PAPER www.rsc.org/njc | New Journal of Chemistry

Biomimetic synthesis of microporous and mesoporous materials at room temperature and neutral pH, with application in electronics, controlled release of chemicals, and catalysis†

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Received (in Montpellier, France) 22nd May 2008, Accepted 27th June 2008
First published as an Advance Article on the web 9th July 2008
DOI: 10.1039/b808697b

Micro- and mesoporous materials molecular sieves have been synthesized at neutral pH and room temperature using a mimic of "silicatein" for mobilizing the silica. This methodology allows preparing molecular sieves materials in where less stable molecules can be encapsulated, leading to a final material with potential applications in electronics (conducting polymers) or for controlled release of chemicals (pheromones). Furthermore, the framework flexibility of the obtained materials allows introducing transition metals in tetrahedral coordination within the silicate in larger amounts than in zeolites, while preserving the activity and selectivity of the metals for selective oxidation reactions.

Introduction

Silica based molecular sieve porous materials present applications in many different fields such as for instance ion-exchange, separation, gas adsorption and in particular, catalysis.[1,2] Recently, new applications have emerged for electronics, magnetism, and medicine.[3–6] Usually, these materials are prepared under hydrothermal or solvothermal conditions,[7,8] requiring high temperatures and pressures.

Moreover, silica is the second most abundant mineral formed by organisms.[9,10] Many living marine organisms are capable of forming in hours skeletons from silica dissolved in sea water at concentrations of 70 μM at temperatures close to 0 °C.[11] It has been found that the proteins occluded within the macroscopic silica needles made by marine sponges can catalyze the synthesis of silica and organically modified silsesquioxanes from the corresponding silicon ethoxides at neutral pH and low temperature.[12] The mechanism has been elucidated, demonstrating that these proteins, called "silicateins", can be used *in vitro* to catalyze the hydrolysis and direct polycondensation of alkoxide precursors by the functional hydroxy and imidazole side chains of serine-26 and histidine-165, which were identified from the structure of silicatein α.[13] Synthetic cysteine-lysine block copolypeptides,[14] or even small molecules, such cysteamine or ethanolamine,[15] can mimic the unique physiochemical environment found in the enzyme active site and can be also used to hydrolyze and condense silica from tetraethylorthosilicate (TEOS), producing non porous silica with different forms.

It would be of much interest to use bioinspiration for synthesizing synthesis micro and mesoporous molecular sieves, within a wide range of porosities, under neutral pH and room temperature.[16] The introduction of different organic structure directing agents (OSDAs) together with the bio-inspired catalyst in the synthesis media, direct the formation of materials with controlled porosity depending on the OSDA selected (see micropore area, pore diameter, and micropore volume in Table 1 and SEM images in Fig. S1 in ESI†) under mild conditions (more information about the characterization of these samples can be consulted in ref. 16).

If this is achieved, then one can use organic structure directing molecules that are not stable under regular synthesis conditions (high temperatures and basic or acid media) and which can be of interest for host–guest chemistry in the fields of electronics, controlled release, light harvesting and even catalysis.

We will show here that by taking into account the mechanism proposed for hydrolyzing and condensing silica from TEOS, it is possible to use simple molecules in combination with selected OSDAs for encapsulating them within microporous or mesoporous silica structures at neutral pH and room temperature. The encapsulated molecules can yield organic conducting polymers or produce hybrid materials for the controlled release of bioactive compounds. The prepared micro- and mesoporous materials have molecular sieve properties, and are stable upon calcination, structurally amorphous and highly flexible. This allows introducing in the structure larger amounts of heteroatoms than in the crystalline counterparts, with the corresponding potential interest in catalysis.

Experimental

Synthesis of microporous molecular silicates with prepolymers

The amorphous microporous molecular sieves were prepared at room temperature and neutral pH with the following molar

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† Electronic supplementary information (ESI) available: Fig. S1: SEM images of the microporous samples obtained by bioinspired methodology. Fig. S2: XRD of the lamellar phase of the MCM family (MCM-50). See DOI: 10.1039/b808697b

Table 1 Textural properties of microporous and mesoporous materials synthesized under bioinspired conditions

Sample	Et/Si[a]	Si source	OSDA/Si[b]	pH	Area/m^2 g^{-1}		Pore diameter/Å	Micropore volume/cm^3 g^{-1}
					BET	Micropore		
TEA	0.05	TEOS	0.5 (TEA)	7.7	387	328	6.3	0.18
TPA	0.05	TEOS	0.5 (TPA)	7.7	471	440	6.7	0.19
TBA	0.05	TEOS	0.5 (TBA)	7.5	525	481	6.9	0.23
CTMA	0.05	TMOS	0.16 (CTMA)	7.1	956	—	~30	—

[a] Molar ratio between biomimetic catalyst (ethanolamine) and silica in the synthesis preparation. [b] Molar ratio between organic structure directing agent (OSDA) and silica in the synthesis preparation. The acronyms are TEA (tetraethylammonium), TPA (tetrapropylammonium), TBA (tetrabutylammonium), and CTMA (cetyltrimetylammonium).

composition (TM = tromethamine, $H_2NC(CH_2OH)_3$, EA = ethanolamine, $H_2NCH_2CH_2OH$):

TEOS : 0.2 TM : 0.05 EA : 0.25 PPV monomer : 12 H_2O.

