Synthesis and Characterization of Porous Clay Heterostructures

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Porous clay heterostructures (PCH) based on modified montmorillonite were synthesized using different reaction conditions (different hydration degrees, pH values and reaction times). The PCH precursors and PCH were characterized using FTIR Spectroscopy and X-Ray Diffractions (XRD). The XRD results showed that basal distance of porous clay heterostructures was significantly influenced by the modified montmorillonite hydration degree and also by pH value of the reaction medium. Low reaction times ensure the synthesis of PCH characterized by high basal distance.

Keywords: Porous Clay Heterostructures, Hexadecyltrimethylammonium Bromide, Montmorillonite, Co-surfactant

Porous clay heterostructures (PCH) are a new class of porous materials characterized by excellent properties like high surface area and porosity, high thermal stability, surface acidity, mechanical strength and adsorption capacity of volatile organic compounds (VOCs) [1-6].

The first PCH based on cationic layered silicates was discovered by Galarneau and co-workers in 1995 [7].

The advantageous properties and combined micro and mesoporous structure of PCHs recommend these materials in a wide range of applications like heterogeneous catalysts, molecular sieves, adsorbents, decontamination agents and encapsulation agents [8-11].

The synthesis of PCH materials involves three main components as follows: a cationic layered silicate (fluorohectorite, vermiculite, laponite, montmorillonite, magadiite and saponite) modified with a surfactant (hexadecyltrimethylammonium bromide), a silica precursor (tetraethylorthosilicate) and a neutral co-surfactant (primary, secondary or tertiary amines) [12, 13]. Using these raw materials the PCH synthesis involves a cationic exchange reaction, a hydrolysis and polycondensation reaction of silica precursor within the modified layered silicates, in the presence of a co-surfactant and finally a thermal treatment (calcination process) [14-15].

The properties of the final product are significantly influenced by the synthesis conditions which include the ratio between raw materials (surfactant: silica precursor: co-surfactant), cationic layered silicate type, cationic exchange capacity of clay and thermal treatment condition.

In the present work we have studied the influence of several factors (montmorillonite hydration degree, reaction time, *p*H value of reaction medium, surfactant concentration) on the PCH synthesis. The porous materials were characterized using FTIR Spectroscopy and X-Ray Diffraction (XRD).

Experimental part

Raw Materials

Nanofil 116, a natural montmorillonite (**MMT-Na**) with a cationic exchange capacity (CEC) of 116 mEq/100 g clay was supplied from Southern Clay Products.

Hexadecyltrimethylammonium bromide (**HDTMA**), tetraethyl orthosilicate (**TEOS**) and dodecylamine (**DDA**) were supplied from Sigma and used as received. The chemical structures of the raw materials are shown in figure 1.

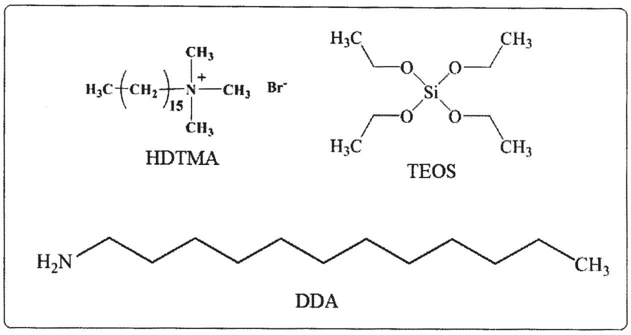

Fig.1. Chemical structures of raw materials

Synthesis of Porous Clay Heterostructures (PCH)

The PCH was synthesized using a modified method described in literature [16]. The PCH synthesis method includes a first step focused on the montmorillonite organophilization and a second step for mesoporous silica generation between the silicate layers.

Organophilization of MMT with HDTMA

The MMT-Na organophilization step was done using a cationic exchange reaction according to the figure 2.

