Synthesis of micro- and mesoporous molecular sieves at room temperature and neutral pH catalyzed by functional analogues of silicatein†

Avelino Corma,* María J. Díaz-Cabañas, Manuel Moliner and Guillermo Rodríguez

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By using functional mimics of the protein silicatein α together with organic structure directing agents, it was possible to produce different mesoporous and microporous molecular sieves at room temperature and neutral pH.

A large variety of marine organisms such as diatoms, silico flagellates, radiolarians, and sponges are able to synthesize silica skeletons by activating and self assembling the silica present in sea water at neutral pH and room temperature. It has been recently shown[1] that silicatein α can hydrolyze and condense silica species while forming non porous silica structures of different shapes. Menzel *et al.*[2] have modeled the polyamines found in diatoms, and showed an accelerating effect on silica condensation, which depends on the chemical nature, chain branching and the degree of polymerisation. In this study, silicic acid condensation takes place at pH of 4.3 to 4.8 and no structured material was obtained.

Synthetic cysteine–lysine block copolypeptides,[3] or even small molecules, such as for instance cysteamine,[4] have also been used to hydrolyze and condense silica from TEOS, producing non porous silicas with different forms. It will be of interest to use bioinspiration not only to produce non porous silicas as has been done up to now, but to synthesize nanoporous materials with well defined and controlled pore diameters.

Crystalline and amorphous mesoporous and microporous molecular sieves are important silica based materials with applications in electronics, magnetism, light emitting devices, adsorption and catalysis among others.[5–9] Their pore diameter ranges from 3.5 to 100 Å and they are usually obtained by hydrothermal synthesis at high pressure and temperature in basic or acid media. When working in nearly neutral conditions, the presence of fluoride ions is required.[10–15] Biotechnological approaches to the synthesis of these important materials, at neutral pH and low temperature, can open new strategies and environmentally friendly routes for the synthesis and structural design of porous silicates and their use in the controlled delivery of encapsulated drugs, in one step synthesis of LEEDS and for molecular separation and catalysis.

Here we show that by using simple molecules such as tromethamine, cysteamine, and ethanolamine, which act as catalysts, *i.e.* functional mimics of the protein silicatein α, together with organic structure directing agents (SDA), it is possible to mobilize and self-assemble the silica and the SDA to produce different microporous and mesoporous molecular sieves at neutral pH and room temperature. This is in contrast to conventional methods which require high temperature and pH or the presence of fluoride ions.

In this work, the synthesis of mesoporous and microporous materials has been performed at room temperature in polypropylene screw cap containers (50 ml) from gels of compositions:

Microporous: $Si(OR)_4$: 0–0.2 T : 0–0.05 E/C : 0.5 SDABr : 12 H_2O

Mesoporous: $Si(OR)_4$: 0–0.05 E : 0.16–0.5 CTMABr : 20 H_2O

The gel was maintained under stirring during the times specified in Table 1. At different times, small samples were extracted. The solids were filtered, washed and dried at room temperature. Finally, the samples were calcined in air at 540 °C for 3 h to eliminate organic material occluded.

In the blank_micro experiment with tromethamine, made in the absence of SDA, TEOS was hydrolyzed, showing that this molecule can be a functional mimic of silicatein. However, it should be remarked that tromethamine also forms small solid particles of silica with no microporosity (see Table 2). A second blank experiment was performed at neutral pH, with TPABr as SDA and without catalyst. Under these conditions the hydrolysis of TEOS is very slow and no appreciable amounts of solid are obtained, since the hydrolysis of TEOS is acid or base catalyzed with a minimum rate at pH = 7.[16] However, when the synthesis was carried out in the presence of the SDA bromide and with catalyst (Table 1), not only was TEOS hydrolyzed, but condensation and self assembly of silica and the organic SDA occur, as

Table 1 Synthesis conditions of microporous and mesoporous materials at room temperature