The gel of synthesis gel was prepared at room temperature (27 °C) in polypropylene screw cap containers (50 ml). In the preparation, 4.79 g of Tris-HCl 1 M buffer pH = 7.0 (Sigma-Aldrich) containing the tromethamine were first added. Then, 2.2 g of PPV (poly-*para*-phenylenevinylene) monomer as bromide salt, and 4.17 g of TEOS (Merck) were also added to the container under magnetic stirring. Finally, 312 mg of ethanolamine (Sigma-Aldrich, >98%) were incorporated into the mixture. After one week stirring, the solid was filtered off and washed, first with abundant water (1 l) and, finally, with acetone (200 ml). The solid was dried at room temperature.

Synthesis of mesoporous materials with encapsulated pheromone

The preparation of the mesoporous materials was carried out at room temperature and neutral pH with the following compositions: TMOS or TEOS : 0.05 EA or NH_4F : X pheromone : Y CTMABr : 40 H_2O.

The gels for synthesis were prepared at room temperature (300 K). In a typical preparation, the cetyltrimetylammonium bromide (CTMABr, Sigma-Aldrich), and the pheromone ((*E*,*E*)-8,10-dodecadien-1-ol) were mixed with water, and the mixture was stirred during 30 min. After this time, tetramethylorthosilicate (TMOS, Sigma-Aldrich, >99%) or TEOS (Sigma-Aldrich, >99%) was added. Finally, the ethanolamine (Sigma-Aldrich, >98%) or NH_4F was incorporated into the mixture under agitation. The gel was covered and stirred during 2 days. The solid was filtered off and washed with abundant water (1 l) and acetone (1 l). The solid was dried at room temperature.

Determination of pheromone emission

Cylindrical tablets of the powder were prepared with a manual hydraulic press at 3 tonne cm^{-2}. The tablets were placed into an aerator, with an air flow rate of 80 ml min^{-1} at 25 °C. Periodically, the tablets were extracted, and the residual loading was obtained by chemical analysis.

Synthesis of Zr-amorphous microporous materials

The preparation of the amorphous microporous materials containing zirconium was carried out at room temperature and neutral pH with the following compositions: TEOS : 0.2 TM : 0.05 EA : x ZrO_2 : 0.5 TPABr : 12 H_2O.

In a typical preparation, Tris-HCl 1 M buffer pH = 7.0 (Sigma-Aldrich) containing the tromethamine was first added. Then, the required quantity of tetrapropylammonium bromide (TPABr, Sigma-Aldrich), $ZrOCl_2{\cdot}8H_2O$ (Sigma-Aldrich) and TEOS (Merck) were also added to the container under magnetic stirring. Finally, ethanolamine (Sigma-Aldrich, >98%) was incorporated into the mixture. After one week stirring, the solid was filtered off and washed, first with abundant water (1 l) and, finally, with acetone (200 ml). The solid was dried at room temperature.

Synthesis of Ti-mesoporous materials

The preparation of Ti-MCM-41 materials was carried out under mild synthesis conditions with the following compositions: TMOS : 0.05 EA : X TiO_2 : 0.5 CTMABr : 20 H_2O.

In a typical preparation, the cetyltrimetylammonium bromide (CTMABr, Sigma-Aldrich) was stirred in water during 30 min. After this time, TMOS (Sigma-Aldrich, >99%) and titanium(IV) ethoxide (Alfa Aesar) were added. Finally, the ethanolamine (Sigma-Aldrich, >98%) was incorporated into the mixture under stirring. The gel was covered and stirred during 2 days at room temperature. After one week stirring, the solid was filtered off and washed, first with abundant water (1 l) and, finally, with acetone (200 ml). The solid was dried at room temperature.

Characterization techniques

XRD measurements were collected by using a Philips X'Pert diffractometer. The X-ray diffraction pattern was measured with Bragg—Brentano geometry using a fixed divergence slit (1/16°), a goniometer arm length of 240 mm, Cu-K$\alpha_{1,2}$ radiation (λ = 1.5406, 1.5441 Å), and a X'Celerator detector. Tube voltage and current were 45 kV and 40 mA, respectively. The IR spectra in the region of framework vibrations (400–1800 cm^{-1}) were recorded in a Nicolet 710 FTIR spectrometer using the KBr pellet technique. The N_2 adsorption isotherms were measured in the calcined samples at 77 K using an ASAP 2000 Micromeritics instrument. The micropore volume of the products was determined by the *t*-plot method. The Ar adsorption isotherms were measured at 85 K. The pore size distributions were calculated using the Howarth–Kawazoe formalism.[17] ^{29}Si solid state NMR spectra were recorded under magic angle spinning (MAS) at ambient temperature with a Varian VXR-S 400 WB spectrometer at 79.5 MHz with an RT CP/MAS

Varian probe with zirconia rotors (7 mm in diameter). The ^{29}Si chemical shifts were referred to TMS and the ^{29}Si Bloch decay (BD) spectra were acquired using pulses of 4 μs to flip the magnetization an angle of 3/4 π radians, and a recycle delay of 60 s.

