimethylammonium bromide (CTAB) as structuring agent and tetraethylorthosilicate (TEOS) as silica source under hydrothermal treatment. The procedure for the catalyst's preparation was thoroughly described elsewhere (Boukoussa et al. 2015c, 2017; Chikh et al. 2015).

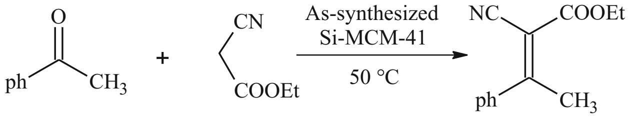
The gel's composition was 1 TEOS, 0.12 CTAB, 0.25 NaOH, 1.5 EtOH, and 100 H_2O. The procedure consists in the preparation of a solution containing CTAB (2.91 g, 98%, Alfa Aesar), distilled water (110 mL), and ethanol (6 mL, 99.5%, Riedel-de-Haën). The second solution containing NaOH (0.66 g, 98% Sigma-Aldrich), distilled water (10 mL), and TEOS (7.4 mL, 98%, Aldrich), was added to the first solution. After stirring at 308 K for 3 h, the obtained mixture was transferred to an autoclave and hydrothermally treated at 423 K for 10 h. The obtained product was removed from the oven and cooled at room temperature. After filtration and washing several times with distilled water, the obtained solid was dried at 333 K during 24 h. The catalyst was then treated with solutions containing ethanol and hydrochloric acid. 1 g of the as-synthesized Si-MCM-41 was dispersed in 100 mL of ethanol containing 1 M HCl, and the mixture was stirred vigorously at 60 °C for 1 or 2 h, then recovered by filtration, washed with ethanol, and finally dried at 60 °C. The obtained catalysts were named as MCM-0, MCM-1, and MCM-2, respectively, according to the time of surfactant extraction treatment. According to this designation, MCM-0 denotes the as-synthesized Si-MCM-41 non treated, MCM-1 and MCM-2 the as-synthesized Si-MCM-41 catalyst treated for 1 and 2 h, respectively.

Characterization

In order to determine the structural and textural properties of the as-synthesized Si-MCM-41 treated with HCl/ETOH, several techniques of analysis have been used such as X-ray diffraction (XRD) using diffractometer Bruker AXS D-8 with Cu-Kα radiation and nitrogen sorption at 77 K using a TriStar 3000 V6.04A volumetric instrument, where the obtained materials were outgassed at 353 K until a 3×10^{-3} Torr static vacuum was reached. The surface area and pore size distributions were calculated by BET and BJH methods, respectively (Brunauer et al. 1938; Barrett et al. 1951). FTIR spectroscopy using JASCO (4200) instrument, Thermogravimetric analysis (LABSYSEvo SETARAM), scanning electronic microscopy (SEM) was performed using a Hitachi 4800S microscope, and transmission electronic microscopy (TEM) was performed on a JEOL 1200 EXII device. The basicity of the catalysts was determined by the Hammett indicator method. First, the samples were heat treated at 100 °C for 24 h to remove the physorbed species. Thereafter, a suspension containing these catalysts (0.15 g of catalyst) was prepared in a methanol solution containing Hammett indicators (0.02 mol/L methanol solution) to determine the total basicity, and the suspension was stirred for 30 min and then titrated with a methanol solution of benzoic acid (0.01 M).

Catalytic test

A mixture of acetophenone (10 mmol), ethyl cyanoacetate (10 mmol), and catalytic amount of catalyst (see scheme 1) was stirred at 50, 80, or 100 °C on an oil bath under reflux.



Scheme 1 Knoevenagel reaction catalyzed by the as-synthesized Si-MCM-41

The reaction mixture was cooled down to room temperature, the catalyst was filtered, and the product was obtained as colorless oil.

We have investigated several parameters that affect the condensation reaction such as the effect of Si/Al ratio (Si/Al = 80, 40, and 20), reaction temperature (50, 80, and 100 °C), reaction kinetics, and the effect of CTA extraction on Si-MCM-41. For this last parameter, we have used the as-synthesized Si-MCM-41 with different CTA percentages obtained after extraction treatment with HCl/ETOH solvent.

