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HOW TO CONTROL THE STRUCTURAL PROPERTIES OF PURELY SILICEOUS MCM-41

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Abstract - This work deals with the possibility of improving the structural and textural proprieties of MCM-41 only by playing with their synthesis reagents. To realize this study, three kind of silicas are chosen; colloidal silica (ludox); fumed silica and tetraethylorthosilicat (TEOS) and three kind of bases; sodium hydroxide (NaOH); tetramethylammonium hydroxide (TMAH) and tetraethylammonium hydroxide (TEAH). Each silica source is tested with three bases separately at three different temperatures 373 K, 403 K and 423 K for duration of 48 h under hydrothermal treatment. As results we noticed when the hydrothermal treatment temperature increase leads to more stable materials by increasing their wall thickness. The use of organic bases promotes the increase of specific surface area, pore sizes and volume pores of MCM-41 materials.

Résumé – Comment contrôler les propriétés structurales de MCM-41 purement silicique. Ce travail porte sur la possibilité d'améliorer les propriétés structurales et texturales de MCM-41 en seulement changeant les réactifs de synthèse. Pour réaliser cette étude, trois sources de silices ont été choisies: silice colloïdale (Ludox), fumée de la silice et tetraethylorthosilicate (TEOS) et trois sources basiques: hydroxyde de sodium (NaOH), l'hydroxyde de tétraméthylammonium (TMAH) et l'hydroxyde de tétraéthylammonium (TEAH). Chaque source de silice est testée avec les trois sources basiques prises séparément à différentes températures de synthèse (373 K, 403 K et 423 K) pendant une durée de 48 heures. Les résultats ont montré que l'augmentation de la température de synthèse conduit à une plus grande stabilité des matériaux en augmentant leur épaisseur de parois. L'utilisation de bases organiques favorise l'augmentation de la surface spécifique, la taille des pores et le volume mésoporeux des matériaux MCM-41.

1. INTRODUCTION

The last few decades have witnessed a great interest in the synthesis and development of ordered porous materials with controlable structures and systematic tailoring pore architecture. The

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structural capabilities at the scale of a few nanometres can meet the demands of the growing applications in various fields, such as adsorption, separation, catalysis, drug delivery, sensors, photonics, and nanodevices. In the early 1990s, Japanese scientists and Mobil scientists separately reported the synthesis of mesostructued silicates [1, 2]. In Mobil's report; quaternary ammonium cationic surfactants such as cetyltrimethylammonium bromide ($C_{16}H_{33}N(CH_3)_3$-Br, CTAB) were first used as templates to prepare highly ordered M41S mesoporous silicate molecular sieves under hydrothermal, basic conditions. This kind of attractive material extends the uniform pore sizes from the range of micropore to mesopore. More importantly, the concept of "template" was first postulated in the synthesis of mesoporous silicate materials [3]. The organic/inorganic self-assembly of mesoporous material is driven by weak noncovalent bonds such as hydrogen bonds, van der Waals forces, and electrovalent bonds between the surfactants and inorganic species. Instead of a simple superposition of the weak interaction, an integrated and complex synergistic reaction facilitates the process. Cooperative assembly between organic surfactants and inorganic precursors is generally involved, forming inorganic/organic mesostructured composites [3]. The main drawback of MCM-41 molecular sieve for practical applications is its rather low hydrothermal stability. The hexagonal arranged silica framework is stable when surfactant template molecules are present. However, the calcined samples, which have no templates in the pores, have very poor structural stability, especially in hot water. By contrast, the crystal structure of pure silica MCM-41 was found to be retained up to 1123 K [4] or in a 100% steam flow under atmospheric pressure at 773 K [5]. Nevertheless, the structure of MCM-41 collapses if it is placed in hot water or aqueous solution for an extended period of time. Partial substitution of Si by other atoms like Ti or Al was reported to improve the thermal and hydrothermal stability to some extent [6]. It was also reported that improved hydrothermal stability could be achieved by adjusting the gel pH several times during the hydrothermal crystallization process [7]. On the basis of the current knowledge on the art of mesoporous synthesis, the textural and structural proprieties can be controlled by playing with silica source, basis source or surfactant length, temperature, pH. Our contribution deals with the improving the structural and textural proprieties of MCM-41 only by playing around with its synthesis reagents without any other reagents which can enhance these properties.

2. EXPERIMENTAL

2.1. Synthesis of Si-MCM-41

The MCM-41 materials are prepared using a procedure developed by our group according to the molar composition described by Mokaya [8]: $1SiO_2$ 0.25CTAB 0.2MOH $40H_2O$, where M represents cations, such as tetramethylammonium (TMA^+), tetraethylammonium (TEA^+), or Na^+ that were added as hydroxides. Each source of silica (ludox, fumed and TEOS) was tested with three different bases source NaOH, TMAH or TEAH and at three different temperatures 373 K, 403 K or 423 K for 48 h under hydrothermal synthesis. Colloidal silica (Ludox, 40% Aldrich), tetraethylorthosilicate (TEOS, 97% Aldrich) and fumed silica (0007 um particle size, Aldrich), Cetyltrimethylammomiun bromide (CTAB, 98% Merck), tetramethylammonium hydroxide (TMAH, $5H_2O$, 97 % Aldrich), tetraethylammonium hydroxide (TEAH, 40% Fulka), sodium hydroxide (NaOH, 99% Prolabo) and deionized water as solvent. We started with the molar composition stœchiometrics described above. The synthesis procedure of Si-MCM-41 was reported in according the following molar composition $1SiO_2$: 0.25CTAB: 0.2base: $40H_2O$. Each silica source was tested with three bases source separately at three different crystallization temperatures for 48 h. The base sources (TMAH, TEAH or NaOH separately) was dissolved in deionised water, and then 2g cetyltrimethylammonium bromide (CTAB) was added into the suspension under

