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Short Communication

Activity of amino-functionalised mesoporous solid bases in microwave-assisted condensation reactions[☆]

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Aminopropylated functionalised hexagonal mesoporous silicas (HMS) and SBA-15 materials with different amino-loadings (5–30 wt.% NH_2) were synthesized, characterised and their catalytic activities were subsequently investigated in the microwave-assisted Knoevenagel condensation of cyclohexanone and ethyl cyanoacetate as well as in the Michael reaction between 2-cyclohexen-1-one and nitromethane. The effects of the quantity of the catalyst in the reaction as well as a variety of microwave parameters including the power, temperature and time of microwave irradiation were optimised. High activities and selectivities to the condensation product could be achieved at short times of microwave irradiation for both base-catalysed processes. The low loaded HMS-5%NH_2 and higher loaded SBA-15-20%NH_2 were found to give the best activities in the reactions. This observation seems to be related to the significant deterioration observed in textural properties of HMS materials at amino-loadings larger than 10%.

1. Introduction

The development of more environmentally friendly methodologies has stimulated the search for solid bases in substitution of homogenous bases currently employed in many industrial processes [1,2]. In this sense, important C – C coupling organic reactions including Michael additions [3], Heck [4,5], Sonogashira [6] and Knoevenagel condensations [7–12] have been reported to be catalysed by solid bases.

Among them, the Knoevenagel condensations are interesting base-catalysed processes for the preparation of high added-value chemicals [2,7–12]. The reaction involves a nucleophilic addition of an active hydrogen compound to a carbonyl group followed by a dehydration reaction that generates an α,β-unsaturated carbonyl compound (Scheme 1). The Michael addition is another relevant reaction for the preparation of high-added value chemicals [13,14]. In this reaction, the nucleophilic addition of a carbanion to an alpha, beta unsaturated carbonyl compound takes place to give the cross-coupled product (Scheme 2).

A wide variety of heterogeneous catalysts have been reported for these particular reactions including $AlPO_4$–Al_2O_3 catalysts [10], clays [11], hydrotalcites [12] and, more recently, aminopropylated functionalised silicas [13–17]. These catalysts have been reported as high efficient materials for condensation reactions, providing quantitative conversions of starting materials in a few hours of reaction.

Microwaves have been proved to be a very useful tool to accelerate conventionally heated reaction experiments which can be efficiently performed at reduced times of reaction under milder reaction conditions [18,19], often with the additional advantage of tuning the selectivity to product distribution by controlling different microwave parameters [20]. We have recently reported an efficient microwave assisted protocol for the Knoevenagel condensation reaction using alkali-modified SBA-1 materials as compared to a conventionally heated protocol. Quantitative conversion in the system could be achieved in less than 45 min reaction (around 3 h for the more challenging substrates) as compared to 4–24 h required under conductive heating [21].

In continuation with the development of designer catalysts for heterogeneous catalysed processes, we report here the effect of microwave irradiation in the Knoevenagel condensation of cyclohexanone and ethyl cyanoacetate over amino-functionalised silica-based materials as well as in the Michael reaction between 2-cyclohexen-1-one and nitromethane (Schemes 1 and 2). Parameters such as the power irradiation, the exposure time and the temperature were monitored in order to obtain the optimum conditions leading to high yields for the condensation product. Different silica-based materials, with varying loadings of aminopropylated groups, were characterised by a number of techniques including N_2 adsorption, DRIFTS, XRD, and CP-MAS ^{13}C and subsequently investigated in the aforementioned reaction.

[☆] In memoriam of Prof. Juan Manuel Campelo, inspiration and friend, who passed away in October 2012.

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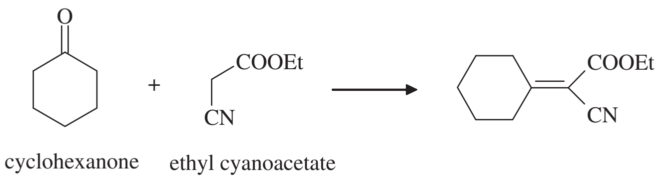


Scheme 1. Knoevenagel reaction of cyclohexanone and ethyl cyanoacetate.

2. Experimental

2.1. Preparation of supports

n-Dodecylamine and Pluronics P123 were utilised as structure directing agents for the synthesis of hexagonal mesoporous silica (HMS) and SBA-15 mesoporous materials, respectively. The synthesis of HMS materials was performed following a previously reported methodology by Macquarrie et al. [22]. Briefly, 20.80 g of TEOS was added under stirring to a solution containing 5.10 g *n*-dodecylamine in 1:1 ACN/H_2O (50 g/50 g) at room temperature. After 18 h of stirring the solid formed is filtered off and dried for 1 h in an oven at 100 °C. In order to remove the template the sample was purified by extraction with ethanol for 8 h using an automatic FexIKA extractor. The solid resulted was oven dried for 16 h at 100 °C.