Results and discussion

Characterization of the catalysts

The XRD patterns of the as-synthesized and extracted Si-MCM-41 are given in Fig. 1. The XRD patterns of all samples exhibit the peaks characteristic of the hexagonal phase, confirming the formation of Si-MCM-41 mesoporous structure. We also note that the treated materials maintain their structure after surfactant extraction. All catalysts (MCM-0, MCM-1, and MCM-2) exhibit a strong peak, respectively, at $2\theta = 2.06$, 2.08, and 2.10 due to (1 0 0) reflection lines and four weak signals around 3.53–3.60, 4.08–4.12, 5.45–5.51, and 6.16–6.23 (2θ) corresponding to (110), (200), (210), and (300) reflections, indicating the formation of well-ordered mesoporous materials with high hexagonal regularity (Pauly et al. 1999). However, there were some slight decreases in peaks (110), (200), (210), and (300) for the sample MCM-2 due to the processing time.

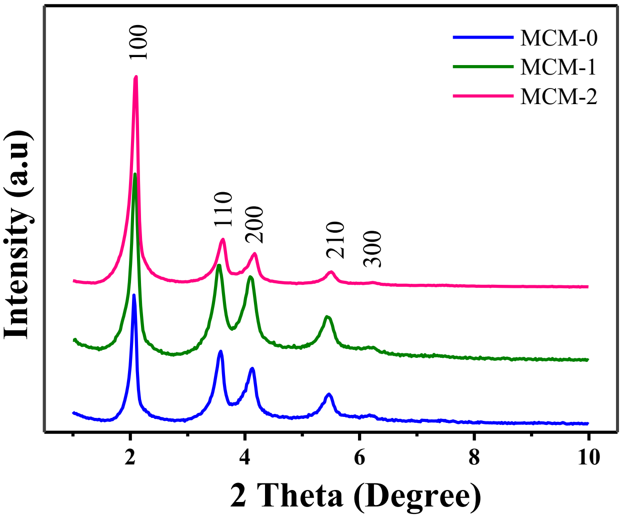


Fig. 1 XRD patterns of MCM-0, MCM-1 and MCM-2 catalysts

The lattice parameter a_0 is calculated using the equation: $a_0 = 2d_{100}/\sqrt{3}$, and the d_{100} value is calculated using Bragg's equation: $n\lambda = 2d\,\sin\theta$. The observed d_{100} and a_0 unit cell parameter results (Table 1) do match well with the hexagonal p6 mm space group. We note that the d_{100} value is about 42.02–42.84 Å for all samples containing the surfactants (MCM-0, MCM-1, and MCM-2). When the template in the sample was completely removed by calcination (823 K under air for 12 h), the d_{100} value decreased to 37.54 Å as shown in Table 1 due to the condensation of the silica framework by deshydroxylation during calcination. However, when the template was partially removed by the solvent extraction, the d_{100} decreased slightly as a consequence of the cell contraction, and after the partial replacement of the big CTA$^+$ cations by protons, the value is maintained ($\approx$42 Å) as shown in Table 1 (the cases of MCM-1 and MCM-2). These results are consistent with the literature (Ariapad et al. 2012).

The BET surface area, pore size, and pore volume of the as-synthesized Si-MCM-41 catalysts treated with HCl/EtOH solvent are also shown in Table 1. There were increases in the mesopore volume and the BET surface area during the removal of the surfactant in Si-MCM-41. We note also that the pore volume and pore size are higher compared with the samples treated in lesser duration of exchange time. Extending the treatment time leads to the removal of higher amount of surfactant inside the pores of Si-MCM-41. However, a higher pore volume was obtained by calcination at 823 K for 12 h ($V = 1.071$ cm^3/g) due the total removal of the surfactant. However, interesting results were obtained during the treatment with HCl/EtOH solvent (the case of MCM-2, $V = 0.91$ cm^3/g) compared to those obtained via calcination.

Figure 2 shows the nitrogen sorption isotherms of different catalysts treated by HCl/EtOH solvent. The isotherms of MCM-1 and MCM-2 samples are of type IV which is a characteristic of the mesoporous materials according to the classification of IUPAC. These isotherms exhibit three stages: the first stage is due to monolayer adsorption of nitrogen to the walls of the mesopores at $P/P_0 < 0.25$. In the second stage, we note a significant increase in nitrogen adsorption at $0.25 < P/P_0 < 0.4$, and the corresponding isotherm exhibits a sharp inflection, a characteristic of the capillary condensation within the uniform mesopores. The third stage takes place at relative pressure higher than 0.4, and this stage is characterized by gradual increase in volume with P/P_0 due to multilayer adsorption on the outer surface of catalysts. For the case of MCM-0 sample, the nitrogen sorption isotherm is distinctly different from the other samples, due to the filling of Si-MCM-41 pores by the CTA surfactant.