stirring. After 30 min, silica (Ludox, fumed or TEOS) was slowly added, giving rise to white slurry. The reaction mixture was continuously stirred for 1 h at room temperature. Afterwards the obtained hydrogel was transferred into a Teflon autoclave vessel for the crystallization, which lasted 48 h at (373 K, 403 K or 423 K). Thereafter, the product was washed several times with demineralised water, filtered and dried at 373 K overnight, afterwards calcined in air at 823 K for 12 h.

2.2. Characterization

The powder samples were washed, dried and heat-treated to 823 K for up to 8 h with a heat rate of 2 °C/min. Powder X-ray diffraction (XRD) patterns were carried using a Philips PW 3710 diffractometer using CuKα (wavelength = 0.15404 nm) radiation, with scanning step 0.035° 2θ between 2° and 80° 2θ.

The specific surface area was evaluated by the BET method (Brunauer- Emmet-Teller) [9] from data in the relative pressure range from 0.01 to 0.025. The mesoporous volume which characterizes the uniform pores of Si-MCM-41 was estimated by using the t-De Boer method. The relation $t(\frac{p}{p_0})$ in equation (1) was given while basing on an adsorption isotherm of macroporous silica gel for the relative pressure range from 10^{-5} to 0.995 [10]. The pore size distribution (D_{BJH}) was calculated from the adsorption branches on the isotherms using the Barret-Joyner-Halenda (BJH) method [11] in conjunction with the corrected Kelvin equation and the statistical film thickness curves derived by Kruk-Jaroniec-Sayari (KJS) [12] in equation (2). The two related equations are the following:

$$t\left(\frac{p}{p_0}\right)[nm] = 0.1\left[\left(\frac{60.65}{0.03071} - \log\left(\frac{p}{p_0}\right)\right)\right]^{0.3986} \qquad (1)$$

$$r\left(\frac{p}{p_0}\right)[nm] = 0.416\left[\log\left(\frac{p_0}{p}\right)\right]^{-1} + t\left(\frac{p}{p_0}\right) + 0.3 \qquad (2)$$

where $r(\frac{p}{p_0})$ is the pores radius, $0.416[\left(log\ \frac{p_0}{p}\right)]^{-1}$ is the Kelvin equation and 0.3 is the corrective term [12]. The pore diameter (D_{DRX}) was calculated by a geometrical method [13] by supposing that the MCM-41 exhibits a hexagonal arrangement of cylindrical pores. The pore diameter is given by:

$$D_{DRX} = C.d_{100}\sqrt{\frac{\rho.V_{meso}}{1+\rho.V_{meso}}} \qquad (3)$$

where V_{meso} is mesoporous volume, ρ is density of the pores walls (2.2 cm^3/g for silica materials) [13, 14], d_{100} is interplanar spacing and C is a constant depending on the pore geometry ($C = 1.213$ for a geometry cylindrical [2]).

Finally, the wall thickness (bp) was estimated from following relation [14]:

$$b_p = a_0 - D_{DRX} \qquad (4)$$

where a_0 is the unit cell given by:

$$a_0 = \frac{2}{\sqrt{3}}d_{100} \qquad (5)$$

3. RESULTS AND DISCUSSIONS

3.1. Colloidal silicate combined with different base sources and temperatures

The XRD pattern of calcined samples of the Si-MCM-41 synthesised by using colloidal silicate with NaOH at 373 K, 403 K and 423 K *(figure 1a)* allowed identification of the peak relative to (100) plane corresponding to an hexagonal structure with symmetry P6mm, which are typical of a MCM-41 product. The absence of the weak reflection relative to (110), (200) and (210) planes indicates that the product is less organized; even the width of the main reflection (100) confirms the result found.

While the XRD pattern of calcined samples of the Si-MCM-41 synthesised by using colloidal silicate with TEAH at 373 K, 403 K and 423 K *(figure 1b)* is better crystallized compared to that one from NaOH as base. The width of the main reflection (100) relative to Si-MCM 41 by using TEAH is smaller than that one from NaOH and the appearance of new reflection (110) confirms the restructuring of the material. Unlike the materials synthesized using NaOH, Si-MCM-41 synthesized by using TEAH presents a structural evolution vs temperature. The XRD patterns of Si-MCM-41 synthesized by using TMAH as base at 373 K, 403 K and 423 K *(figure 1c)* present large structuring improvement compared to TEAH and NaOH. There is appearance of the weak reflection (110) and (200) which indicates an improvement of the long-ranged ordered of Si-MCM-41. Compared Si-MCM-41 synthesized using TMAH at different temperatures; we note that the temperature affects the crystallinity. At 403 K and 423 K, the obtained materials show the appearance of the peaks (110) and (200). The temperature acts by evaporation of water which leads to promote the formation of siloxane bridges (i) and (ii).

$$\equiv\text{Si-OH} + \equiv\text{Si-OH} \rightleftharpoons \equiv\text{Si-O-Si}\equiv + H_2O \qquad \text{(i)}$$

$$\equiv SiO^- + HO\text{–}SiO \equiv \rightleftharpoons \equiv \text{Si-O-Si} \equiv + OH^- \qquad \text{(ii)}$$