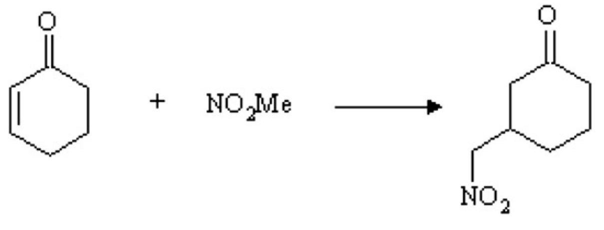
SBA-15 materials were prepared following the previously reported methodology by Bonardet et al. [23]. The triblock copolymer Pluronic P123 surfactant (0.41 mmol) was dissolved in water (1.25 mol) and HCl (2 M, 1.23 mol) with stirring at RT. On complete dissolution TEOS (25 mmol) is added drop wise to the above solution. The mixture was then allowed to be stirred for 24 h at RT. After that was subjected to a hydrothermal treatment at 100 °C for 48 h in an oven. The solid formed was filtered off and dried at 60 °C. The template was removed by calcination at 550 °C for 8 h.

2.2. Synthesis of functionalised materials

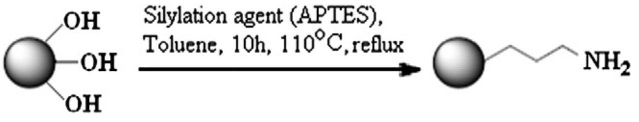
The synthesis of functionalised silicates was carried out by a grafting method using the amino reactant aminopropyltriethoxysilane (APTES) in different concentrations (5, 10, 20 and 30 wt.%) over the silica-based support. The required amounts of APTES to achieve these loadings were dissolved in 50 mL of toluene, stirred for 1 min for a better mixing and finally added to a round bottom flask containing the mesoporous material (1.5 g). The mixture was refluxed at 110 °C for 10 h under stirring, cooled to room temperature and filtered under vacuum to obtain the grafted solid. The final catalysts were washed at RT with acetone and toluene to ensure the removal of any physisorbed species on the materials prior to reaction. The schematic representation of the grafting of amino-moieties on the surface of HMS and SBA-15 materials has been included in Scheme 3.

2.3. Characterisation and kinetic experiments

The structure regularity of the samples was determined by XRD on a Siemens D-5000 (40 kV, 30 mA) using Cu*Kα* radiation. Scans were performed over the 2θ range from 0.5 to 10.



Scheme 2. Michael reaction of 2-cyclohexen-1-one and nitromethane.



Scheme 3. General pathway of mesoporous silica functionalisation via classical grafting method.

DRIFTS spectra for the catalysts were recorded in a Bomen MB-Series 100 FTIR spectrophotometer equipped with an environmental chamber (Spectra Tech, P/N 0030-100) that includes a diffuse reflectance device (Spectra Tech, Collector) at a resolution of 8 cm^{-1} and 256 scans. Samples were prepared by mixing the powdered solids with KBr (15 wt.%). All materials were evacuated for 1 h at 150 °C in the environmental chamber prior to spectra adquisition at temperatures ranging from 50 to 150 °C. In all cases the spectra were obtained starting with the lowest temperature and subtracting the corresponding reference signal.

Thermogravimetric (TG) experiments were carried out in a Setaram Setsys 12 or Netzsch 409 STA derivatograph in a static air atmosphere. The sample was loaded in ceramic crucibles with α-Al_2O_3 as reference compound and a Pt/Pt-Rh (10%) thermocouple. The heating rate employed was 10 K min^{-1} in all cases.

TG-IR measurements were conducted to quantify the amounts of aminopropyl loading in the materials. These were carried out on a Netsch STA409 interfaced to a Bruker Equinox-55 FTIR instrument equipped with a liquid N_2 cooled MCT detector.

Nitrogen adsorption measurements were carried out at 77 K using an ASAP 2000 volumetric adsorption analyzer from Micromeritics. Samples were previously degassed for 24 h at 110 °C before performing adsorption measurements. Surface areas were calculated according to the BET (Brunauer–Emmet–Teller) equation. Pore volumes (V_{BJH}) and pore size distributions (D_{BJH}) were obtained from the N_2 adsorption branch.

CP-MAS ^{13}C experiments were conducted on a Bruker Avance 400 MHz, WB with a resonance frequency of 100.6 MHz. The spin rate of the sample was 8 kHz, the proton pulse length 2.5 μs (90 flip) a 2.4 ms contact time and a 3 s repetition time.