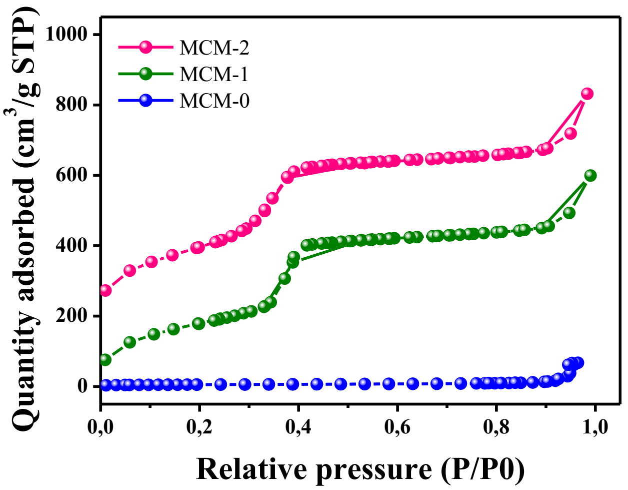


Fig. 2 Nitrogen adsorption–desorption isotherms of MCM-0, MCM-1 and MCM-2 catalysts

We have used infrared spectroscopy in order to confirm the removal of CTA surfactant during the extraction process. Figure 3 shows the IR spectra of the as-synthesized Si-MCM-41 and its modified counterparts. The broad band around 3458 cm^{-1} is assigned to the O–H stretching of surface hydroxyl groups, bridged hydroxyl groups, and adsorbed water molecules, while deformational vibrations of adsorbed water molecules cause the adsorption bands at 1633 cm^{-1}. Both bands between 1239 and 1066 cm^{-1} are attributed to the asymmetric stretching of Si–O–Si band. Other groups observed around 955 and 434 cm^{-1} are due

Table 1 Structural and textural parameters for the prepared Si-MCM-41 samples

Samples	2θ	d_{100} (Å)	a_0^a (Å)	S_{BET}^b (m^2/g)	Pore size (Å)^d	Pore volume (cm^3/g)
MCM-0	2.06	42.84	49.46	17	//	0.07
MCM-1	2.08	42.43	48.99	800	28.1	0.62
MCM-2	2.10	42.02	48.52	1060	32.8	0.91
Si-MCM-41^c	2.35	37.54	43.34	1430	35.2	1.071

[a] XRD unit cell parameter equals to $a_0 = 2d_{100}/\sqrt{3}$

[b] S_{BET}: specific surface area

[c] Si-MCM-41 calcined in air at 823 K for 12 h (Boukoussa et al. 2015c)

[d] Pore size was calculated by the BJH method

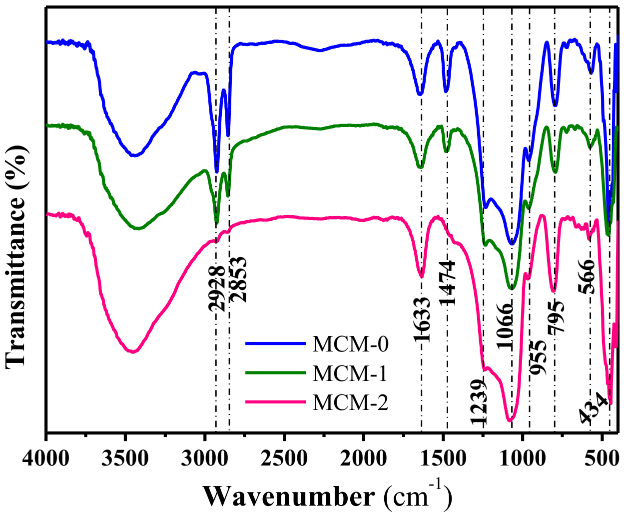


Fig. 3 FTIR spectra of the as-synthesized Si-MCM-41 mesoporous catalysts obtained at different extraction proportions of surfactant

to the bending mode of Si–O–Si band. The presence of two absorption bands around 2928 and 2853 cm^{-1} are assigned to asymmetric and symmetric C–H vibrations of –CH_3 and –CH_2, respectively, and also another band located at 1474 cm^{-1} is due to the carbon chain of surfactant CTA (Berquier et al. 1998). These bands became weaker when the treatment time was extended to 2 h. This clearly shows that a larger part of CTA surfactant was removed out of the Si-MCM-41 upon increasing the treatment time.