TMAH and TEAH are found to be the most effective auxiliary templates to improve the long-range ordered of the molecular sieves, when tetraalkylammine ion is added the wall thickness decreases with a decrease of tetraalkylammine length or with decrease of its hydrophobic chain. It is found that alkylamine takes part in templating mesostructures as co-structurant. Unlike to Lee et al. [15] results, where they found that if alkylamine incorporates into micelles together with CTAB, micelle contrast by small surfactant and consequently resulting mesostructures will contain smaller mesopores, we found also when small alkylamine is used the wall thickness of mesoporous materials decrease and the pore sizes increase. We note as also that the silonate groups of surface are constant when hydrocarbon length chain of co-structurant changes. The interaction decreases for low hydrocarbon chain in tail of co-structurant because cohesion energy between head groups of surfactant and counter-ion decreases and the charge density of surface decreases. TMAH and TEAH play role as dispersant of silicate entities and reduce the silonate groups (ii). TMAH leads to more uniform silica species than TEAH.

The evolution of the unit cell for the Si-MCM from colloidal and NaOH *(table I)* varies from 4.42 nm at 373 K to reach its maxima 4.49 nm at 403 K and decrease to 4.21 nm at 423 K. The same evolution is noted for the wall thickness. Unlike to unit cell and wall thickness evolution, the specific surface area decrease from 981 m^2/g at 373 K then 840 m^2/g at 403 K to 795 m^2/g at 423 K. The last results seem better than found when TEAH is applied as base source but it is still weak to that one found when TMAH is applied. Referring to N_2-sorption for samples synthesized from NaOH at different temperatures present type IV according to IUPAC classification [16] with the same reflection point which reflects the same pore sizes centred at 3.33 nm. Contrary to these results, the pore sizes of the same materials calculated from geometrical method *(3)* exhibit a

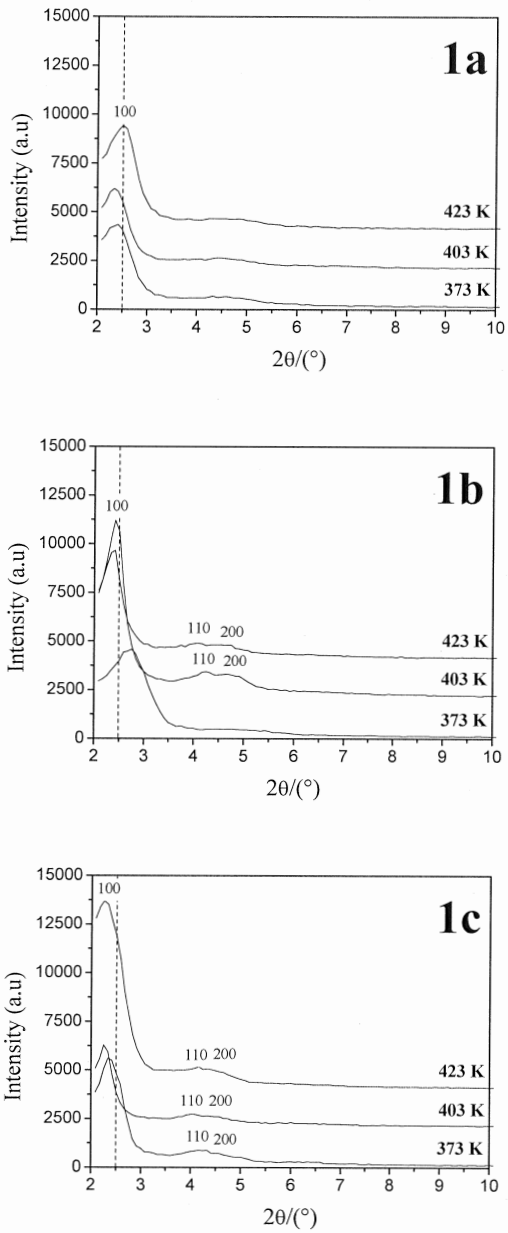


Figure 1. XRD diffraction samples of Si-MCM-41 synthesized with colloidal silicate combined with different base sources and temperatures: 1a (NaOH); 1b (TEAH); 1c (TMAH).