Laser flash photolysis measurements. The laser flash photolysis experiments were carried out by using the third (355 nm) harmonic of a Q-switched Nd:YAG laser (Spectron Laser Systems, UK; pulse width *ca.* 9 ns and 20 mJ $pulse^{-1}$). The signal from the monochromator/photomultiplier detection system was captured by using a Tektronix TDS640A digitizer and transferred to a PC computer that controlled the experiment and provided suitable processing and data-storage capabilities.

Conductivity measurements. Measurements of the electrical conductivity were carried out in a cell having aluminum as cathode and a transparent conductive indium tin oxide (ITO) surface on a glass substrate as anode. Measurements were carried out by using ambient-equilibrated zeolite powders deposited as self-supported dry thin films of 50 mm.

Catalytic tests

Meerwein–Ponndorf–Verley (MPV) reaction. The test reaction was carried out in 2 ml glass flasks with magnetic stirring, and heated by means of a temperature-controlled aluminium rack. The molar ratio cyclohexanone : 2-propanol was 1.5 : 98.5, using and 20 mg of catalyst per 1 ml of reaction mixture. The reaction temperature was 85 °C. Aliquots were taken at different reaction times and the evolution of the composition was evaluated by using ultra-fast gas chromatography.

Cyclohexene epoxidation reaction. Catalytic tests were performed at 333 K with the titanium containing mesoporous materials as catalysts and cyclohexene (Fluka >98%) and *tert*-butyl hydroperoxide (TBHP, Aldrich) as reactants. More specifically, 785 mg of cyclohexene were reacted with 215 mg of TBHP (molar ratio olefin : oxidant = 4 : 1), using 5 mg of catalyst. Aliquots were taken at different reaction times and the evolution of composition was evaluated by means of ultrafast gas chromatography. Conversion percentages are referred to TBHP and selectivities to the epoxide.

Results and discussion

Synthesis of microporous molecular silicates at room temperature and pH = 7 with prepolymers as OSDAs

Conducting organic polymers are interesting materials for electric conductivity, charge storage capacity, photovoltaic activity, and electroluminescence.[18,19] One of the objectives in the preparation of the conducting organic polymers, as for instance poly-*para*-phenylenevinylene (PPV), is to prepare materials more stable towards oxidative degradation of their π conjugation.[20] This has been partially achieved by forming the PPV conducting polymer within the pores of zeolite Y.[21] Nevertheless, the method of preparation requires four consecutive steps: zeolite synthesis, calcination, monomer adsorption, and final polymerization.

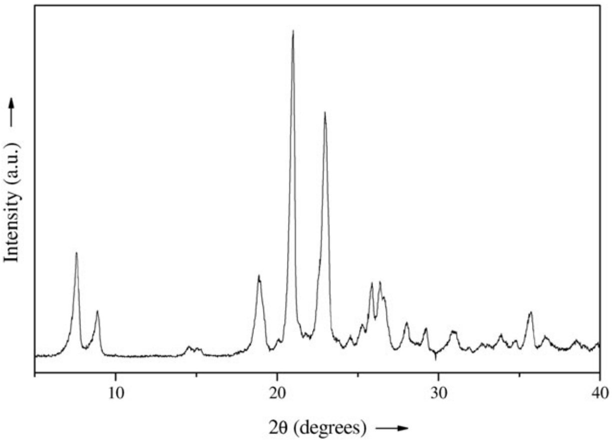

Fig. 1 XRD of the ZSM-12 zeolite obtained using the *para*-phenylenemethylene-bis(trimethylamonium) cation as OSDA under hydrothermal conditions.

It appears to us that by means of the synthesis method described before to produce microporous silicates under neutral pH and room temperature, it should be possible to use the monomers of PPV, *i.e.* *para*-phenylenemethylene-bis(1-tetrahydrothiophenium) (**1**) or *para*-phenylenemethylene-bis(trimethylamonium) (**2**), as directing agents.[22]

In a first approximation, the synthesis of the encapsulating silicate was carried out at moderate pH (pH ~ 8) by working in fluoride media for silica mobilization under hydrothermal conditions. In this media, molecule **2** was stable, but not **1**. Therefore, by using **2** as the OSDA, a gel of the following composition SiO_2 : 0.20 PPV monomer (**2**) : 0.40 HF : 7 H_2O was crystallized at 150 °C, and after 7 days, a crystalline material with the structure of ZSM-12 was obtained (see Fig. 1). The chemical analysis and thermogravimetry gave a composition for the encapsulated organic of 10 wt% and confirmed that the *para*-phenylenemethylene-bis(trimethylamonium) had been preserved during the synthesis and it had been encapsulated within the micropores of the ZSM-12 zeolite. At this point, we attempted the polymerization of the monomer by heating at different temperatures, even in basic media. All attempts to obtain the encapsulated PPV by polymerization of the encapsulated monomer in ZSM-12 zeolite were unsuccessful. In this situation, it is possible to infer that the rigidity of the structure does not allow the monomers to approach in an adequate geometrical orientation for achieving the polymerization.

