Influence of cationic phosphorus dendrimers on the surfactant-induced synthesis of mesostructured nanoporous silica†‡

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The concomitant use of polycationic dendrimers and cationic surfactants for the elaboration of periodic mesoporous silica of type MCM-41 is described. The hexagonal structure is preserved up to about 26% in weight of dendrimer included in the silica. The cationic surfactant can be selectively removed to liberate the pores, while preserving the non-covalently incorporated dendrimers. These dendrimers included in the mesoporous silica are fully accessible through the mesoporous volume to small molecules such as HCl and tetrahydrofuran.

Introduction

Periodic mesostructures synthesized by the cooperative assembly and organization of organic and inorganic components play a key role in the development of nanotechnologies, with great promise for diverse applications such as catalysis or drug release.[1] The controlled porosity of the material is of paramount importance; it is often achieved by using surfactants for the templated synthesis of the inorganic walls between ordered micelles.[2] In recent years, several attempts to replace surfactant micelles by dendrimers have been reported,[3] but only a poor control of the porosity is generally observed both before and after removal of the dendrimer. Furthermore, if the properties of the dendrimers have to remain usable in the silica, such approach is not suitable. Alternately, the grafting[4] or the growing[5] of dendrimers on or inside the pores of preformed mesoporous silica has been reported.

To the best of our knowledge, there is no report to date about the concomitant use of dendrimers and surfactants for the synthesis of mesostructured nanoporous silica including dendrimers. Performing such experiments raises fundamental questions: (i) what will the influence of the dendrimer be on the structuration process; (ii) whether it is possible to eliminate only the surfactant after the synthesis and not the dendrimer included in a non covalent way; (iii) if it is possible to preserve the nanometric size of the pores even after this process; (iv) whether the dendrimer included in the material will be accessible. We report here the answers to these questions.

Results and discussion

Cetyltrimethylammonium bromide (CTAB) is classically used for the synthesis of the well-known MCM-41 hexagonal silica phase[1,2,6] from sodium silicate in water. In association with this system, we decided to use the water-soluble cationic phosphorus dendrimers displaying similar cationic end groups **1-G$_4$**,[7] **2-Gc$_4$** and **2-Gc$_8$**.[8] These dendrimers differ both by the nature of their core (P═S: trifunctional; N_3P_3: hexafunctional) which modifies the number of end groups at each generation, and by the type of ammonium end groups they carry (quaternary or tertiary) (Fig. 1).

These dendrimers could play the role of a second surfactant; it has been shown previously that a double surfactant system may modify the morphology of the silica and offer a better control.[9] The ratio dendrimer/Si, the size (generation 4 or 8) of the dendrimer, and the nature of the end groups R have been varied (Table 1). The ratio used is $1SiO_2/0.21CTAB/0.8NaOH/xdendrimer/100H_2O$ for all experiments.

The perturbations induced by the dendrimers on the classical hexagonal MCM-41 phase have been characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM) (Fig. 2). XRD shows that the diffraction pattern is not perturbed by relatively small amounts of dendrimers; the diffractograms show peak characteristics d_{100}, d_{110}, d_{200}, and d_{210} which could be attributed to a hexagonal phase with the $d_{100} \cong 40$ Å. The perturbation increases with increasing amounts of dendrimer, both for **1-G$_4$** and **2-Gc$_4$**, but the type of end groups plays an important role on the intensity of the perturbation; dendrimer **2-Gc$_4$** has a more destabilizing effect than **1-G$_4$** on the hexagonal phase for analogous concentrations (compare pattern *C* with *F* in Fig. 2). This fact might be

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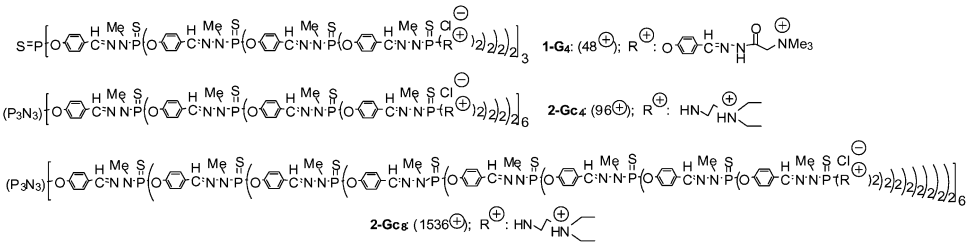

Fig. 1 Chemical structure of the cationic dendrimers used in this study.

related to the presence of tertiary ammonium end groups: we have shown that the whole end groups of this dendrimer are protonated only in acidic conditions,[10] thus part of the surfactant properties are lost in the basic conditions used with **2-Gc$_4$** but not with **1-G$_4$**, which bears stable quaternary ammonium end groups.