Microwave experiments were carried out in a CEM-DISCOVER model with PC control. Experiments were performed on a closed vessel (pressure controlled) under continuous stirring. The microwave method was generally power-controlled where reactions mixture were irradiated with the maximum power output (300 W), achieving different temperatures in the 70–90 °C range, as measured by an infra-red probe.

In a typical Knoevenagel condensation reaction, 10 mmol (1.036 mL) of cyclohexanone and 1.2 mmol (0.123 mL) ethyl cyanoacetate were stirred together with the solid base (0.25–0.1 g) in 2 mL toluene for up to 30–45 min at 300 W. This reaction was selected on the basis of a challenging substrate (e.g. cyclohexanone as compared to more reactive aldehydes) for the formation of the Knoevenagel condensation product as test reaction for the synthesized solid base catalysts. Reaction reached completion for most catalysts after 30 min of microwave irradiation. Conversions at 15 min reaction have been included to establish a comparison of activities between catalysts.

Table 1
Textural properties of the HMS materials functionalised with various quantities of aminopropyl groups.

Sample	Mean pore size (nm)	Pore volume (mL g^{-1})	S_{BET} (m^2 g^{-1})	Amino propyl loading (wt.%, TG-IR)
HMS	2.8	0.80	736	–
HMS-5%APTES	2.6	0.45	496	7
HMS-10%APTES	2.6	0.36	407	9.6
HMS-20%APTES	<2.0	0.39	550	8.2
HMS-30%APTES	<2.0	0.28	332	11.5

Table 2
Textural properties of the SBA-15 materials functionalised with various amounts of aminopropyl groups.

Sample	Mean pore size (nm)	Pore volume (mL g^{-1})	S_{BET} (m^2 g^{-1})	Aminopropyl loading (wt.%)
SBA-15	5.4	0.54	706	–
SBA-15-5%APTES	2.4	0.21	221	5.4
SBA-15-10%APTES	<2.0	0.35	256	7.0
SBA-15-20%APTES	<2.0	0.32	226	9.0
SBA-15-30%APTES	<2.0	0.21	239	8.6

In a typical Michael reaction, 10 mmol 2-cyclohexen-1-one and 2 mL nitromethane (35 mmol) were microwaved with the solid base (0.05–0.2 g) for 15-30 min at 300 W (100 °C, maximum temperature reached). Reaction reached completion for most catalysts after 45 min

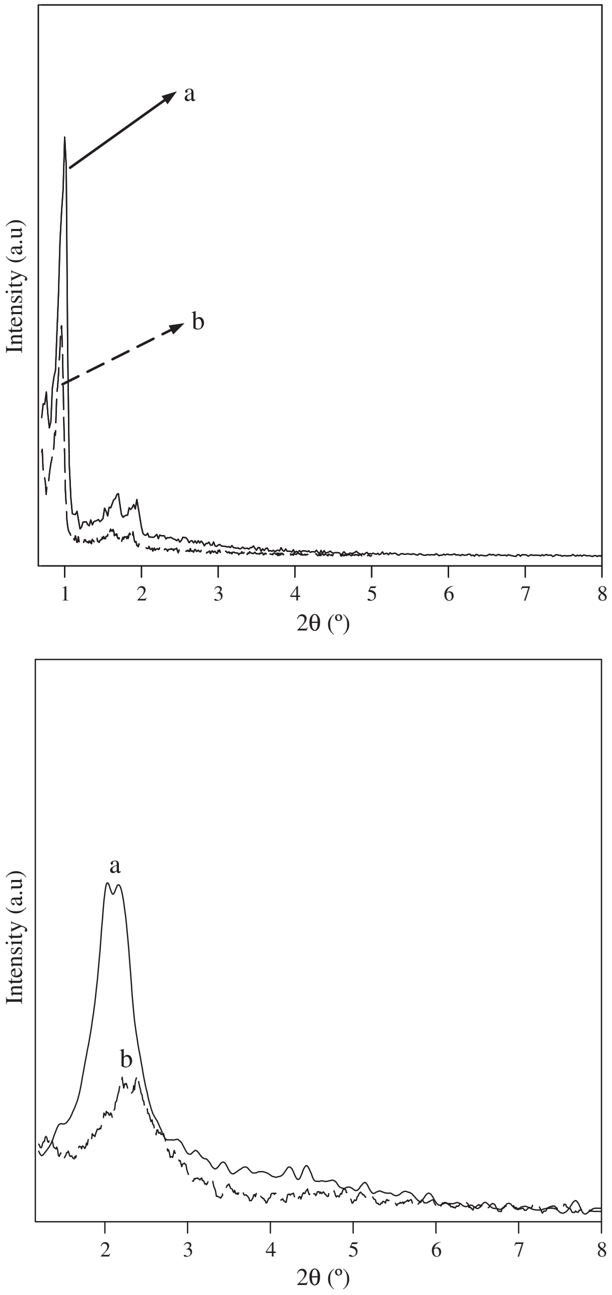


Fig. 1. XRD patterns of: a) SBA-15; and b) SBA-15-10%APTES (top) and a) HMS and b) HMS-10%APTES (bottom).