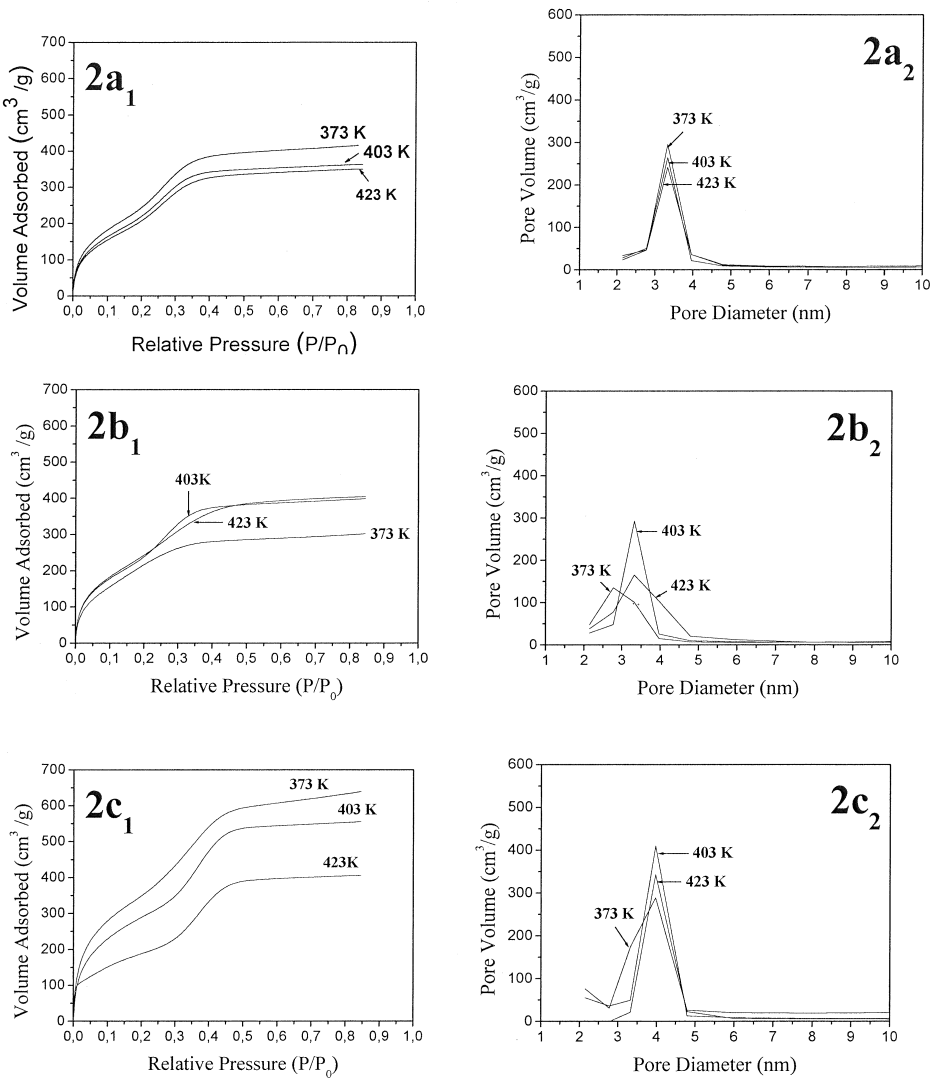


Figure 2. Adsorption isotherms (index 1) and pores size distribution (index 2) samples of Si-MCM-41 synthesized with colloidal silicate combined with different base sources and temperatures: 2a (NaOH); 2b (TEAH); 2c (TMAH).

difference, where we note a decrease of the pore sizes when the temperature increase *(table I)* this difference is still not important and BJH model cannot be applied because the pore size of these materials is in the range of mesoporous (Although Das et al., [17] argued their results basing on the BJH method). The BJH model is not taken in consideration; it is used just to have an idea about the pore distribution. Though that TEAH presents great physical results such as unit cell, specific surface area and pore sizes. Despite these results, TMAH is not appropriate to be used as a base

with colloidal silica using the chemical composition proposed by Mokaya [8] referring to N_2-sorption Si-MCM-41(colloidal + TEAH) at 373 K exhibit a mixture between type I and type IV. On the other hand all isotherms of Si-MCM (colloidal + TMAH) are types IV according to IUPAC classification [16], we note a slight difference between the pore size calculated from geometrical formulae *(3)* and by using BJH model basing on adsorption branch.

Table I. Results of the XRD and N_2-sorption at 77 K of samples synthesized with colloidal silicate.

Basic source	Temperature (K)	a_0 (nm)	S_{BET} (m^2g^{-1})	V_{meso} (cm^3g^{-1})	D_{DRX} (nm)	D_{BJH} (nm)	b_p (nm)	Isoterm type
NaOH	373	4.42	918	0.55	3.43	3.33	0.99	IV
	403	4.49	840	0.50	3.42	3.33	1.07	IV
	423	4.21	795	0.49	3.18	3.33	1.03	IV
TEAOH	373	3.89	975	0.40	2.80	2.70	1.09	I+IV
	403	4.34	900	0.55	3.38	3.33	0.96	IV
	423	4.44	822	0.56	3.47	3.33	0.97	I+IV
TMAOH	373	4.48	1274	0.82	3.77	4.00	0.71	IV
	403	4.65	1075	0.80	3.90	4.00	0.75	IV
	423	4.69	826	0.58	3.61	4.00	1.08	IV

As a short conclusion of this part, basing on the results obtained from XRD and N_2-sorption, the higher specific surface area and pore volume of the final product are obtained when TMAH at different temperatures is used. The wall thickness shown an improvement, when NaOH and TEAH are used. Nevertheless the specific surface area and pore size are still important.

3.2. Fumed silica combined with different base sources and temperatures

The XRD pattern of calcined samples of the Si-MCM-41 synthesised by using fumed silica with NaOH at 373 K, 403 K and 423 K *(figure 2a)* allowed identification of the peak relative to (100) plane corresponding to an hexagonal structure with symmetry P6mm, which are typical of MCM-41 product at both temperatures 403 K and 423 K. The existence of a bump between 3-4° 2θ represents an overlap of the two peaks relative to (110) and (200). That can be attributed either to the experimental conditions or to the width of the lenses used for the measurement or even to slight disorder at long-rang. At 373 K the MCM structure is very disordered referring to the broad peak (100) which characterizes the hexagonal structure.