The influence of the dendrimer on the silica structure is also shown by TEM. The honeycomb structure characteristic of the hexagonal arrangement is easily seen for relatively low amounts of **1-G$_4$** (Fig. 2 image *A*, Si/R = 31, CTAB/R = 4.4); this structure is perturbed by high amounts of **1-G$_4$** (Fig. 2 image *C*, Si/R = 6, CTAB/R = 0.4), but there are still large domains in which it persists, confirming the diffraction data. The generation of the dendrimer has also an influence on the morphology of silica, as shown by the comparison between dendrimers **2-Gc$_4$** and **2-Gc$_8$** (possessing the same type of end groups) used in experiments *E* and *H* with the same initial ratio between the end groups and SiO_2 (1/5). Hexagonal domains are observed in the presence of the lowest generation (**2-Gc$_4$**), whereas only disordered phases are observed with the highest generation (**2-Gc$_8$**).

The determination of the chemical composition of the hybrid composite (silica–surfactant–dendrimer) has been carried out by FT-Raman spectroscopy, thermogravimetric analyses (TGA) coupled with differential scanning calorimetry (DSC), and elemental analyses. Raman spectroscopy allows the characterization of the organic part included in the silica. In all cases, the signals characteristics of CTAB (2800–3000 cm^{-1}) and of the dendrimer (1570–1600 cm^{-1} for the internal skeleton, 2800–3000 cm^{-1} for the end groups) are detected showing the inclusion of both the dendrimer and the CTAB in the material (Fig. 3). The dendrimer is generally incorporated intact in the silica, except if the silica is elaborated by heating when **1-G$_4$** is used. This has to be related to the lower thermal stability imparted by the $COCH_2NMe_3$ groups compared to the $CH_2CH_2NEt_2H$ groups shown by TGA analyses of the dendrimers alone.[11]

The TGA-DSC analyses of the silica composite allowed the determination of the quantity of organic components included; the relative amount of dendrimer was measured by Si, P, and S elemental analyses (Table 2). The percentage of organic components included in silica is high in all cases (47 to 61%), and significantly higher than the percentage obtained with dendrons included in silica without the help of surfactants (14 to 45%),[3d] measured by weight loss in TGA-DSC analyses in both cases. The incorporation of dendrimers occurs to the detriment of CTAB: the weight loss is relatively similar in all cases, whereas the percentage of CTAB diminishes dramatically when the amount of dendrimer increases. In case

Table 1 Characteristics of the hybrid composite silica synthesized with dendrimers

No	Compound	Initial R/Si[a]	*m*R/Si[b]	*m*Weight **Gn**/SiO_2[c]	Phase[d]
A	**1-G$_4$**	1/20	1/31	0.25	Hex.
B	**1-G$_4$**	1/10	1/21	0.38	Hex.
C	**1-G$_4$**	1/2	1/6	1.25	Hex. Dis.
D	**2-Gc$_4$**	1/10	1/25	0.23	Hex.
E	**2-Gc$_4$**	1/5	1/8	0.75	Hex. Dis.
F	**2-Gc$_4$**	1/3.5	1/4	1.40	Dis.
G	**2-Gc$_8$**	1/10	1/11	0.55	Hex.
H	**2-Gc$_8$**	1/5	1/6	1.03	Dis.

[a] Ratio of the number of end groups of dendrimers/SiO_2 for the starting components. [b] In the material, measured by elemental analyses (from the ratio P/Si). [c] Weight of dendrimer/weight of SiO_2 in the hybrid composite silica, measured by the ratio P/Si. [d] XRD, TEM (Hex.: hexagonal; Hex. Dis.: hexagonal domains visible by TEM; Dis.: disordered).