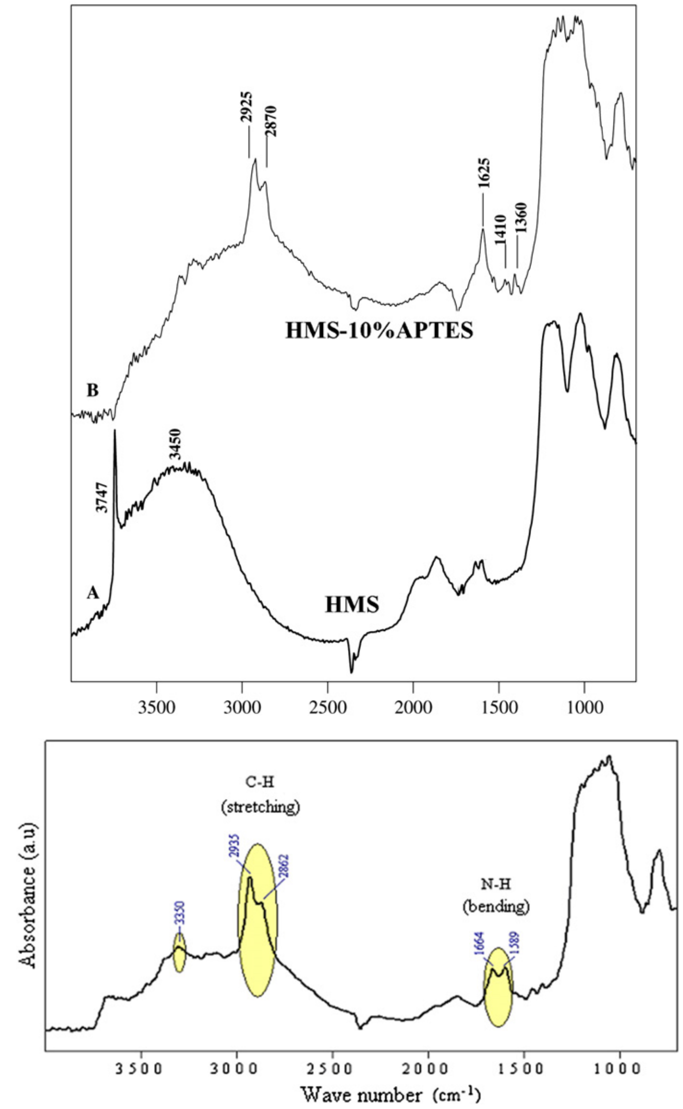


Fig. 2. DRIFT spectra of functionalised HMS (HMS-APTES-10%) as compared to the parent HMS support (top image), clearly showing the disappearance of the 3747 cm^{-1} band. SBA-15-10%APTES spectra acquired at 473 K (reference KBr, bottom image).

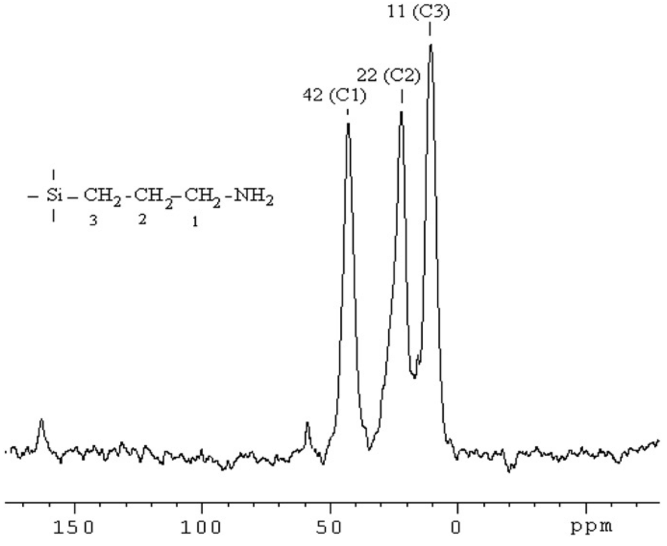


Fig. 3. Representative ^{13}C CP-MAS NMR spectra of HMS-10%APTES, displaying the characteristic peaks of the C atoms in the aminopropyl groups ($\delta^{13}C = 42$, 22 y 11 ppm).