Briefly, in a round bottom flask, 10 g of MMT were swelled in 900 ml deionized water for 1 h at 50°C under mechanically stirring. After the montmorillonite swelling

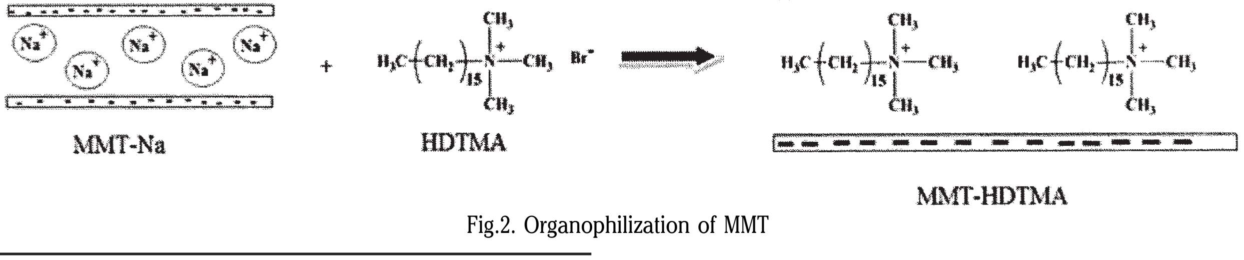

Fig.2. Organophilization of MMT

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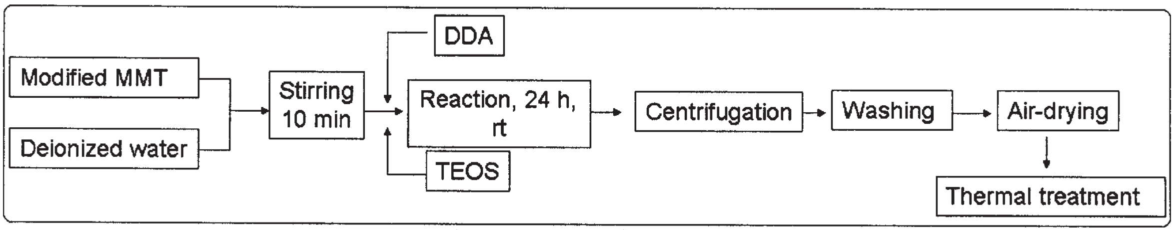

Fig.3. PCH synthesis steps

step a precise amount of organic cation (HDTMA) was added. The presence of HDTMA leads to a cationic exchange reaction between sodium cations from the clay gallery and organic cation. The final suspension was maintained for 5 h at 50°C. After the cationic exchange reaction the modified clay was filtered and washed with water. The modified MMT was air dried for 24 h.

According to the procedure previously described different HDTMA amounts (0.25; 0.5; 1; 2; 3; 4; 5; 6 g) were used in the cationic exchange reaction in order to identify the optimal concentration of modifier agent. The modified clays were abbreviated as follows: MMT-HDTMA-0.25, MMT-HDTMA-0.5, MMT-HDTMA-1, MMT-HDTMA-2, MMT-HDTMA-3, MMT-HDTMA-4, MMT-HDTMA-5, MMT-HDTMA-6.

Synthesis of PCH

The modified MMT which exhibits the highest basal distance was further used for PCH synthesis according to the strategy schematically presented in figure 3.

Using this strategy for PCH synthesis we aimed to study the influence of several factors (MMT hydration degree, reaction time, pH value) that could have a strong influence on the PCH properties.

The influence of MMT-HDTMA hydration degree

For this study 0.5 g of air-dried modified MMT (MMT-HDTMA-6) were hydrated using different water amounts (200μL, 400μL, 1mL, 2mL, 5mL) and then the co-surfactant (DDA) was added under stirring for 10 min In the next step the silica precursor (TEOS) was slowly added and the reaction was maintained for 24 h under stirring. In the final step the reaction product was washed with 15 mL of ethanol and air-dried. After drying the PCH was subject to a thermal treatment (calcination) at 650°C for 11h with a heating rate of 1°C/min in order to remove the organic fractions. The PCH synthesis involved the using of a 1:20:120 molar ratio between MMT-HDTMA: DDA: TEOS.

The samples were abbreviated as PCH-1w-n, PCH-2w-n, PCH-3w-n, PCH-4w-n, PCH-5w-n (for non-calcinated samples) and PCH-1w-c, PCH-2w-c, PCH-3w-c, PCH-4w-c, PCH-5w-c.