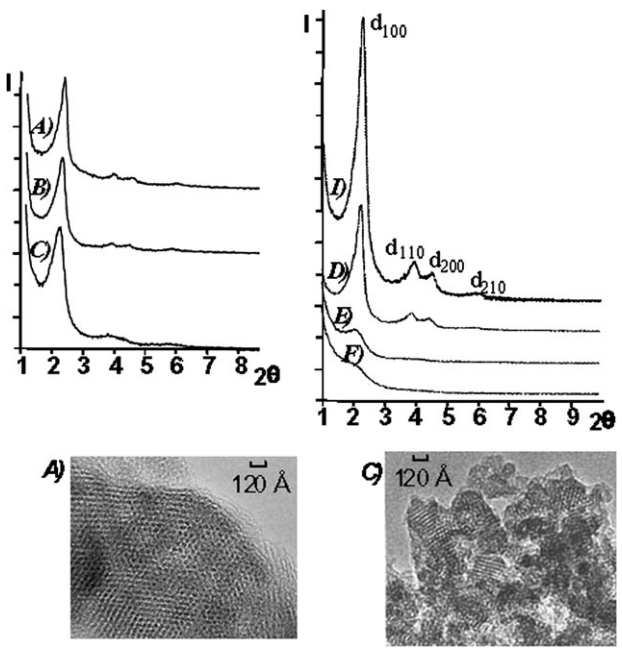

Fig. 2 Upper part: XRD patterns for mesoporous silica containing dendrimers **1-G$_4$** (*A*: Si/**1-G$_4$** = 1500; *B*: Si/**1-G$_4$** = 1000; *C*: Si/**1-G$_4$** = 300), **2-Gc$_4$** (*D*: Si/**2-Gc$_4$** = 2400; *E*: Si/**2-Gc$_4$** = 750; *F*: Si/**2-Gc$_4$** = 400), and after extraction of CTAB from *D*) (I) (molar ratios measured by elemental analyses in all cases). Lower part: TEM images of *A*) and *C*).

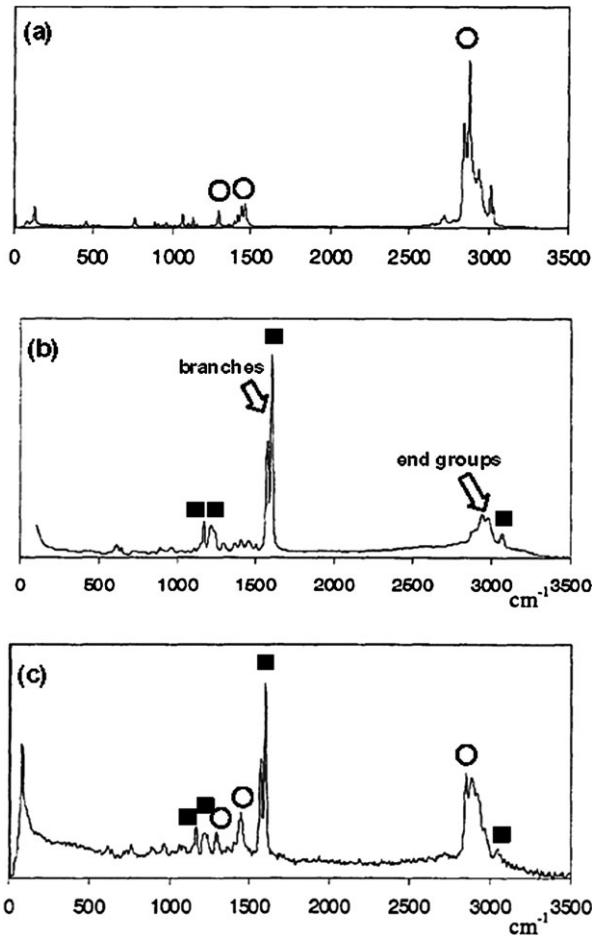

Fig. 3 FT-Raman spectra of CTAB (○) (a), dendrimer **2-Gc$_4$** (■) (b), and hybrid composite (silica-surfactant-dendrimer) obtained in experiment *D* (c).

of experiment *F*, the percentage of dendrimer incorporated in the silica is very high (50%) whereas the percentage of CTAB is very low (0.6%), but this ratio has a detrimental effect on the structure of the silica, which is disordered. The ratio in weight dendrimer/CTAB measured in the hybrid composite silica is relatively close to the ratio used in the initial mixture for **1-G$_4$**, whereas it is totally different (much higher) for **2-Gc$_4$**, showing a very good affinity of this compound for silica. Comparison between Tables 1 and 2 also shows that the hexagonal structure is lost for the highest amounts of dendrimers (experiments *F*, *H*, and *C*, 50, 42 and 41wt% of dendrimer in silica, respectively).