On the contrary, the much larger flexibility of the amorphous microporous structure that can be synthesized through the bioinspired synthesis should increase the mobility of the monomer within the micropores and allow polymerization. Thus, a synthesis was carried out using the *para*-phenylenemethylene-bis(1-tetrahydrothiophenium) as OSDA and ethanolamine as the silica mobilizing agent, while working at pH = 7 and room temperature, with the following starting synthesis gel TEOS : 0.2 TM : 0.05 EA : 0.25 PPV monomer (**1**) : 12 H_2O.

After 7 days, an amorphous sample was obtained according to XRD measurements, which contained 14 wt% of the encapsulated monomer. When a portion of this sample was

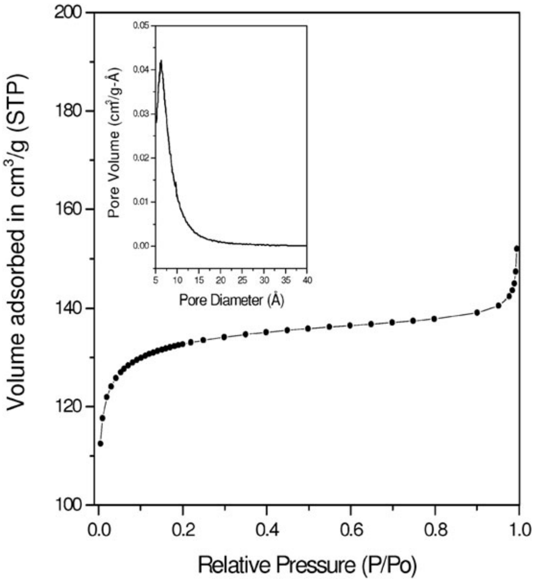

Fig. 2 N_2 adsorption isotherm of the calcined microporous material. The inset shows the pore size distribution measured by means of Ar adsorption.

calcined in air at 540 °C, the organic was removed, leading to a microporous silicate (see N_2 adsorption isotherm in Fig. 2) with 0.20 cm^3 g^{-1} micropore volume, and a pore diameter of ~0.65 nm as measured by Ar adsorption (see Fig. 2). This amorphous structure should be more flexible than the crystalline counterpart owing to the larger number of defects present in the structure of the former, as can be inferred from the ^{29}Si MAS NMR bands associated to Q^3 [Si(3Si)(1OH)] and Q^2 [Si(2Si)(2OH)] in Fig. 3.

When the polymerization of the monomer encapsulated in the amorphous microporous material was now attempted, a simple heat treatment with a solution of tetrabutylammonium hydroxide at 250 °C allowed achieving the PPV. Indeed, this was confirmed by comparing the IR spectra of the solid resulting after the polymerization treatment with the pure PPV polymer (Fig. 4). Adsorption measures with N_2 were performed to the sample, before (monomer **1**@SiO_2) and after polymerization (PPV@SiO_2), to show that the polymerization occurs inside of the pores. In both cases, the low values obtained for the BET surface areas (~2–3 m^2 g^{-1}) confirm that the polymerization occurs inside of the pores. Moreover, chemical analysis for two samples shows that the C content is maintained before (9.6 wt% C) and after (9.2 wt% C) polymerization.

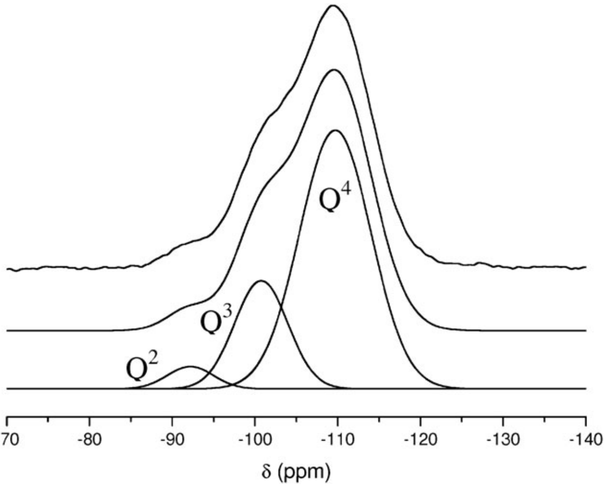

Fig. 3 ^{29}Si MAS NMR spectra of the calcined microporous material. From top to bottom: spectrum of the calcined material, simulation with deconvoluted components and individual deconvoluted Q^2, Q^3 and Q^4 components.