Figure 2b presents the XRD pattern of calcined samples of the Si-MCM-41 synthesised by using fumed silica with TEAH at 373 K, 403 K and 423 K. We note an enhancement in crystallinity of sample synthesized at 373 K. The main peak (100) corresponding to hexagonal structure is well defined and the appearance of the weak peaks (110) and (200) confirms the restructuring of the material and an improvement of the long-rang ordered of Si-MCM-41. At 403 K we note a slight decrease in crystallinity and disappearance of the weak peaks (110) and (200). This disappearance can be attributed to a decrease in crystallinity of the materials at that temperature promotes the creation of silonate groups in the medium. Badiei et al., (2008) [18] found that when the silonate groups decrease, the best hexagonal structure is obtained. At 423 K we noted a drastically decrease in crystallinity and the main peak (100) becomes broad. The hexagonal structure is lost.

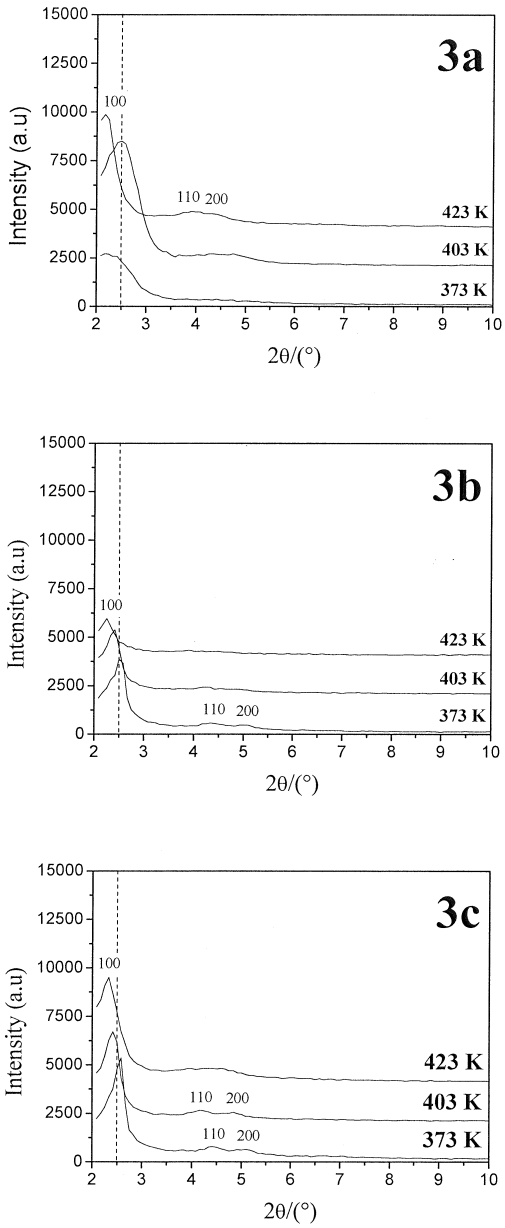
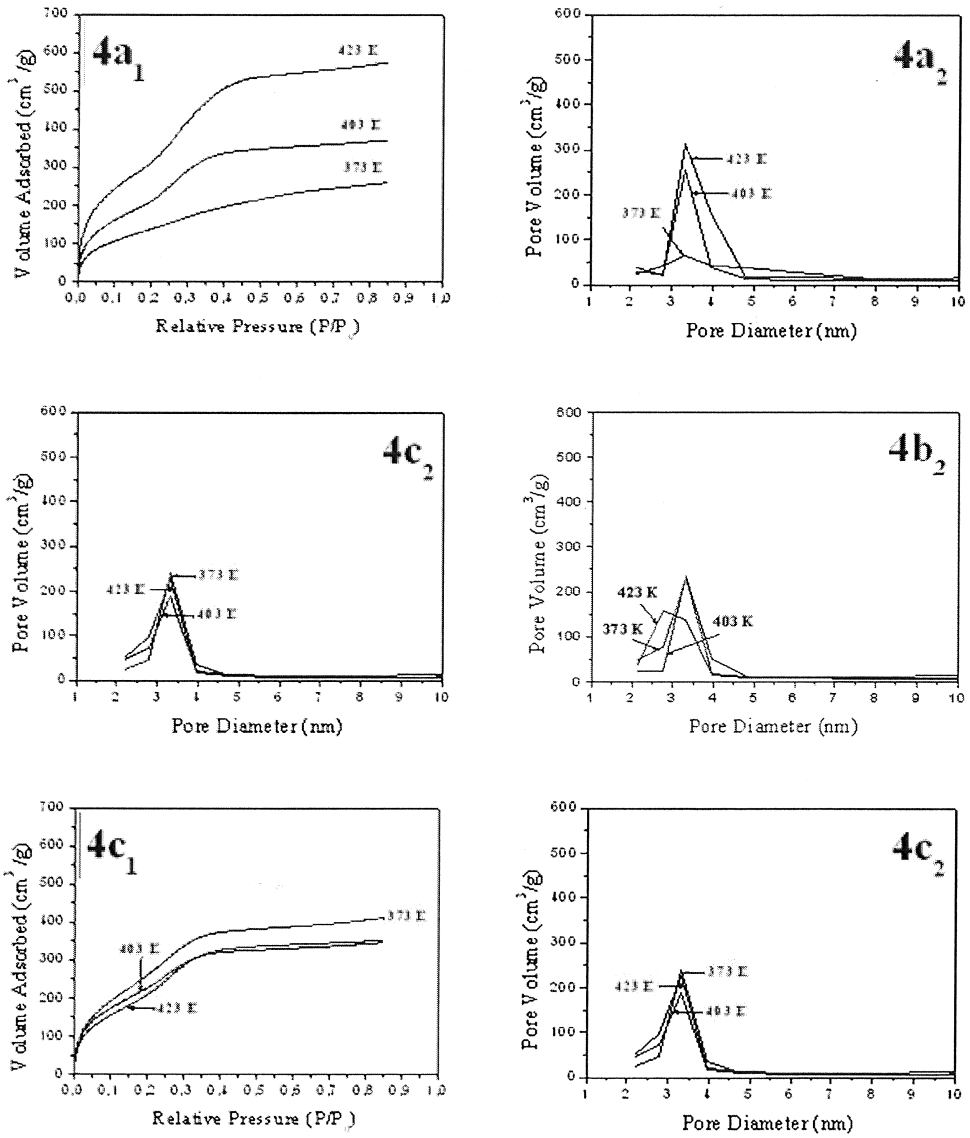