Thermogravimetric analysis TGA (Fig. 4) was used to determine the amount of the CTA surfactant in the modified catalysts. Our results are in agreement with the previous studies which assessed that all of the surfactant is burned out, when using this temperature range (Ariapad et al. 2012). The calculated values show that the samples MCM-0, MCM-1, and MCM-2 contain about 59, 40, and 9%, respectively, of CTA species inside the channels of Si-MCM-41. Thus, one-third of surfactant molecules were eliminated out of the pores of Si-MCM-41 after 1 h of treatment, whereas increasing the treatment time to 2 h leads to interesting results with better elimination of CTA (the case of sample MCM-2). These results are consistent with the measurements of the pore volume previously described which revealed that the elimination of CTA leads to higher pore volume (Table 1).

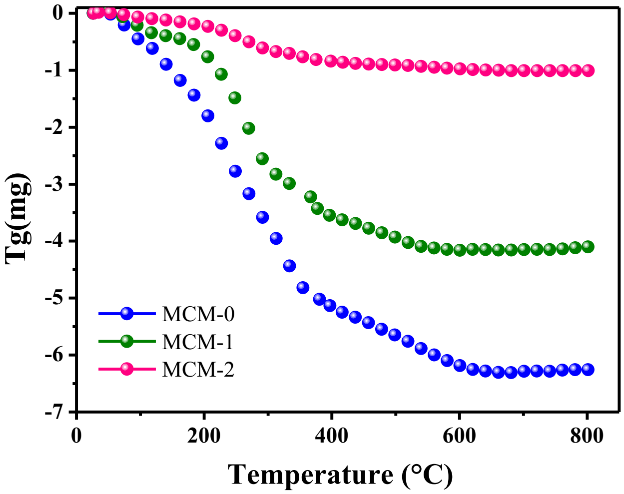


Fig. 4 TGA analysis curves of the as-synthesized Si-MCM-41 mesoporous catalysts obtained at different extraction proportions of surfactant

Scanning electronic microscopy images of the as-synthesized Si-MCM-41 treated by HCl/ETOH solvent are shown in Fig. 5. This analysis may provide more information on the relationship between the particle size, morphology, and their catalytic properties. The SEM pictures of the samples are typical of silicate mesoporous materials and show a different morphology with some large elongated agglomerates (the cases of MCM-0 and MCM-1); however, a rod-like morphology of coils is observed for the catalyst MCM-2, and this shows that the extraction using a solvent can affect the morphology of Si-MCM-41.

TEM images of the samples MCM-0, MCM-1, and MCM-2 are illustrated in Fig. 6. The treated mesoporous catalysts display parallel channel-like porous structure which confirms regular arrangement of hexagonal pores. We also observe that the MCM-1 and MCM-0 samples are characterized by black zone which confirms the presence of a significant amount of the surfactant into the pores of Si-MCM-41. These results are in agreement with the characterizations cited previously.

Catalytic experiments

Based on the results obtained in Fig. 7, we note that all the catalysts have a significant catalytic activity for the condensation of acetophenone with cyanoacetate at 50 °C. The catalyst MCM-0, displayed the best catalytic activity for condensation of acetophenone with a yield of 96% obtained at 60 min. However, medium and low yields were obtained with the MCM-1 and MCM-2, respectively; this is due to the ion exchange treatment which reduces the basicity of the solid as explained below. The untreated catalyst (MCM-0) showed strong base sites $\equiv SiO^-$ which combined with the cations CTA^+ (Martins et al. 2006, 2010; Boukoussa et al. 2015c), and the extraction by a HCl/ETOH solvent generated the formation of silanol groups according to the following reaction Eq. (1):

$$\equiv \mathrm{SiO^-CTA^+} + \mathrm{HCl} \rightarrow \equiv \mathrm{SiOH} + \mathrm{CTA^+} + \mathrm{Cl^-}. \tag{1}$$

The high removal of CTA^+ leads to significant formation of SiOH groups, with the latter having a weak-acid