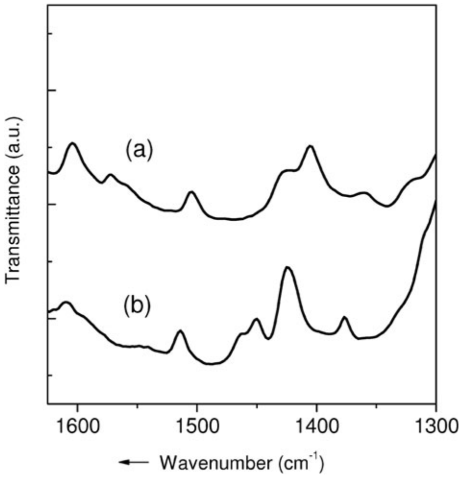

Fig. 4 IR spectra of pure PPV (a) and PPV@SiO_2 sample (b) after outgassing at 100 °C under 10^{-2} Torr for 1 h.

The resulting material showed electroluminescence, with a strong fluorescence at λ_{em} = 530 nm upon excitation at 400 nm (see Fig. 5(a)). The PPV@SiO_2 shows electrical conductivity, producing an intense increase in conductivity when the voltage was increased to 3–4 volts (see Fig. 5(b)). It is most important the fact that the stability of the encapsulated polymer is much higher than the free PPV. Indeed, extended exposure of the sample PPV@SiO_2 to the laser flash (7 mJ $pulse^{-1}$) did not lead to spectroscopic changes, indicating the photochemical excitation does not produce decomposition of the sample. In contrast, analogous treatment of pure PPV film led to degradation of the polymer.

Pheromone encapsulation and release

The development of materials for controlled drug release is a matter of much interest.[23] However, the controlled release of chemicals goes now beyond drugs, since environmental concern is limiting the use of massive amounts of pesticides for agricultural uses, especially in environmental sensitive areas. Nevertheless plagues of harmful insects should be fought, and more natural systems are used that involve the use of semiochemicals, such as pheromones. These natural chemicals can be used either to trace the insects into the traps in where the pesticide is concentrated (Attract and Kill) or to decrease the probabilities of reproduction by sexual confusion (Mating Disruption).[24]

Both systems require the use of devices for the controlled release of the pheromone. The environmental limitations preclude the commonly used plastic bottles with a controlled neck diameter or other non biodegradable polymeric devices

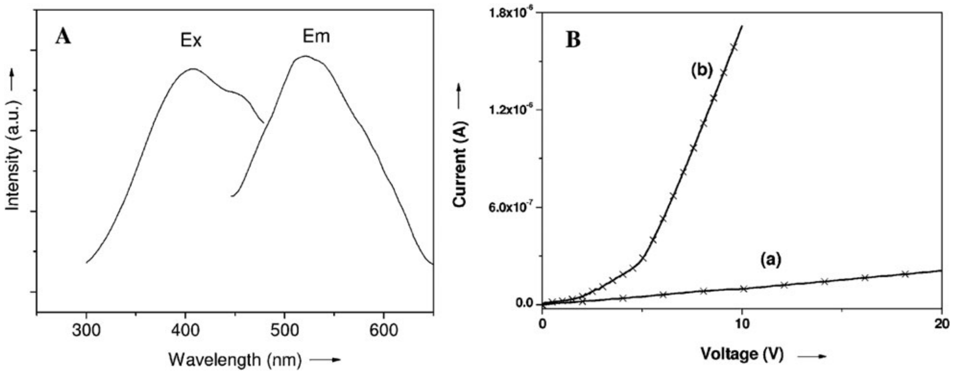

Fig. 5 (a) Emission spectra (Em, λ_{ex} = 400 nm) and excitation spectra (Ex, λ_{em} = 530 nm) of PPV@SiO_2. (b) I–V curve before (a) and after the polymerization (b) for the bioinspired material.

for controlled release of the pheromone. However, micro- and mesoporous silicates are perfectly compatible with environmental demands and could be used for encapsulating and controlling the release of pheromones.

In our case, we have considered, among others, the pheromone of the codling moth (*Cydia pomenella*). Codling moth is the major insect pest of pome fruit that has been traditionally controlled by organophosphorus insecticides sprayed 2–4 times per growing season. This pheromone ((*E*,*E*)-8,10-dodecadien-1-ol) has a lineal carbon chain with 12 carbons, one OH group and two double bonds (see Fig. 6(b)). The *E* configuration of the two double bonds is a key parameter for insect recognition. Thus, if one wants to design a dispenser for controlled release of the pheromone based on a porous structured silicate, has to consider that any $E \rightarrow Z$ isomerization should be avoided, and a regular level of pheromone, above the insect detection limit, has to be maintained during a period of, at least, 120 days.

To accomplish the above requirements, we have synthesized mesoporous materials of the M41S family at room temperature and neutral pH using as OSDA a supramolecular organization of the pheromone and the surfactant (see Fig. 6(a)).[25]

By following our methodology, we avoid $E \rightarrow Z$ isomerization and achieve a much better controlled release than when impregnating the pheromone on calcined MCM-41. Indeed, in this latter case most of the pheromone is already released in a period of 60 days.