In order to characterize more precisely the porosity of these materials, the BET specific surfaces have been measured after calcination of the samples at 550 °C. In most cases, the BET surface is comparable to that of classical MCM-41 (*ca.* 1000 $m^2\ g^{-1}$), except for the most disordered samples (experiments *F* and *H*). These experiments emphasize the destabilizing role played by the generation; for the same type of end groups R and the same R/CTAB ratio (1/1.1) and initial R/Si ratio (1/5), the specific surface is 1117 $m^2\ g^{-1}$ for **2-Gc$_4$** and only 172 $m^2\ g^{-1}$ for **2-Gc$_8$**. The pore size and the pore size monodispersity are measured for the silica issued from **1-G$_4$** by nitrogen absorption/desorption isotherms. The isotherm obtained for the lowest amount of dendrimer is similar to that of classical MCM-41, with a narrow pore size distribution of about 25 Å (Fig. 4). The highest amount of dendrimer produces a material possessing a larger pore size distribution, with meso- and microporosities, and also textural porosity between particles (cases *F* and *H*).

After analyzing the chemical and physical composition of the hybrid nanocomposites, some experiments were carried out to emphasize their original properties due to the presence of the dendrimers. We believed that the high number of end groups of dendrimers able to interact with silica should more firmly bind the dendrimer to silica than CTAB, and that CTAB could be selectively removed. To check our assumption, NH_4Cl in refluxing ethanol was used with the sample including **2-Gc$_4$**, issued from experiment *D*, a classical way to remove CTAB. The efficiency and the selectivity of the extraction of CTAB are measured by Raman, elemental analyses, and TGA-DSC analyses. These techniques show that the Si/**2-Gc$_4$** molar ratio is 2600 after extraction (2400 before), whereas the % in weight of CTAB in the sample after extraction is 4% (31% before); thus, the extraction of CTAB is carried out with a good selectivity and the loss of dendrimer is minimal (Fig. 5). Furthermore, the hexagonal structure is preserved by the extraction, as shown by the high intensity of the XRD pattern (see traces *D* and *I* in Fig. 2). The average pore size is 25 Å with a wall thickness of about 15 Å, thus the hexagonal MCM-41 structure is preserved. The BET surface of this sample without calcination is 875 ± 6 $m^2\ g^{-1}$, a value close to that of the classical MCM-41 phase after removal of the surfactant.

The next experiments were carried out to determine the accessibility to the dendrimer **2-Gc$_4$** incorporated in the silica.

Table 2 Composition (wt%) of the silica (by TGA and elemental analysis)

No	Composition	*i*Gn/CTAB[a]	*m*Gn/CTAB[b]	CTAB/%	Gn%	Weight loss/%	BET[c]
A	**1-G$_4$**	0.29	0.24	42	10	58	995 ± 6
B	**1-G$_4$**	0.59	0.83	23	19	48	1010 ± 7
C	**1-G$_4$**	2.95	3.15	13	41	61	798 ± 13
D	**2-Gc$_4$**	0.44	0.35	31	11	47	1108 ± 8
E	**2-Gc$_4$**	0.88	4.38	8	25	47	1117 ± 12
F	**2-Gc$_4$**	1.32	83.3	0.6	50	53	174 ± 2
G	**2-Gc$_8$**	0.45	1.53	17	26	49	985 ± 12
H	**2-Gc$_8$**	0.91	8.4	5	42	51	172 ± 2

[a] Initial ratio in weight of dendrimers and CTAB. [b] Ratio dendrimer/CTAB measured in the material. [c] Brunauer–Emmet–Teller specific surface after calcination of the sample at 550 °C ($m^2\ g^{-1}$).