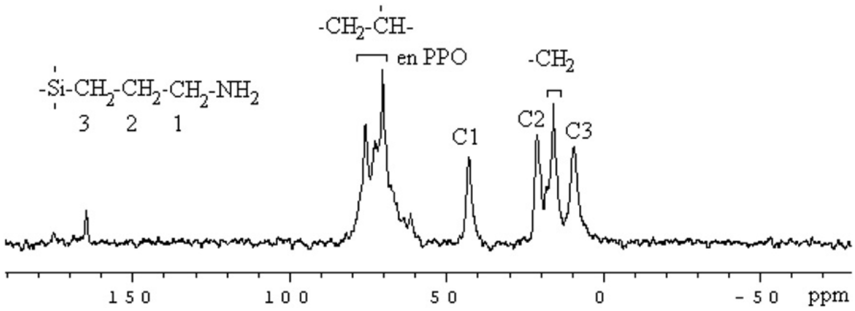


Fig. 4. Representative example of a CP-MAS ^{13}C NMR spectrum of an uncalcined P123-containing APTES functionalised SBA-15 material, showing the characteristic peaks of APTES ($\delta^{13}C = 42$, 21 y 10 ppm) as well as bands correlated to the presence of P123 (CH_2-CH- and $-CH_2-$ at 67-77 ppm and ~15 ppm, respectively).

of microwave irradiation. Conversions at 15 min reaction have been included to establish a comparison of activities between catalysts and conditions.

Sampling aliquots for both chemistries were subsequently analyzed by GC/GC–MS using an Agilent 6890N GC model equipped with a 7683B series autosampler fitted with a DB-5 capillary column and an FID detector.

3. Results and discussion

N_2 adsorption–desorption isotherms of the synthesized materials (not shown) exhibited the characteristic type IV isotherms corresponding to mesoporous materials. Textural properties as well as aminopropyl loading (obtained by thermogravimetric analysis) of both HMS and SBA-15 functionalised materials have been summarised in Tables 1 and 2, respectively. It can be seen that, based on thermal analysis, the maximum content of amino groups in the samples reached around 10 wt.% of aminopropyl groups. The discrepancy between the nominal and actual aminopropyl content could be explain on the basis of saturation of the functionalisable groups on the surface and within the pores of the materials (free silanols) which may not allow a further chemical functionalisation in the materials. Aminopropyl moieties will be surely physisorbed in the materials during the functionalisation step but these are subsequently removed in the washing and filtration step as observed by the presence of N-containing groups in the washings (results not shown).

Results included in Tables 1 and 2 indicate that the grafting of aminopropyl groups also caused a partial blocking of the porosity in HMS and SBA-15 materials, as suggested by the simultaneous decrease in BET surface area and pore volume with aminopropyl loading. Interestingly, this decrease was generally more severe in the case of SBA-15-based materials (5 wt.% loading of aminopropyl already produced a decrease in BET surface from 706 to 211 $m^2\ g^{-1}$ along with a drop in the mean pore size from 5.4 to 2.4 nm). These findings will have an important implication in terms of catalytic activity of SBA-functionalised materials (with generally reduced activities) compared to those of functionalised HMS (improved activities), as described in the section on catalytic results.

XRD patterns of the prepared HMS and SBA-15 materials are typical of hexagonal mesoporous silicas. As an example, Fig. 1 shows the XRD pattern of SBA-15 support vs SBA-15 functionalised materials (and their HMS analogues) with 10 wt.% amino groups. We note that diffractograms of HMS materials prepared by a neutral route using dodecylamine as template are not well resolved as compared to those of SBA-15, although patterns indicate that the materials present a hexagonal symmetry. SBA-15 showed broad diffraction peaks in the low angle region (2θ 0–5°) which is indicative of the long range hexagonal order. These include three well-resolved XRD diffraction peaks in the region of $2\theta = 0.5–2.5°$, which can be indexed to the (100), (110) and (200) reflections, respectively [24]. As shown in Fig. 1, the peak intensity of the functionalised SBA-15 materials decreases at increasing amino loadings, implying a partial structural deterioration due to the aminopropyl groups bound to the surface (see also supporting information for all XRD patterns). This partial structure deterioration could also explain the severe change in textural properties observed for SBA-15 materials upon functionalisation (Table 2). In some cases, materials with over 20%APTES exhibited very low intensity and broad bands which correlated well with the reduction observed in both textural and surface properties (see Tables 1 and 2).