A unique synthesis step was required for the preparation of the mesoporous material containing the pheromone at room temperature and neutral pH when starting from mixtures with the following composition: TMOS or TEOS : 0.05 EA or NH_4F : X pheromone : Y CTMABr : 40 H_2O. The different samples synthesized in this work are summarized in Table 2.

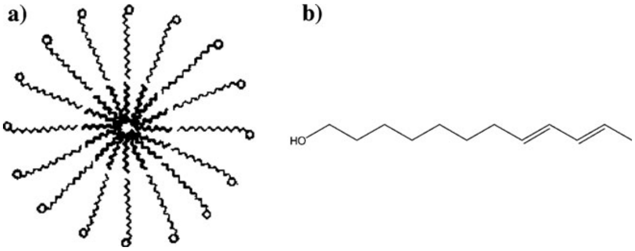

Fig. 6 (a) Schematic drawing of micelle surfactant molecules in presence of *n*-alkane molecules. (b) Pheromone used in this work.

Scientists at Mobil have synthesized mesoporous materials MCM-41, MCM-48 and MCM-50 with hexagonal, cubic and lamellar structures, respectively (see Fig. 7).[26] The formation of each particular material is determined by surfactant packing, which depends on the nature of surfactant and the interaction between surfactant and silica.

The materials obtained here are shown in Table 2, together with the synthesis conditions. When the synthesis was done with no pheromone in the gel (Fer0), the material MCM-41 was formed. If the same ratio of cationic surfactant than for Fer0 is used, but also introducing the pheromone at same molar ratio, the material obtained is not MCM-41 but MCM-50 (Fer1), as can be inferred by comparison with the corresponding XRD data[27] (see also Fig. S2 in ESI†). The difference between both phases stays on the arrangement of the surfactant, which forms cylindrical micelles in the case of MCM-41, and a "sandwich" type layered arrangement in MCM-50 (see Fig. 7). The introduction of other organic molecules in the media, such as pheromone, favours the lamellar structure, decreasing the interactions between water and the non polar group. If the surfactant and pheromone ratios are decreased (Fer3), the hexagonal structure is obtained again. The XRD of the ordered samples obtained in this study is shown in Fig. 8. We have also synthesized an amorphous material using a less reactive silica source (TEOS) with F^- as mobilizing agent (Fer2).

The amount of pheromone charged in each sample is given in Table 3. MCM-50 and the amorphous material have larger amounts of pheromone, while in the MCM-41 material the amount of pheromone is somewhat lower.

The pheromone release for the different materials is presented in Fig. 9 from which it can be seen that the amorphous material (Fer2) presents a lower release than the ordered materials. This could be explained by considering that during the encapsulation of the organic molecules in the synthesis procedure, most of the pheromone is confined inside the amorphous silica framework, that contains pores with bottle necks that slow down the rate of release with respect to that with the ordered materials. The difference between MCM-41 and MCM-50 is related with the initial amount of pheromone that is charged, with the kinetic release being similar, as is

Table 2 Synthesis conditions of the pheromone containing samples

Sample	Si source	*X*	*Y*	Catalyst	Phase
Fer0	TMOS	0	0.16	Ethanolamine	MCM-41
Fer1	TMOS	0.16	0.16	Ethanolamine	MCM-50
Fer2	TEOS	0.16	0.16	NH_4F	Amorphous
Fer3	TMOS	0.10	0.10	Ethanolamine	MCM-41

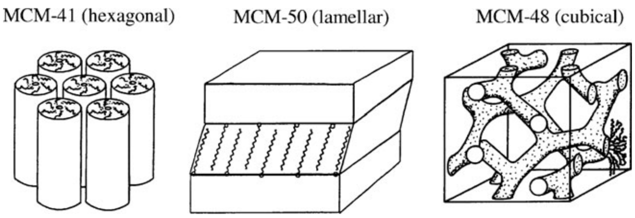

Fig. 7 Mesoporous materials (MCM-41, MCM-48 and MCM-50) with hexagonal, cubic and lamellar structures, respectively.

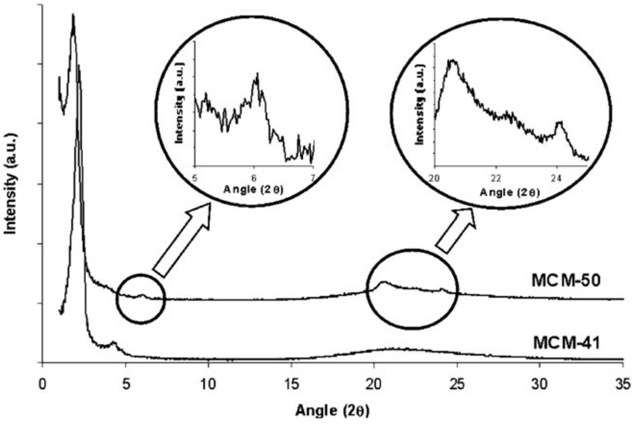

Fig. 8 XRD patterns of the ordered mesoporous samples, MCM-50 and MCM-41.