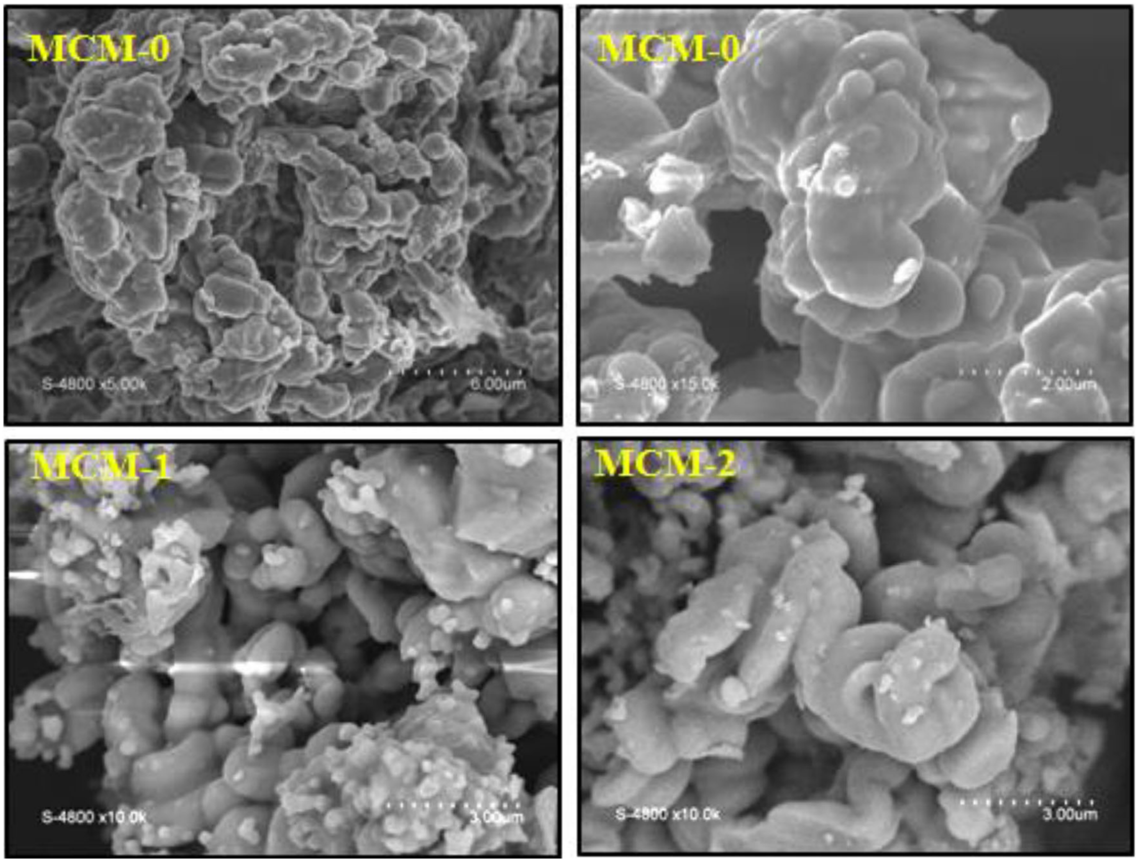
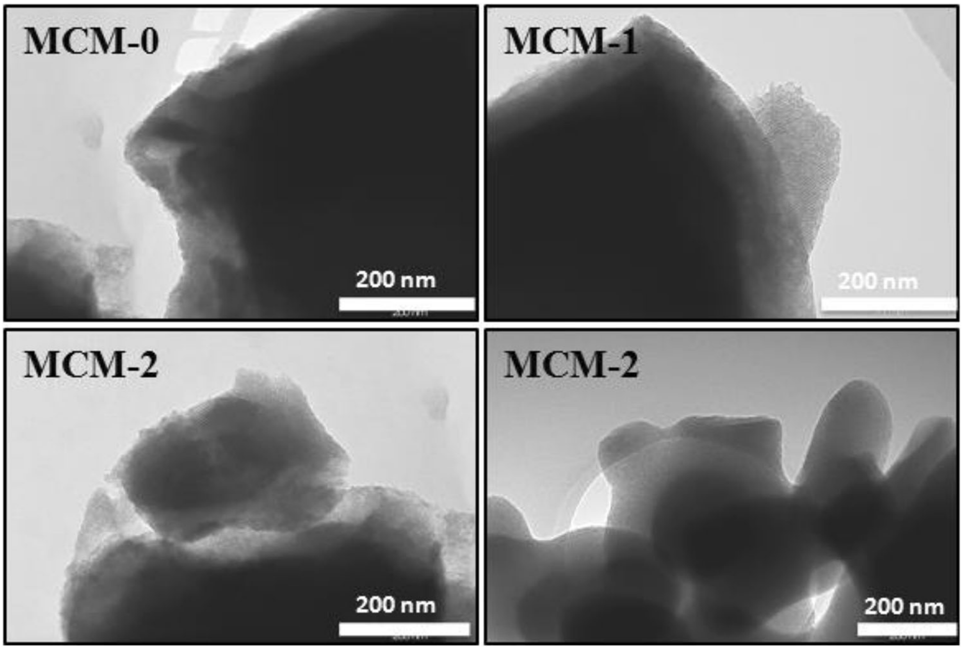