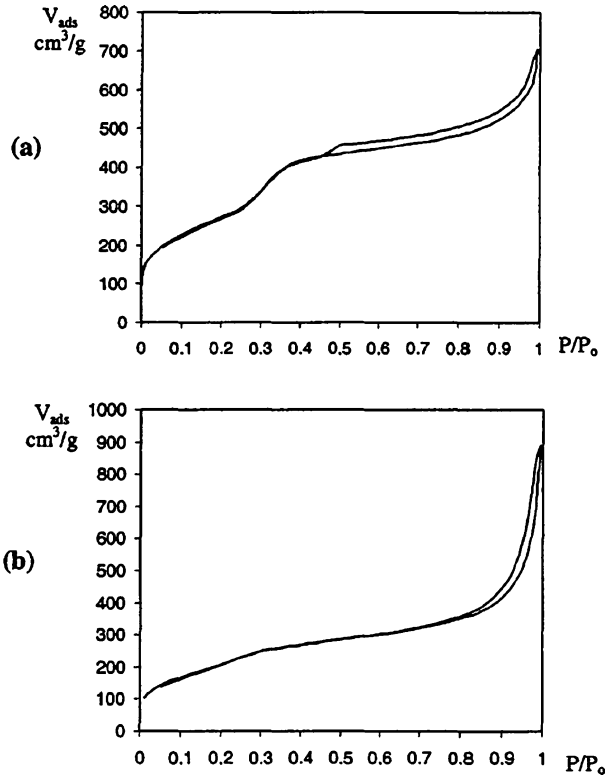

Fig. 4 Isotherms of adsorption and desorption of N_2 (gas) after calcination of the samples *A* (a) and *C* (b). Correspondence to liquid adsorbed volume usually used, V_{ads} in cm^3 g^{-1} will be obtained by multiplying the *Y* axis values by the factor 0.001547.

It must be emphasized that the presence of phosphorus in the skeleton of these dendrimers offers a unique opportunity for their detection inside silica by a simple and unequivocal method (^{31}P NMR). We have previously demonstrated that the internal structure of water-soluble phosphorus dendrimers is hydrophobic, inducing the loss of signals in ^{1}H and ^{31}P NMR spectra when water is used as solvent.[8b] The ^{31}P NMR spectrum of the extracted sample in suspension in D_2O displays no signal; if THF is added to this suspension, a broad signal at 70 ppm corresponding to the dendrimer clearly

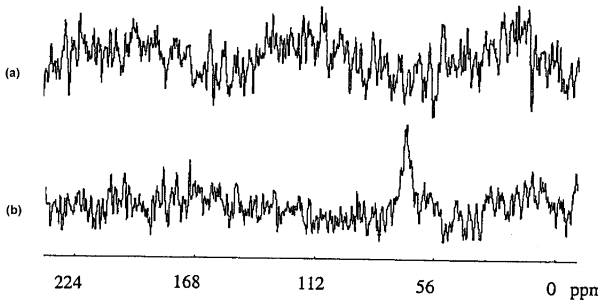

Fig. 6 ^{31}P NMR spectra of sample *G* in suspension in D_2O (a) or in D_2O + THF (b).

appears (Fig. 6). In order to be sure that this signal comes exclusively from dendrimers included in the silica, the solution is separated from the solid. No signal is detected for this solution; thus the dendrimers were not extracted by THF, and the signal really came from the dendrimers included in the silica, showing that they are accessible to THF. However, this experiment does not indicate if all the dendrimers are accessible.

To check the full accessibility of the dendrimers, we decided to use HCl. Indeed, addition of HCl in refluxing ethanol to the dendrimer alone in solution induces a breakage, detectable by ^{31}P NMR and Raman spectroscopy; the end groups are particularly sensitive to the reaction, as shown by the total disappearance of the signals associated to the end groups at 2800–3000 cm^{-1}. The same experiment was carried out with the sample *I* containing **2-Gc$_4$**; the silica meso structure was preserved as confirmed by XRD characterization. Raman spectroscopy shows the total disappearance of the signals at 2800–3000 cm^{-1}, indicating that all the end groups of all the dendrimers included in the silica are destroyed, and thus that all the molecules of dendrimer included in the silica are really accessible. On the other hand, the signals associated to the skeleton of the dendrimers (1570–1600 cm^{-1}), are still present and intense (Fig. 7).

From all theses observations, we suggest that the dendrimers are partially embedded in the silica walls, collapsing on the surface. Indeed, the size of the fourth generation

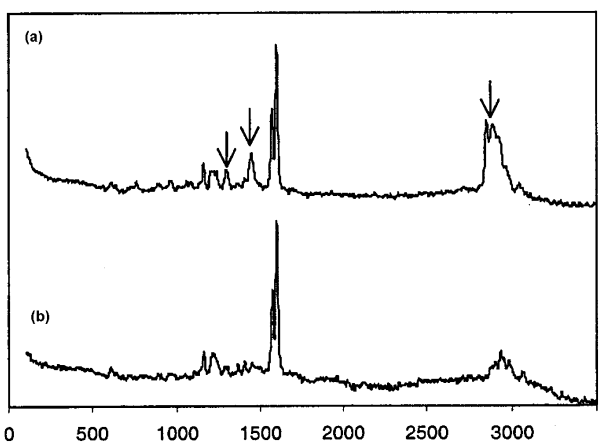

Fig. 5 FT-Raman spectra of sample *D* (a) and sample *I* (b) (obtained from *D* after extraction of CTAB, indicated by the arrows).