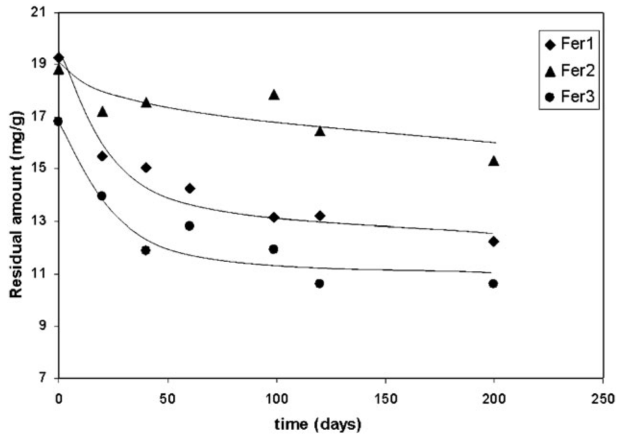

Fig. 9 Release of pheromone for synthesized materials.

shown in Fig. 9. These release kinetics results with a low and constant emission rate are excellent for practical purposes and not easy to obtain with polymeric or other commercial devices.

The example presented here corresponds to a controlled pheromone release, but there is no doubt that this methodology can also be applied for controlled drug delivery since silica is biocompatible and we can also use biocompatible surfactants during the synthesis.

Catalytic materials through bioinspired synthesis

The introduction of heteroatoms in the structure of micro- and mesoporous materials has opened new possibilities for catalysis. For instance, the introduction of Ti in medium[28] and large pore zeolites[29,30] and mesoporous materials,[31] Sn in zeolites and mesoporous molecular sieves[32,33] and Fe in silicalite[34] have opened new possibilities for oxidation catalysis.

The introduction of transition metals, with larger atomic radius than Si, in tetrahedral coordination is not an easy task, and it is normally facilitated in the case of more flexible structures. In the case of mesoporous molecular sieves, the short distance amorphous nature of the materials makes the introduction of transition metals easier in larger amounts that in the case of zeolites. If this is the case, we should be able, by bioinspired synthesis at neutral pH and room temperature, to synthesize micro- and mesoporous molecular sieve materials with relatively large contents of tetrahedrally coordinated metal atoms in the structure.

For instance, the introduction of Zr in the structure of beta zeolite allows the synthesis of active materials for catalyzing the Meerwein–Ponndorf–Verley (MPV) reduction of carbonyls by secondary alcohols.[35,36] However, the size of Zr precludes the introduction of larger amounts of Zr within the framework, and an important loss of crystallinity is observed when decreasing the Si/Zr ratio below 75.[37] However, in the microporous materials synthesized by the bioinspired method described here, using TPA as structure directing agent with the following gel composition TEOS : x ZrO_2 : 0.5 TPABr : 12 H_2O and the synthesis conditions listed in Table 4, a series of microporous materials have been obtained that

Table 3 Chemical composition of the pheromone charged samples

	Weight loss (wt%)		Composition (wt%)			
Sample	30–150 °C	150–800 °C	N	C	H	wt% pheromone
Fer0	8.10	33.10	1.49	23.60	5.01	—
Fer1	2.13	55.02	1.44	38.92	7.46	19.6
Fer2	2.15	49.94	1.08	32.41	6.31	18.8
Fer3	2.68	44.18	1.13	31.77	5.95	16.8

Table 4 Synthesis conditions of the metal containing microporous samples (Zr source $ZrOCl_2{\cdot}8H_2O$)

Sample	Catalyst/Si	Si/Zr (1/x)
Zr1	0.2 TM + 0.05 EA	30
Zr2	0.2 TM + 0.05 EA	60
Zr3	0.2 TM + 0.05 EA	120

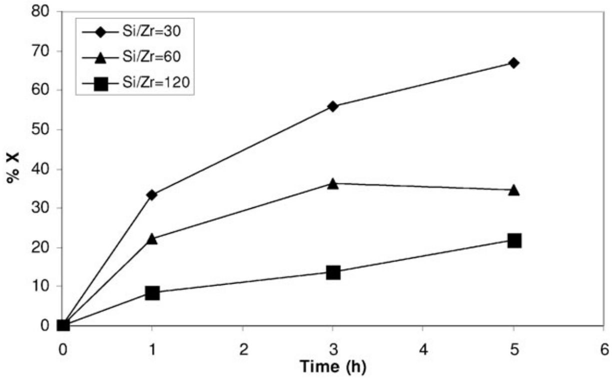

Fig. 10 MPV reduction of cyclohexanone over Zr-amorphous bioinspired materials (T = 85 °C; 2-propanol : cyclohexanone (98.5 : 1.5); 20 mg catalyst).

contain different levels of Zr. They are amorphous and microporous with micropore volume of 0.18 $cm^3\ g^{-1}$ and a pore diameter of 0.65 nm.