Fig. 5 SEM images of the as-synthesized Si-MCM-41 mesoporous catalysts obtained at different extraction proportions of surfactant

Fig. 6 TEM images of the as-synthesized Si-MCM-41 and its modified counterparts



characteristic which causes a progressive decrease in the basicity of the mesoporous catalysts (the case of MCM-2). Despite the higher pore volume and specific area developed by template-extracted MCM-41 solids (MCM-1 and MCM-2), their low basicities had a detrimental effect on their catalytic activity.

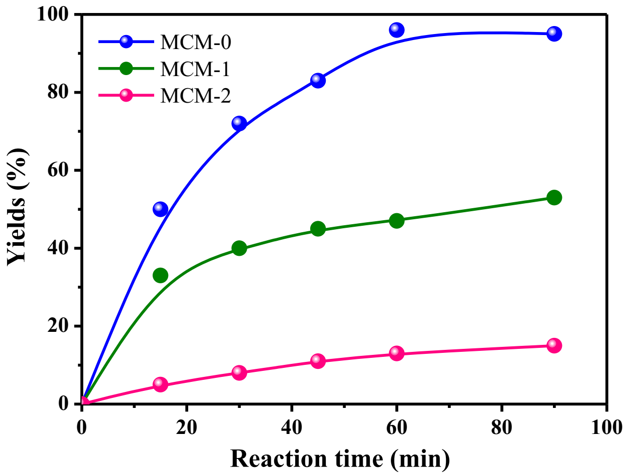


Fig. 7 Kinetics condensation of acetophenone with ethyl cyanoacetate obtained at 50 °C

Effect of different temperatures on the condensation of acetophenone with ethyl cyanoacetate is also investigated as shown in Fig. S1 (see additional file). All the obtained yields were calculated for 30 min of reaction time, and the results indicate that the as-synthesized Si-MCM-41 (MCM-0) catalyst presents higher activity, even at temperatures inferior to the ones reported in our previous work (Kibou et al. 2011).

Table 2 shows the effect of mesoporous catalysts on the yields of the condensation of acetophenone; in all cases, the MCM-0 (the as-synthesized Si-MCM-41) is the best catalyst for this reaction. However, it is noted that the catalysts with a large amount of aluminum have less $\equiv SiO^-$ ions, which causes a decrease in yield of product. For instance, Oliveira et al. studied a variety of the as-synthesized molecular sieves and assessed that they have basic sites and can be employed as catalysts for Knoevenagel condensation under mild conditions (Oliveira et al. 2009). Their catalytic activity is mostly dependent on the fraction of silicon framework. Pure siliceous molecular sieves are suggested to contain the highest number of siloxy anions, which constitute the strong basic sites. The occluded organic cations can interact with the molecular sieves framework, providing the highest catalytic activity. Calcined siliceous catalysts having only silanol groups do not show any activity. The difference in the catalytic activities between the as-synthesized Si- and Al-MCM-41 catalysts could be attributed to a higher concentration of siloxy anions in Si-MCM-41 since it has more silica species than Al-MCM-41 (Si/Al = 80, 40, and 20) (see Table 2, EDX results), and these results are consistent with the literature (Oliveira et al. 2009; Koller et al. 1995). Koller et al. have also shown that increasing the aluminum content in MFI zeolites generated a decrease in the quantity of anion siloxy, which involves a progressive decrease in the basicity of the catalyst (Koller et al. 1995). The same findings were observed by Oliveira et al. (2009). Our results are in agreement with the literature, as shown in Table 2, and there are relationships among the Si/Al ratio, the basicity of the catalysts, and the yields of products.