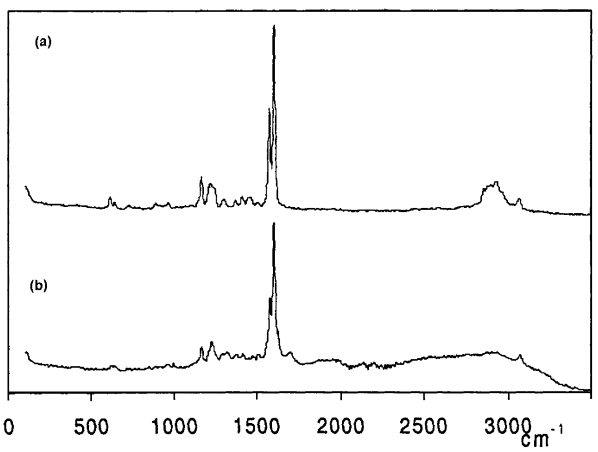

Fig. 7 FT-Raman spectra of sample *I* (a), and the same sample after reaction with HCl 1 N (b).

dendrimer is about 75 Å,[12] a value larger both than the pore diameter (25 Å) and than the wall thickness (15 Å), thus dendrimers should not be totally embedded within the walls. A collapse of our phosphorus dendrimers on the surface is proposed, as previously observed when contacting a surface.[13] This collapse was described by twenty bilayers of an alternation of positively and negatively charged fourth generation dendrimers having only a thickness of 30 nm instead of the expected 300 nm.[14]

Conclusions

The presence of phosphorus in the skeleton of the dendrimers used in this work has facilitated their unambiguous detection in the materials, in particular by elemental analyses (P/Si ratio) and by ^{31}P NMR. Using these specific techniques as well as X-ray diffraction, FT-Raman and measurements of BET specific surfaces allowed us to draw several conclusions. We have shown that relatively important amounts of polycationic phosphorus-containing dendrimers (up to 26% in weight) can be incorporated into hexagonal silica phases during the structuring process, using CTAB as surfactant. In these conditions, the inclusion of dendrimers does not modify the honeycomb structure characteristic of the MCM-41 phase, as well as its narrow pore size distribution of about 25 Å and its specific surface. These hybrid nanocomposites possess original properties, in particular the unprecedented possibility to selectively remove the surfactant while keeping the dendrimer inside the material, while noncovalently linked. Furthermore, all the dendrimers, and particularly their end groups are fully accessible. This fact is of paramount importance when considering future uses of this technique. One may think for instance to catalytically activate dendrimers partially embedded in the silica walls for a better stability and an easier recovery, while keeping a full access of the substrates to the catalytic sites, thanks to the controlled porosity.

Experimental

Dendrimers **1-G$_4$**[7] and **2-Gc$_n$**[8] were synthesized according to published methods.

General method of synthesis of silica

The procedure used is adapted from a classical procedure of synthesis of the silica phase MCM-41.[15] The molar composition of the starting mixture is $1SiO_2 : 0.21CTAB : 0.8NaOH : 100H_2O$: xdendrimer. The synthesis of the silica phase was carried out in polypropylene flasks, and the reagents were mixed using the following procedure: Cetyltrimethylammonium bromide (CTAB, 1.91 g) was solved in a sodium hydroxide solution (0.22 g of NaOH in 42 g of distilled H_2O) under stirring at 50 °C. The dendrimer was then added at the same temperature in an appropriate concentration. Then 5.05 g sodium silicate in water (29.25% SiO_2, 8.86% Na_2O, 61.88% H_2O) was added under stirring to the previous mixture to afford an opaque dispersion. After mixing, a HCl 1 N solution was introduced dropwise into the dispersion under vigorous stirring to reach a final pH of 9. The dispersion thus obtained was aged in closed vessel at 60 °C for 24 h. The obtained white solid was filtered and washed with distilled water and ethanol, and finally dried at 60 °C for 16 h.

Calcination of the samples was carried out as follows: heating for 1.5 h from 20 to 200 °C, keeping at 200 °C for 1 h, heating for 3 h from 200 to 550 °C, then keeping at 550 °C for 4 h.

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