Sample	Catalyst/Si[a]	Si Source	SDA	pH	*t*/d
B_micro[b]	0.2 T	TEOS	—	7.4	7
1TPA	0.05 T	TEOS	0.5 TPA	7	7
2TPA	0.2 T	TEOS	0.5 TPA	7.3	7
3TPA	0.2 T + 0.05 C	TEOS	0.5 TPA	7.2	7
4TPA	0.2 T+ 0.05 E	TEOS	0.5 TPA	7.7	7
1TEA	0.2 T+ 0.05 E	TEOS	0.5 TEA	7.7	7
1TBA	0.2 T+ 0.05 E	TEOS	0.5 TBA	7.5	7
B_meso[b]	—	TMOS	0.5 CTMA	7.0	2
1CTMA	0.05 E	TMOS	0.5 CTMA	7.2	2
2CTMA	0.05 E	TMOS	0.16 CTMA	7.1	2

[a] Molar ratio, T = Tromethamine, C = Cysteamine and E = Ethanolamine. [b] B_micro and B_meso: blank experiments.

Instituto de Tecnología Química (CSIC-UPV), Universidad Politécnica de Valencia, Avda. de los Naranjos s/n., 46022, Valencia, Spain. E-mail: acorma@itq.upv.es; Fax: (+34) 96-387-7809; Tel: (+34) 96-387-7800 Tel: (+34) 96-387-7800

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Table 2 Chemical composition and textural properties of the synthesized samples

	Weight loss (%)		Composition (wt%)				Area/m^2 g^{-1}			
Sample	30–150 °C	150–800 °C	N	C	H	C/N	BET	Micropore	Pore diameter/Å	Micropore volume/cm^3 g^{-1}
B_micro	6.4	5.0	0.29	1.30	1.26	5.2	165	0	—	—
1TPA	5.0	17.6	0.77	11.84	2.96	17.8	550	450	—	—
2TPA	5.8	14.0	0.73	9.57	2.69	15.2	496	432	—	—
3TPA	5.5	13.4	0.74	8.04	2.36	12.6	461	405	—	—
4TPA	5.4	14.7	0.90	8.71	2.67	11.3	471	440	6.7	0.19
1TEA	6.5	16.1	1.14	7.69	2.56	7.8	387	328	6.3	0.18
1TBA	3.2	15.4	0.62	8.90	2.47	16.7	525	481	6.9	0.23
B_meso	3.3	16.8	0.55	9.05	2.30	19.1	704	—	—	—
1CTMA	6.1	37.0	1.60	25.51	5.37	18.6	995	—	~30	—
2CTMA	8.1	33.1	1.49	23.60	5.01	18.5	956	—	~30	—

evidenced by the organic content of the resulting materials[17] (see Table 2).

When using CTMA bromide as SDA at room temperature (22 °C) and pH = 7.2, ethanolamine as silica mobilizing agent and TMOS as silica source, well ordered MCM-41 mesoporous molecular sieve material was obtained, as can be seen by XRD and TEM (see Fig. 1a and 1b, respectively). Accordingly, the BET surface area after calcination at 540 °C is approximately 1000 m^2 g^{-1} (Table 2) and the pore size distribution is very narrow and centered at ~30 Å (see Fig. 2a), as expected. When no mobilizing agents are added, a material with a very broad pore distribution is obtained, and no MCM-41 is formed. Moreover, it has to be remarked that, in the presence of catalyst but without CTMA, an amorphous material is obtained with a BET surface area of 165 m^2 g^{-1}. The synthesis of MCM-41 may take place through a liquid-crystalline templating mechanism as introduced by Göltner *et al.*,[18] though at neutral pH.

In order to optimise the MCM-41 synthesis, an experiment (2CTMA) at much lower concentration of CTMA (see Table 1 and Table 2) was performed, which also yielded a well ordered mesoporous material.