We performed Diffuse Reflectance Infrared Fourier Transform (DRIFT) and ^{13}C CP-MAS NMR experiments aiming to check the efficiency of the grafting methodology used herein to functionalise HMS and SBA-15 materials. The DRIFT spectra of the HMS and SBA-15 supports exhibited in all cases the characteristic bands of amorphous silicas (not shown) with an intense band at 3747 cm^{-1} corresponding to the O–H stretching due to the superficial Si–OH groups. Remarkably, this band disappears completely in the case of functionalised materials (Fig. 2) confirming

Table 3
Catalytic activity [total conversion (X_T, mol%) and selectivity to Knoevenagel condensation product (S_K, %)] of basic mesoporous HMS–APTES type materials in the condensation of cyclohexanone and ethyl cyanoacetate under microwave irradiation.[a]

Entry	Catalyst	Amount of catalyst (g)	X_T (mol%)	S_K (mol%)
1	HMS-5%APTES	0.025	35	>99
2		0.05	64	>99
3		0.1	>99	>99
4	HMS-10%APTES	0.025	26	>99
5		0.05	59	>99
6		0.1	77	>99
7	HMS-20%APTES	0.025	12	>99
8		0.05	29	>99
9		0.1	62	>99
10	HMS-30%APTES	0.025	38	>99
11		0.05	61	>99
12		0.1	>90	>99

[a] 10 mmol cyclohexanone, 1.2 mmol ethyl cyanoacetate, 2 mL toluene, 300 W and 15 min (max. temperature set at 150 °C).

Table 4
Catalytic activity [total conversion (X_T, mol%) and selectivity to Knoevenagel condensation product (S_K, %)] of basic mesoporous SBA-15–APTES type materials in the condensation of cyclohexanone and ethyl cyanoacetate under microwave irradiation.[a]

Entry	Catalyst	Amount of catalyst (g)	X_T (mol%)	S_K (mol%)
1	SBA15-5%APTES	0.05	30	>99
2		0.1	54	>99
3	SBA15-10%APTES	0.05	29	>99
4		0.1	70	>99
5	SBA15-20%APTES	0.05	31	>99
6		0.1	80	>99
7	SBA15-30%APTES	0.05	27	>99
8		0.1	57	>99

[a] 10 mmol cyclohexanone, 1.2 mmol ethyl cyanoacetate, 2 mL toluene, 300 W and 15 min (max. temperature set at 150 °C).

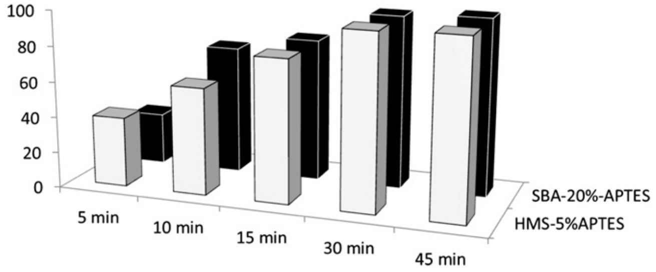


Fig. 5. Conversion of cyclohexanone as a function of time for HMS-5%APTES (front, white columns) and SBA-15-20%APTES (back, black columns) materials. Reaction conditions: 10 mmol cyclohexanone, 1.2 mmol ethyl cyanoacetate, 2 mL toluene, 300 W and 0.1 g catalyst.

Table 6
Total conversion (X_T) and selectivity to Michael addition product (S_M) of APTES functionalised HMS materials in the microwave-assisted Michael addition of 2-cyclohexen-1-one and nitromethane.[a]

Entry	Catalyst	Quantity of catalyst (g)	X_T (mol%)	S_M (mol%)
1	Blank (no catalyst)	–	–[b]	–
2	Blank (HMS support)	0.1	<5	–
3	HMS-5%APTES	0.05	<10	>99
4		0.1	35	>99
5		0.2	69	>99
6	HMS-10%APTES	0.05	<5	>99
7		0.1	12	>99
8		0.2	40	>99
9	HMS-20%APTES	0.05	<10	>99
10		0.1	26	>99
11		0.2	63	>99
12	HMS-30%APTES	0.05	–[b]	–
13		0.1	–[b]	–
14		0.2	<15	>99

[a] Reaction conditions: 10 mmol 2-cyclohexen-1-one, 35 mmol (2 mL) nitromethane, 300 W and 15 min.
[b] No reaction.

the grafting of aminopropyl groups on the mesoporous material. The presence of aminopropyl groups was further confirmed by the presence of bands at 2925 and 2870 cm^{-1} which correspond to stretching of C–H groups along with bands at 1664–1589 cm^{-1} ascribed to the N–H bending, which are more clearly observed operating at higher temperatures, in good agreement with previous literature results (Fig. 2) [25].