Table 3 shows a comparative study between the NH_4OAc and the as-synthesized Si-MCM-41 (MCM-0) catalysts; the catalyst MCM-0 shows interesting results compared with the NH_4OAc at lower temperature and short reaction times. This catalyst leads to efficient yields (between 96 and 70%) using different ketones. Compared with our previously published work (Kibou et al. 2011), we note that not only we were able to reduce the reaction time, but also that we have developed a simpler process for the separation of final product via filtration.

Reusability of the MCM-0 catalyst has been studied in the condensation reaction of acetophenone with ethyl cyanoacetate under the following conditions: acetophenone (10 mmol), ethyl cyanoacetate (10 mmol), MCM-0 catalyst (25 mol%), different temperatures (50, 80, and

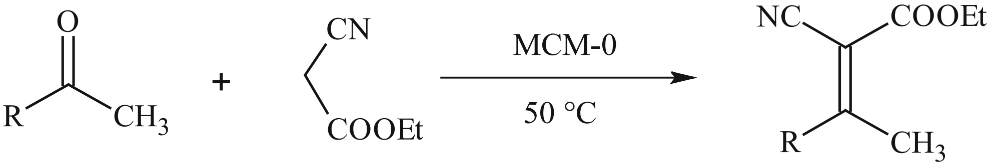
Table 2 Effects of catalysts on the condensation of acetophenone with cyanoacetate

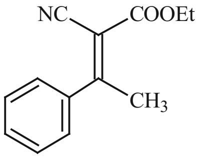
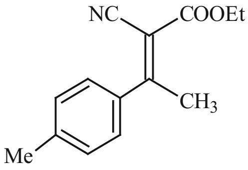
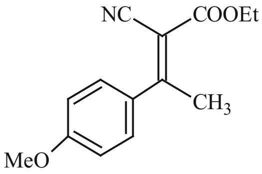
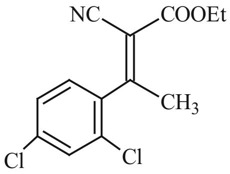
Catalysts	Si/Al	Total basicity (mmol/g) × 10^{-1}	Reaction time (min)	Reaction temperature (°C)	Yields
MCM-0	∞	9.6	60	50	96
MCM-1	∞	6.4	60	50	49
MCM-2	∞	1.9	60	50	13
Si-MCM-41[a]	∞	//	60	50	No products
Al-MCM-41(80)[b]	90.74	7.5	60	50	57
Al-MCM-41(40)[b]	45.94	4.8	60	50	38
Al-MCM-41(20)[b]	29.67	2.1	60	50	15
NH_4OAc	//	//	180	100	70

[a] MCM-0 after calcinations at 823 K under air during 12 h

[b] As-synthesized Al-MCM-41 with (Si/Al = 20, 40, and 80) were synthesized and characterized in our previous work (Boukoussa et al. 2017)

Table 3 Condensation of different ketones using MCM-0 and NH_4OAc catalysts



Entry	A	Product	Yield (%)[a]	Yield (%)[b]
1	C_6H_5–		70	96
2	*p*-$CH_3C_6H_4$–		65	86
3	*p*-$CH_3OC_6H_4$–		80	87
4	2,4-$Cl_2C_6H_3$–		68	70

[a] Products obtained in homogeneous catalysis using NH_4OAc, 100 °C, 3 h

[b] Products obtained in heterogeneous catalysis using the as-synthesize Si-MCM-41(MCM-0), 50 °C, 1 h

100 °C), and 60-min reaction time. The catalysts were filtered and dried before use in the subsequent cycles; the results are represented in Fig. 8. For the case of MCM-0 catalyst treated at 50 °C, it can be seen that the catalyst could be reused up to five times with little loss of activity, confirming its stability; the slight decrease in yields may be due to the weak CTA^+ leaching from the reaction medium (Boukoussa et al. 2015c). However, for MCM-0 catalysts treated at 80 and 100 °C, there is a progressive decrease in yields after the third reuse, due to the influence of temperature on the stability of the Si-MCM-41 and the leaching of surfactant in the reaction medium. These results have been confirmed by XRD analysis as shown in Fig. S2 (see additional file). The XRD patterns of the fresh and the reused catalyst MCM-0 at 50 °C or at 100 °C show that there was a decline in the intensity of the peak hkl (100) in the following order: MCM-0 (100 °C) < MCM-0 (50 °C) <fresh MCM-0. Besides, the catalyst treated at 100 °C shows the disappearance of peaks (110) and (200) showing slight destruction of the catalyst framework at 100 °C probably caused by the water generated from the condensation reaction which combined with the temperature 100 °C.