Interestingly, it was possible by this method to achieve a sample with a Si/Zr ratio as low as 30. The materials obtained are active for the MPV reduction of cyclohexanone with 2-propanol (see Fig. 10), and what is interesting is that there is a direct correlation between the initial reaction rate and the Zr/(Zr + Si) ratio (see Fig. 11). This is an indication that all the Zr sites give the same TOF regardless of the Zr content, suggesting that if the Zr is tetrahedrally coordinated in samples with high Si/Zr ratio, it should also be tetrahedrally coordinated in the case of the sample with Si/Zr = 30.

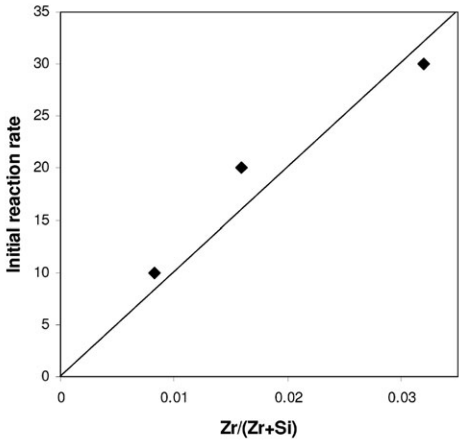

Fig. 11 Direct correlation between the initial reaction rate and the Zr/(Zr + Si) ratio.

Table 5 Synthesis conditions of Ti-containing mesoporous samples (Si source TMOS)

Sample	Catalyst/Si	TiO_2 (wt%) Gel	TiO_2 (wt%) Analysis
Ti1	0.05 EA	1	0.9
Ti2	0.05 EA	2	1.4
Ti3	0.05 EA	2.4[a]	2.4

[a] By grafting.

Table 6 Cyclohexene epoxidation over Ti containing mesoporous samples

Sample	TiO_2 (wt%)	Conversion (%)	Selectivity (%)
Ti1	0.9	49.8	>98
Ti2	1.4	65.6	>98
Ti3	2.4[a]	67.1	>98
Ti-MCM 41	2.0	72.0	>98

[a] By grafting.

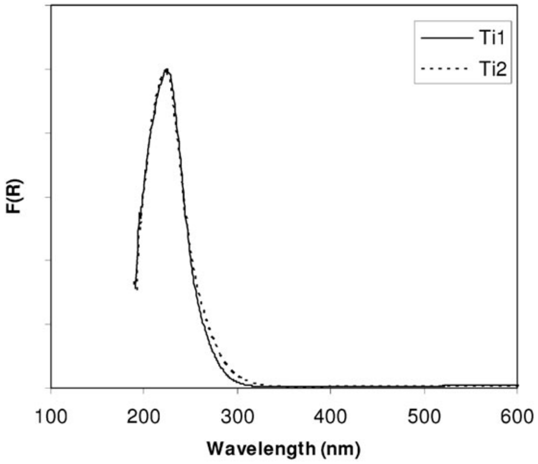

Fig. 12 UV-Vis DRS spectra of bio-inspired Ti-mesoporous materials.

Mesoporous titanosilicates of the MCM-41 type have also been synthesized by the same method with good crystallinities. The synthesis conditions are given in Table 5 and the composition of the starting gel was TMOS : x TiO_2 : 0.05 EA : 0.5 CTMABr : 20 H_2O. The catalytic behaviour has been tested for the epoxidation of cyclohexene with *tert*-butyl hydroperoxide, and the results are given in Table 6. Activity and selectivity of the Ti-MCM-41 samples prepared by the bioinspired method is, at least, as good as those obtained by well optimized conventional methods through either direct synthesis,[31] or by Ti grafting on pure silica MCM-41.[38] These results would imply that in the samples prepared here, Ti is also tetrahedrally coordinated in the walls of the mesoporous materials. Indeed, UV-visible spectra of Ti-MCM-41 samples (Ti1 and Ti2) show a band at 220 nm, which is typical of Ti^{IV},[38–42] while no band is observed at 240–260 nm, which would be associated to the presence of Ti^{VI} (see Fig. 12).

Conclusions

It has been shown[15] that proteins of the "silicatein" type containing the hydroxy group of serine-26 and the imidazole group of histidine-165 close enough to act in a concerted way are able to hydrolyze and condense silica from TEOS. From this, we have proposed that a similar effect could be expected by having hydroxy or thiol and a primary amine group in close enough proximity. Indeed, we have synthesized micro- and mesoporous molecular sieve materials at neutral pH and room temperature, using ethanolamine to mobilize the silica. This methodology allows the preparing of amorphous micro- and mesoporous molecular sieve materials, where less stable molecules can be encapsulated and the final material used in electronics (conducting polymers) or for the controlled release of chemicals (pheromones). Furthermore, the framework flexibility of the materials formed allows the introduction of transition metals with tetrahedral coordination within the silicate in larger amounts than in the zeolites, while preserving the activity and selectivity of the metals for selective oxidation reactions.

Acknowledgements

The authors thank the CICYT for financial support (Project MAT 2006-14274-C02-01).

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