Figure 3. XRD diffraction samples of Si-MCM-41 synthesized with fumed silica combined with different base sources and temperatures: 3a (NaOH); 3b (TEAH); 3c (TMAH).



Figue 4. Adsorption isotherms (index 1) and pores size distribution (index 2) samples of Si-MCM-41 sythesized with fumed silica combined with different base sources and temperatures: 4a (NaOH); 4b (TEAH); 4c (TMAH).

The XRD patterns of Si-MCM-41 synthesized by using TMAH as base at 373 K, 403 K and 423 K *(figure 2c)* present an regular increase of the crystallinity with the increase of temperature. The appearance of the weak peaks (110) and (200) indicate the improvement of the long-ordered materials. The unit cell increase from 4.14 nm at 373 K, 4.37 nm at 403 K to 4.58 nm at 423 K.

Basing on N_2-sorption for samples synthesized from fumed silica and different base sources at different temperatures and combined with XRD results the samples synthesized from NaOH at different temperatures present type IV only for both temperatures 373 K and 403 K. At 373 K the isotherm is more type I than type IV according to IUPAC classification. The specific surface area of samples decreases with the increase of temperature. That can be also deduced from the width of the main peak which characterizes the hexagonal phase of the samples. The geometrical formulae *(3)* is used to calculate the average pore size, difference is noticed. This difference is missed when BJH model is applied. In all samples synthesised from fumed silica with different base sources at different temperatures. It is noted also an increase of the pore sizes when the temperature increase *(table II)*. Contrary to the evolution noticed when colloidal silica with different base sources is used.

Table II. Results of the XRD and N_2-sorption at 77 K of samples synthesized with fumed silica.

Basic source	Temperature (K)	a_o (nm)	S_{BET} (m^2g^{-1})	V_{meso} (cm^3g^{-1})	D_{DRX} (nm)	D_{BJH} (nm)	b_p (nm)	Isotherm type
NaOH	373	-	544	0.28	-	-	-	IV
	403	4.25	770	0.47	3.18	3.33	1.07	IV
	423	4.88	1009	0.73	4.03	3.33	0.85	IV
TEAOH	373	4.18	950	0.47	3.13	3.33	1.05	IV
	403	4.41	845	0.48	3.32	3.33	1.09	IV
	423	4.71	719	0.47	3.53	-	1.08	I+IV
TMAOH	373	4.14	1044	0.51	3.16	3.33	0.98	IV
	403	4.37	874	0.44	3.22	3.33	1.15	IV
	423	4.58	868	0.49	3.46	3.33	1.12	IV

As conclusion of this part, when NaOH is used at 373 K the MCM-41 is not obtained referring to N_2-sorption and XRD results. The MCM is obtained is obtained at 403 K and 423 K with higher specific surface area and wall thickness. Nevertheless the pore volume at 403 K is weak ca. 0.47 cm^3/g compared to that one obtained at 423 K which is around 0.73 cm^3/g. TMAH and TEAH showed an important enhancement either concerning specific surface area, pore size or even wall thickness. The better results are attributed to TMAH.

3.3. Tetraethylorthosilicate combined with different base source and temperature

The XRD pattern of calcined samples of the Si-MCM-41 synthesised by using Tetraethylorthosilicate as silica source with NaOH at 373 K, 403 K and 423 K *(figure 3a)* showed a typical reflection relative to (100) plane of hexagonal mesoporous structure with symmetry P6mm at both temperatures 403 K and 423 K. The XRD pattern of calcined Si-MCM-41 at 403 K presents a bump between 3-4° 2θ corresponding to an overlap of (110) and (200) reflection. It is noticed that the unit cell increases with the increase of the temperature and even the average pore size calculated by the geometrical formula *(3)* increases *(table III)*. This increase is not raised in the case of the wall thickness. The important wall thickness around 1.02 nm is attributed to the sample synthesized at 423 K, where at the same temperature the pore volume decreases dramatically to reach 0.59 cm^3/g. The inverse result was noticed at 403 K, where the biggest pore volume is obtained ca. 0.96

cm^3/g compared to its wall thickness ca. 0.60 nm. This can be explained by the polymerization of the silica preference, in this case we assume that the micelle rods, interact with silicate species to form several monolayer of silica on the outer surface of the micelles, followed by a spontaneously assembled to produce the hexagonal MCM-41.