^{13}C CP MAS NMR spectrum of SBA-15 and HMS functionalised samples (Fig. 3 shows a representative spectrum for HMS-10%) clearly displayed three peaks at 10–11, 21–22 and 42 ppm respectively, corresponding to the C atoms on the $Si-CH_2-CH_2-CH_2-NH_2$ chain in sequence from left to right [26,27]. These results are relevant in that they demonstrate that the aminopropyl groups were not decomposed during the synthesis procedure and confirm the incorporation of such functionalities in the materials. The absence of any additional bands related to the surfactant indicated its complete removal upon calcination. In fact, a comparative spectrum of an unextracted template containing amino-functionalised SBA-15 material (Fig. 4) shows distinctive peaks in the 67–77 ppm range corresponding to the C species from P123 [28].

Tables 3 and 4 summarise the main catalytic data for the condensation of cyclohexanone with ethyl cyanoacetate under microwave irradiation using different loadings of amino moieties grafted on mesoporous silicas. Most catalysts provided quantitative conversion to the target Knoevenagel product after 30 min microwave irradiation (see supporting information) and results at 15 min reaction were only selected to establish an activity comparison between catalysts.

The use of microwave irradiation is beneficial in that it reduces reaction times (from over 12 h typically reported in literature [10–12,15] up to 15 min upon microwave heating) and increases at the same time conversions to products. Importantly, the blank reaction (in absence of the catalyst) gave no conversion in the systems under the investigated conditions. At optimised conditions, the microwave irradiated protocol afforded moderate to very good conversions of cyclohexanone with almost complete selectivites to the principal product of reaction. By comparison of Tables 3 and 4 it can be seen that, in general, aminopropyl functionalised-HMS materials showed higher activity than their counterparts supported on SBA-15 at the same conditions of power, temperature and catalyst loading. This result could be correlated with the higher surface area and pore volume of the HMS materials after functionalisation, as reported in Table 1. Aminopropyl loading could not be correlated directly with activity in the case of HMS materials since, for example, HMS-5%APTES (aminopropyl content 7 wt.%) and HMS-30%APTES (aminopropyl content 11.5 wt.%) showed similar activities at comparable conditions. In the case of SBA-15 based materials, whilst a catalyst loading of 0.05 g showed similar activity for all the materials, a positive trend of the activity with the aminopropyl content was found at catalyst loadings of 0.1 g, except for the material SBA-15-30% APTES. An excessive loading of aminopropyl groups that are not grafted to the surface (as indicated before) could lead to excessive blocking of porosity in this sample leading to the observed decrease in activity. For these samples, SBA-15-20%APTES exhibited the best catalytic results.

A variety of microwave parameters including power and time of microwave irradiation were investigated for the most active catalysts (HMS-5%APTES and SBA-15-20%APTES) in order to find the optimal conditions to run this condensation. As expected, an increase in power produced an enhancement of activity in all cases without affecting the selectivity to the condensation product, although a power increase above 200 W did not significantly improve conversion In the case of reaction time, 15 min allowed to reach very high activity for both samples (Fig. 5), with slight increases at 30 min. Interestingly, an increase of the time of reaction above this time did not produce significant increase in conversion (Fig. 5). A comparison of our system with related literature reports showed the possibility to work under mild reaction conditions and low quantities of catalyst to achieve good conversions with complete selectivity to the target product under the investigated conditions. Similar reports gave as much as comparable yields under slightly milder conditions (entry 3, Table 5).

The base catalysts were subsequently investigated in another important base-catalysed process such as the Michael addition of 2-cyclohexen-1-one to nitromethane under microwave irradiation (Scheme 2). Optimised results for both HMS and SBA-15 functionalised materials have been summarised in Tables 6 and 7. In general, short

Table 5
Comparison between our solid base system and related literature work of the same reaction under similar conditions.

Catalyst	Reaction conditions	Temp. (°C)	Reaction time (h)	Product yield (%)	Reference
HMS-5%APTES	10 mmol cyclohexanone, 1 mmol ethyl cyanoacetate, 0.1 g cat., toluene (solvent)	80	0.3	>99	Current work
SBA-15-20%APTES	10 mmol cyclohexanone, 1 mmol ethyl cyanoacetate, 0.1 g cat., toluene (solvent)	70	0.3	80	Current work
Diamine-MCM-41	2 mmol cyclohexanone, 2 mmol ethyl cyanoacetate, 0.02 g cat., toluene (solvent)	50	0.3	81	[29]
Mg–Al-HT	2 mmol cyclohexanone, 2 mmol ethyl cyanoacetate, 0.05 g cat., DMF (solvent)	RT	1	33	[30]
Silica gel-APTMS	10 mmol cyclohexanone, 10 mmol ethyl cyanoacetate, 10 g cat., toluene (solvent)	RT	–	66	[31]
γ-Aminopropyl silica	20 mmol cyclohexanone, 20 mmol ethyl cyanoacetate, 0.25 g cat., cyclohexane (solvent)	82	1	98	[32]
AMS–HMS	20 mmol cyclohexanone, 20 mmol ethyl cyanoacetate, 0.25 g cat., toluene (solvent)	110	0.5	98	[33]