By this method, it was also possible to synthesize metal-containing MCM-41, as for instance Ti-MCM-41, with a UV–Visible spectrum that indicates that most Ti is tetrahedrally coordinated (see Fig. 1 in ESI†) and which gives activities and selectivities for epoxidation of cyclohexene very close to those reported for conventionally prepared Ti-MCM-41 epoxidation catalyst.[19–21]

The material obtained with TPA as SDA remains stable after removing the organics by calcination in air at 540 °C. It possesses a BET surface area close to 500 m^2 g^{-1}, most of that being microporous area (Table 2). Furthermore, Ar adsorption experiments show that the majority of the micropores are within a very narrow pore size distribution, with the maximum located at ~6.7 Å, indicating that a microporous molecular sieve material has been obtained (Fig. 2b). The micropore size distribution and the maximum are higher than those of the medium pore size ZSM-5 zeolite (6.2 Å), which is also synthesized using TPA as SDA, but at a rather high pH (pH ~11) and temperature (150 °C).

The X-ray diffraction pattern of the biomimetically synthesized microporous material shows that it is an amorphous material. The amorphous nature of the material was also confirmed by IR spectroscopy (see Fig. 2 of ESI). Indeed, IR allows detection of the presence of crystalline silicates even as small nuclei of two or three unit cells.[22,23] As can be seen in Fig. 2 of the ESI, bands in the 400–650 cm^{-1} region associated with rings in crystalline silicates are present in the zeolite ZSM-5, while only a broad band at ~460 cm^{-1} in the spectrum of our material is observed.[24] This broad band at ~460 cm^{-1} is similar to what is observed in amorphous silica or MCM-41 type materials.[25] Electron diffraction experiments showed no crystallinity in agreement with the IR results.

^{29}Si MAS NMR spectra of the calcined material (Fig. 3 of ESI) show the presence of Q^4, Q^3 and Q^2 species in the ratio 73 : 23 : 4. The proportion of Q^3 and Q^2 species (silanols) is much higher than in pure silica ZSM-5 zeolite,[26] but lower than in a mesostructured silica form of MCM-41 synthesized in basic media, with a Q^3/Q^4 ratio around 0.60. This indicates that the amorphous microporous

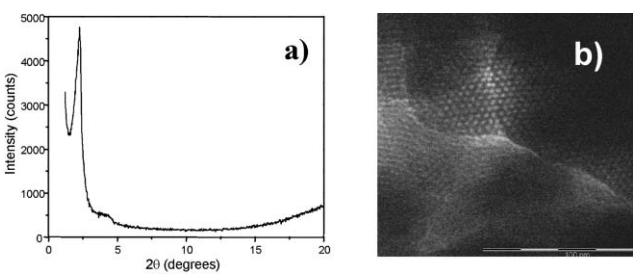


Fig. 1 (a) XRD pattern of the mesoporous material obtained with ethanolamine, (b) TEM image for the mesoporous MCM-41.