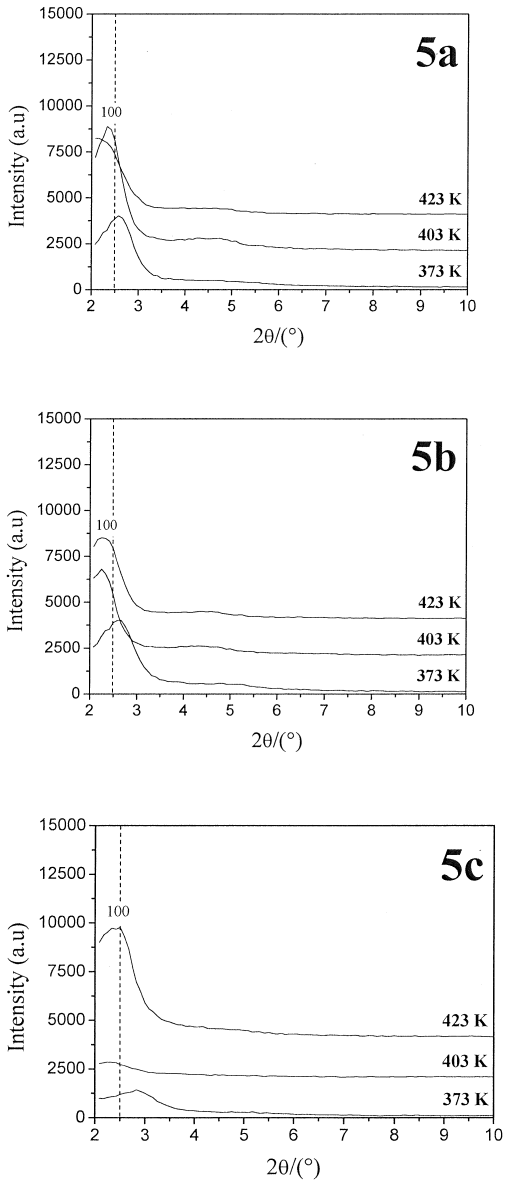


Figure 5. XRD diffraction samples of Si-MCM-41 synthesized with tetraethylorthosilicate combined with different base sources and temperatures: 5a (NaOH); 5b (TEAH); 5c (TMAH).

Figure 5b presents a XRD pattern of Si-MCM-41 synthesized from Tetraethylorthosilicate as silica source with TEAH as base source. The XRD showed a broad peak between 2° and 3° 2θ corresponding to (100) reflection and the absence of the weak peaks corresponding to (110) and (200) confirms the disorder in the long-rang of Si.MCM-41 synthesized at 373 K. At least the MCM-41 structure is obtained. The XRD of sample synthesized at 403 K presents an enhancement of the crystallinity.

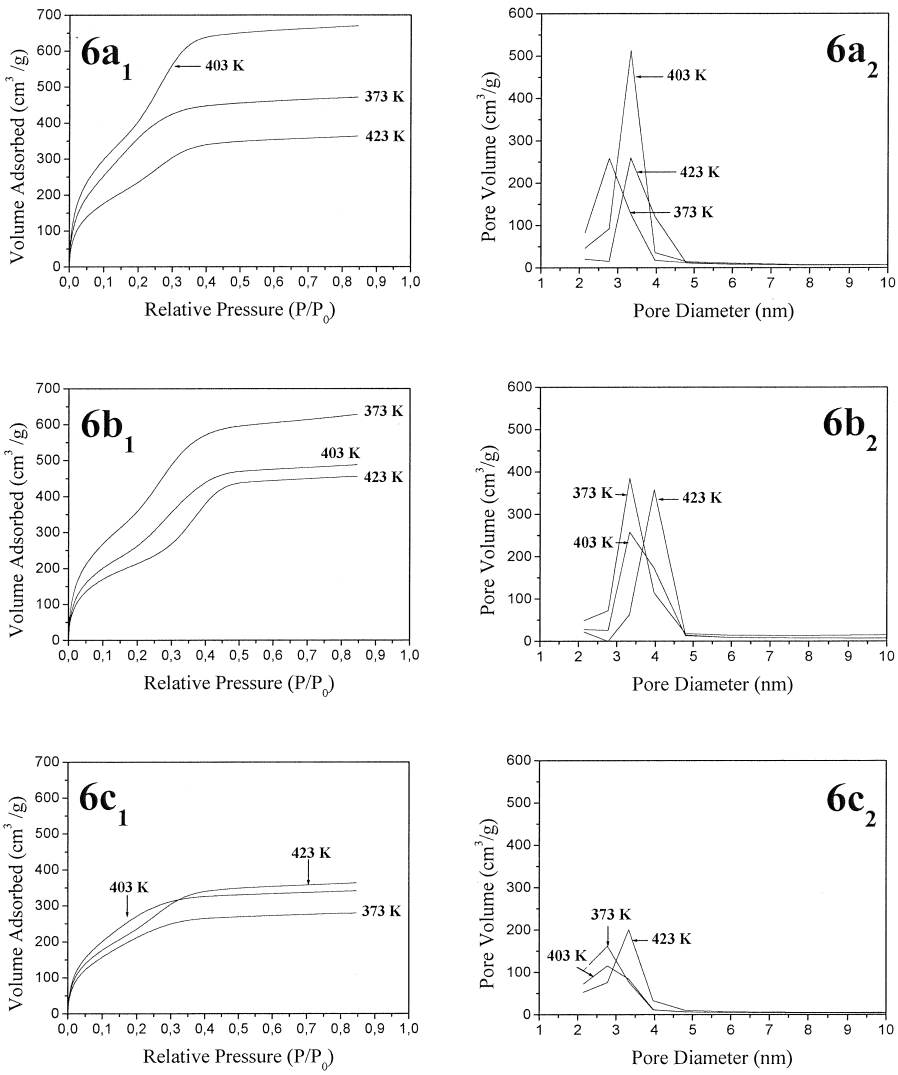


Figure 6. Adsorption isotherms (index 1) and pores size distribution (index 2) samples of Si-MCM-41 synthesized with tetraethlorthoilicate combined with different base sources and temperatures: 6a (NaOH); 6b (TEAH); 6c (TMAH).