Table 7
Total conversion (X_T) and selectivity to Michael addition product (S_M) of APTES functionalised SBA-15 materials in the microwave-assisted Michael addition of 2-cyclohexen-1-one and nitromethane.[a]

Entry	Catalyst	Quantity of catalyst (g)	X_T (mol%)	S_M (mol%)
1	Blank (no catalyst)	–	–	–
2	Blank (SBA-15 support)	0.2	<5	–
3	SBA-15-5%APTES	0.05	<10	>99
4		0.1	<20	>99
5		0.2	39	>99
6	SBA-15-10%APTES	0.05	<5	>99
7		0.1	<10	>99
8		0.2	28	>99
9	SBA-15-20%APTES	0.05	<20	>99
10		0.1	45	>99
11		0.2	72	>99
12	SBA-15-30%APTES	0.05	<5	>99
13		0.1	22	>99
14		0.2	39	>99

[a] Reaction conditions: 10 mmol 2-cyclohexen-1-one, 35 mmol (2 mL) nitromethane, 300 W and 15 min.

times of reaction (typically 15 min) were selected to compare the activities between the different functionalised solid bases. Results clearly demonstrate HMS-5%APTES (69%) and SBA-15-20%APTES (72%) were once again the most active catalysts in the base-catalysed process, with remarkably different activities to those obtained for the other functionalised materials, with the exception of comparable activities observed for HMS-20%APTES (63% conversion). Both an increase in the quantity of catalyst (from 0.05 to 0.2 g) and time of reaction (from 15 to 45 min) had a dramatic increase in the activity of the systems (Tables 6 and 7, supporting information) as expected. Selectivity to the Michael addition product was found to be complete for all investigated catalysts under microwave irradiation at the studied conditions.

Catalyst recycling tests were also performed for both samples in both base-catalysed processes. Solids were isolated by filtration, washed and dried at a low pressure. Remarkably, no significant loss of activity was observed after 3 reuses in any of the two investigated chemistries under the studied conditions (Fig. 6, data included for the Knoevenagel condensation). Potential leaching leading to homogeneous catalysis under the reaction conditions used was discarded by stopping reaction at a low conversion level (15%), removing the catalyst in the hot solution and washing several times with toluene at 55 °C and allowing the reaction to proceed for another 24 h; no further conversion of the reactants into products was thus observed.

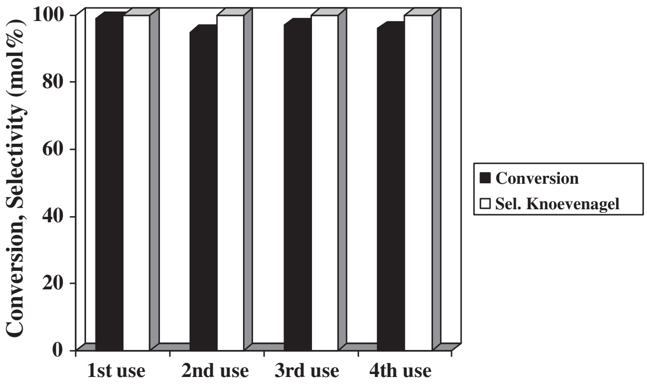


Fig. 6. Reusability experiments of HMS-5%APTES in the Knoevenagel condensation. Reaction conditions (for each cycle): 10 mmol cyclohexanone, 1.2 mmol ethyl cyanoacetate, 2 mL toluene, 300 W, 15 min reaction and 0.1 g catalyst.

4. Conclusions

Aminopropyl functionalised silica mesoporous materials have been found to be effective catalysts in the Knoevenagel condensation of cyclohexanone with ethyl cyanoacetate. Mild reaction conditions and short reaction times (typically 30–45 min) are the obvious advantages of the presented method which allowed excellent yields to target products with a complete selectivity. The investigated materials have been also found to be useful for a series of related chemistries (e.g. Michael additions) providing also excellent conversion and selectivities to target products under microwave-assisted conditions.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2012.12.005.

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