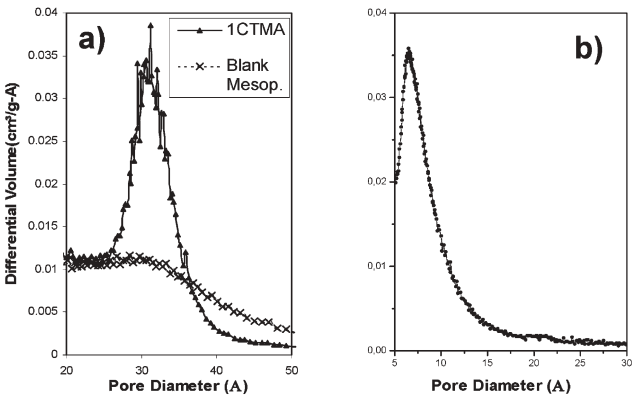
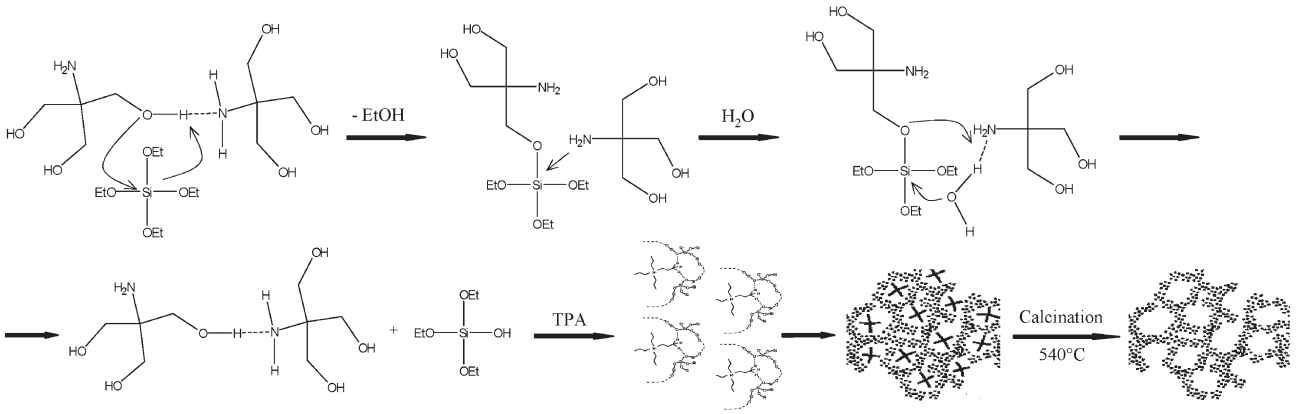


Fig. 2 Pore distribution of (a) the mesoporous sample and (b) the microporous material obtained with TPA.



Scheme 1 Mechanism of the hydrolysis and condensation of silica species to form microporous and mesoporous materials.

molecular sieve synthesized here has an incompletely formed framework but with a high degree of connectivity. An schematic mechanism for the hydrolysis and condensation of the silica source to form the microporous materials is proposed in Scheme 1, following the mechanism described by Zhou *et al.*[1]

Aqueous solutions of cysteamine and ethanolamine, both molecules with a nucleophilic and a hydrogen bonding group, give a pH not neutral, that can be adjusted to neutral in the presence of tromethamine (3TPA and 4TPA in Table 1). Fig. 4 in the ESI shows that the rate of hydrolysis of TEOS with tromethamine increases in the presence of ethanolamine (4TPA) and shows only a slight increase with cysteamine (3TPA). Nevertheless, the final products obtained in these syntheses occlude similar amounts of organics and the total surface area and microporosity developed after calcination is very close in all cases (Table 2).

Once hydrolysis of silica precursors and self-assembly with the organic compounds have occurred, the next step was to check if the micropore diameter and micropore volume could be modified by changing the SDA. Several organic molecules of different sizes were selected: TEA, TPA and TBA. The syntheses were carried out at room temperature with the buffered solution of ethanolamine and tromethamine (Table 1). Under these conditions, microporous materials were obtained (1TEA, 4TPA, and 1TBA) and the characteristics are shown in Table 2. The BET surface area and the micropore volume of the microporous materials obtained are higher for bigger SDAs. Ar adsorption measurements (Table 2) indicate that the maximum of the micropores for 1TEA is located at ~6.3 Å, for 4TPA is ~6.7 Å, and in the case of 1TBA is ~6.9 Å. This gradation corresponds to the size of the organic SDA. Then, we have found that the concept can be extended to other organic structure directing agents yielding microporous materials with different pore diameters and micropore volumes.

In conclusion, it is possible to synthesize micro and mesoporous molecular sieve materials by working at nearly neutral pH and room temperature, by using organic SDAs and simple organic molecules, that act as functional mimics of natural proteins.

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