The influence of reaction time

The PCH synthesis was performed using similar steps previously presented with the reaction times variation (1h, 3h, 5h, 22h, 67h). For this study the PCH synthesis was done using a modified MMT (MMT-HDTMA-6) hydrated with 5 mL of water. The samples were abbreviated as PCH-1h-n, PCH-3h-n, PCH-5h-n, PCH-22h-n, PCH-67h-n (for samples before thermal treatment) and PCH-1h-c, PCH-3h-c, PCH-5h-c, PCH-22h-c, PCH-67h-c (for samples after thermal treatment).

The influence of pH value

Similar PCH synthesis steps were followed using a reaction medium with different *p*H values (*p*H=1, 2, 3, 4, 7, 8, 9). For this study we used a MMT-HDTMA hydrated with 2 mL of water and a reaction time of 5 h.

The samples were abbreviated as PCH-pH1-n, PCH-pH2-n, PCH-pH3-n, PCH-pH4-n, PCH-pH7-n, PCH-pH8-n, PCH-pH9-n (for samples before thermal treatment) and PCH-pH1-c, PCH-pH2-c, PCH-pH3-c, PCH-pH4-c, PCH-pH7-c, PCH-pH8-c, PCH-pH9-c (for samples after thermal treatment).

Characterization Techniques

X-Ray Diffraction (XRD) analysis was performed on a X'Pert PRO MPD Panalytical equipment.

FTIR spectra were recorded on a Bruker VERTEX 70 spectrometer using 32 scans with a 4 cm^{-1} resolution.

Results and discussions

The PCH synthesis was performed varying the reaction parameters (HDTMA amount used for MMT organophilization, MMT-HDTMA hydration degree, reaction time and *p*H value) in order to identify the optimal reaction conditions. The reaction products were characterized using FTIR Spectroscopy and XRD analysis.

The influence of HDTMA concentration used for MMT organophilization

FTIR Analysis

FTIR Spectroscopy analysis is recognized as a suitable technique used in order to study the interactions of layered silicates with different surfactants or to evaluate the molecular conformation of the modifier agent in the clay gallery. This analysis was also used for studying the structural change in the synthesis of porous clay heterostructures or other mesoporous materials [12, 17, 18].

The modified clays (MMT-HDTMA) with different amounts of HDTMA were firstly characterized by FTIR Spectroscopy to identify if some interactions occurred between organic-inorganic components involved in the cationic exchange reaction (fig. 4).

As one may observe the FTIR spectra of modified MMT showed some new peaks at 3017 cm^{-1}, 2917 cm^{-1}, 2849 cm^{-1} and 721 cm^{-1}. These peaks were assigned as follows: 3017 cm^{-1} corresponding to C-H stretching vibrations involved in CH_3-N; 2917 cm^{-1} and 2849 cm^{-1} correspond to C-H asymmetric and symmetric vibrations and 721 cm^{-1} was assigned to C-H bending vibration.

The appearance of peaks at 3017 and 721 cm^{-1} in the FTIR spectra of modified MMT was found to be dependent on the HDTMA concentration used. These two peaks were detected only for the montmorillonites treated with higher HDTMA amounts (1-6 g).

The FTIR analysis results highlighted an increase of peak intensity corresponding to the C-H bending vibrations for modified montmorillonite with high HDTMA amounts. The changing of this peak position (from 1482 to1470 cm^{-1}) indicates the presence of additional interactions (like hydrophobic interactions) in case of montmorillonites modified with different HDTMA concentration.