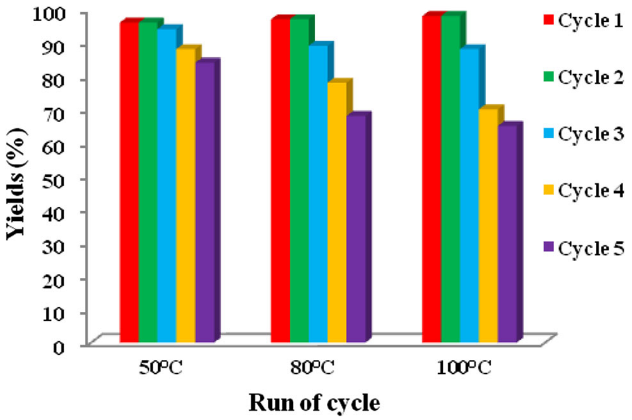
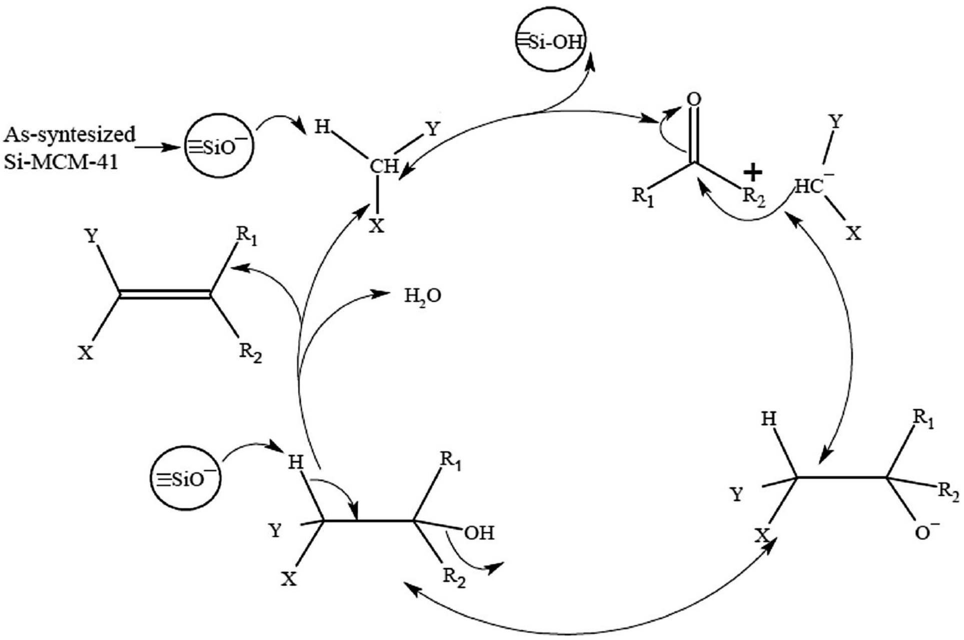


Fig. 8 Reusability of MCM-0 catalyst at different temperature



Scheme 2 Mechanism of the Knovenagel condensation in the presence of the as-synthesized mesoporous silica, Si-MCM-41

According to the obtained results, we have proposed a mechanism of Knoevenagel reaction catalyzed by the as-synthesized Si-MCM-41 mesoporous silica. The scheme 2 illustrates the proposed mechanism of Knoevenagel condensation that is started by the formation of the carbanion on the methylenic group upon the action of the basic catalyst (the as-synthesized Si-MCM-41); this carbanion intermediate attacks the carbonyl group to form an intermediate molecule which, in turn, yields the desired Knoevenagel compound after the removal of water molecule.

Conclusions

The as-synthesized Si-MCM-41 has been employed as an efficient catalyst for the preparation of olefinic compounds by a Knoevenagel reaction. This procedure results in high yields, has operational simplicity, and involves short reaction times. It has been well evidenced that the reaction is affected by the Si/Al ratio, temperature, and the percentage removal of CTA out of Si-MCM-41. At average temperatures (50 °C), this catalyst can be reused for five cycles, but at higher temperatures, it can be reused only for three cycles due to the combined effect of temperature and water generated by condensation reaction on the structure of the as-synthesized Si-MCM-41. The partial removal of the surfactant despite increases in the textural proprieties of the catalyst did not permit an enhancement of the activity for the Knoevenagel reaction.

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