The main peak which characterizes the hexagonal structure become narrow compared to that obtained at either 373 K or 423 K, we noticed a shift towards small 2θ. This shift is accompanied with an increase in the unit cell of the sample which reach 4.70 nm and in the pore size and even in the wall thickness around 0.87 nm. At 423 K a slight shift towards a high 2θ is noticed. Consequently the unit cell will slightly decrease to 4.63 nm accompanied by slight decrease of pore volume. On the other hand the wall thickness increases to 0.91 nm.

XRD patterns of Si-MCM-41 synthesized by using tetraethylorthosilicate as silica source with TMAH as base source at different temperatures are presented in *figure 3c*. The Hexagonal structure which characterizes the Si MCM-41 is not obtained for both temperatures 373 K and 403K, referring to the large width of both main peaks (100) of Si-MCM-41 synthesized at both temperatures 373 K and 403 K. At 423 K, referring to its XRD pattern, the main peak of Si-MCM-41 is obtained and we noticed an improvement of the crystallinity and the hexagonal structure is obtained.

According to N_2 adsorption-desorption for samples synthesized from tetraethylorthosilicate and different base sources at different temperatures and combined with XRD results the samples synthesized from NaOH at different temperatures present type IV for both temperatures 373 K and 403 K except for the sample synthesized from NaOH at 373 K the isotherm is type I according to IUPAC classification [16]. The specific surface area of samples decreases with the increase of temperature *(table. III)*. At 403 K the specific surface area is ca.1589 m^2/g.

Table III. Results of the XRD and N_2-sorption at 77 K of samples synthesized with tetraethylorthosilicate.

Basic source	Temperature (K)	a_o (nm)	S_{BET} (m^2g^{-1})	V_{meso} (cm^3g^{-1})	D_{DRX} (nm)	D_{BJH} (nm)	b_p (nm)	Isotherm type
	373	4.08	1282	0.67	3.31	2.70	0.77	I
NaOH	403	4.47	1589	0.96	3.87	3.33	0.60	IV
	423	5.02	834	0.59	4.00	3.33	1.02	IV
	373	4.06	1367	0.84	3.43	3.32	0.63	IV
TEAOH	403	4.70	966	0.69	3.83	-	0.87	IV
	423	4.63	774	0.64	3.72	4.00	0.91	IV
TMAOH	423	4.40	921	0.51	3.36	3.33	1.04	IV

As conclusion of this part, we not that when TMAH is used no results are obtained either at 373 K or at 403 K. MCM-41 is obtained at 423 K with high wall thickness. NaOH and TEAH displayed great results at different temperature, excepted at 373 K for NaOH where the structure is lost.

Thanabodeekij et al. [19], found that when electrical repulsion between ionic heads decreases, thus resulting in a decrease in CMC of CTAB. They found at high ionic concentrations charge repulsion occurs, inhibiting the hexagonal array to form else. Consequently, when the electrical repulsion between ionic heads decreases either by using a weak electrolyte or even a weak concentration of strong one the specific surface area increase because of the liquid crystal in the solution containing a weak electrolyte or even a weak concentration of strong one is more compact than that which contain strong one or high concentration of the weak one. This result is also obtained when low crystallization temperature is used. The increase of thermal treatment led to the increase of the charge repulsions. Lee et al. [15], found a tendency of decrease in pore-to-pore distance is noticed with increasing hydrophobicity of alkylamine. They suggested that alkylamine

which is smaller than the CTAB takes part in templating mesostructure as a cosurfactant. They assumed if the alkylamine incorporates into micelles together with CTAB, micelles will contract by small surfactants and consequently resulting mesostructure will contain smaller. Das et al. [17], found that during the formation of the surfactant–silicate mesostructure, the electrostatic interaction between the cationic surfactant micelles and the surrounding silicate anions is altered by the presence of the additional cations. Referring to the ^{29}Si MAS NMR results of the samples prepared with and without TPA^+. They found that the Q_4/Q_3 ratio in the as-synthesized samples was much higher for that prepared in the presence of TPA^+. The higher Q_4/Q_3 ratio indicates that there is increased condensation between the silanol groups during the formation of the mesostructure. They suggested that MCM-41 type mesoporous materials with a high degree of hydrothermal stability can be directly obtained without tedious pH adjustment steps by adding additional cations in the synthesis gel. Although the exact roles of these additional cations are still not clear, their presence seems to facilitate increased condensation of the silanol groups during the formation of the mesostructure. The highly condensed silica wall is considered to have better structural stability under hydrothermal treatment conditions.

4. CONCLUSION

The structural and textural properties of pure Si-MCM-41 can be controlled just by their main reagents without need to add other reagents. The knowledge of the reactivity of each reagent towards the other reagents and depending of the property wanted, the silica source, base source and the crystallization temperature are chosen. Despite the low basicity of organic bases like TMAH and TEAH, the interesting results are obtained. The organic bases like TMAH and TEAH play two roles in the synthesis of nanomaterials, as dispersant of ionic silicate and co-structurant. The sodium hydroxide gives better results when tetraethylorthosilicat (TEOS) is used. The wall thickness could be very important if it is derived from pore size calculated from BJH.

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