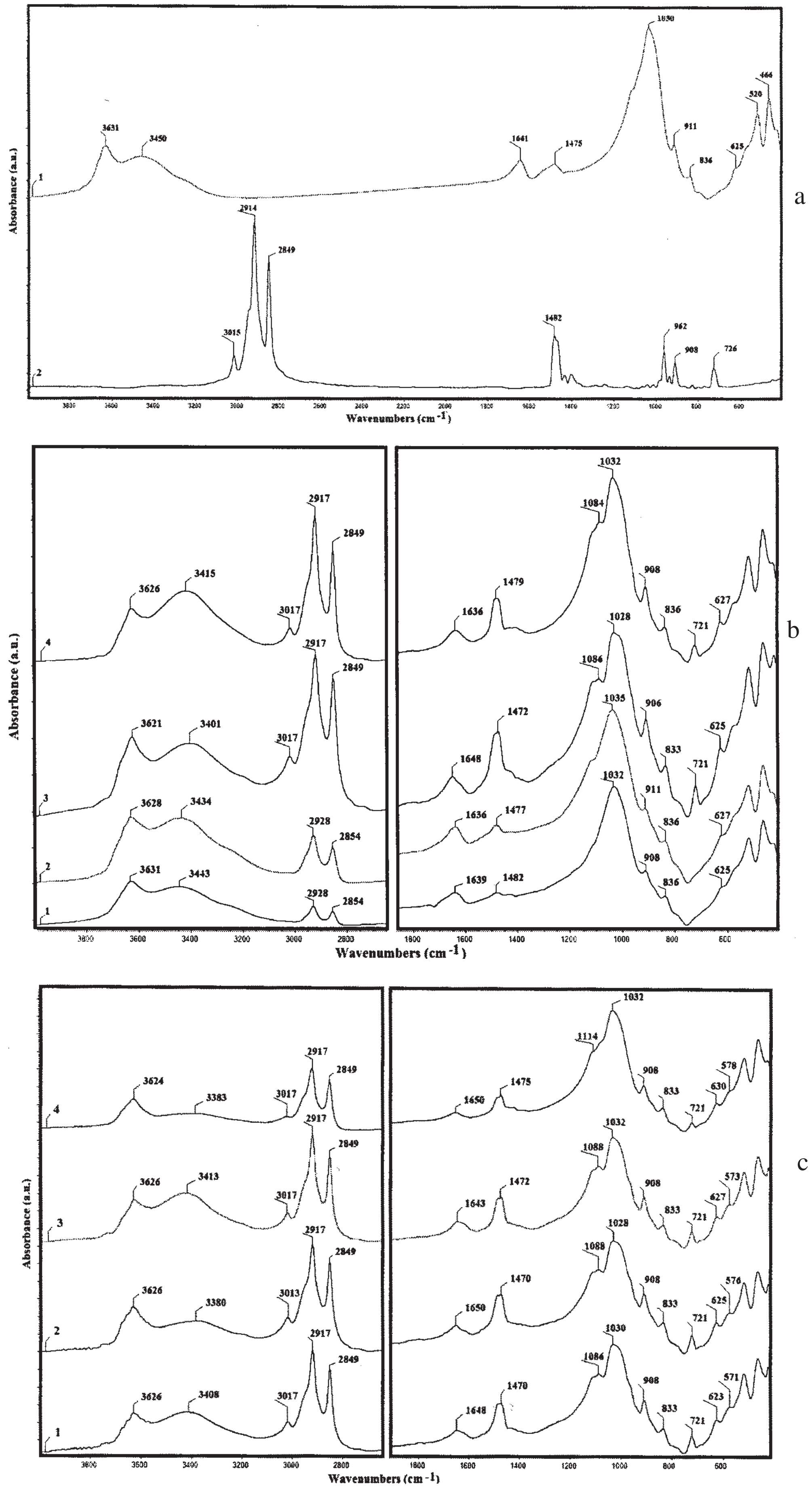

Fig. 4. FTIR spectra of a: 1-MMT-Na, 2-HDTMA; b: 1-MMT-HDTMA-0.25, 2- MMT-HDTMA-0.5, 3- MMT-HDTMA-1; 4- MMT-HDTMA-2; c: 1-MMT-HDTMA-3, 2-MMT-HDTMA-4, 3-MMT-HDTMA-5, 4-MMT-HDTMA-6

In addition the FTIR analysis was usefull for assessing the chain conformational changes [18]. Only for modified MMT with lower HDTMA amounts (0.25 and 0.5 g) a small change of asymmetric and symmetric CH_2 stretching absorption bands position was recorded. Similar results were obtained by Hongping and co-workers for a HDTMA modified montmorillonite which exhibits a lower cationic exchange capacity (57.9 meq/100 g) than in our case. He Hongping and co-workers demonstrate by FTIR spectroscopy that intercalated HDTMA within activated montmorillonite with Na_2CO_3 adopts an ordered conformation for higher HDTMA concentrations [18].

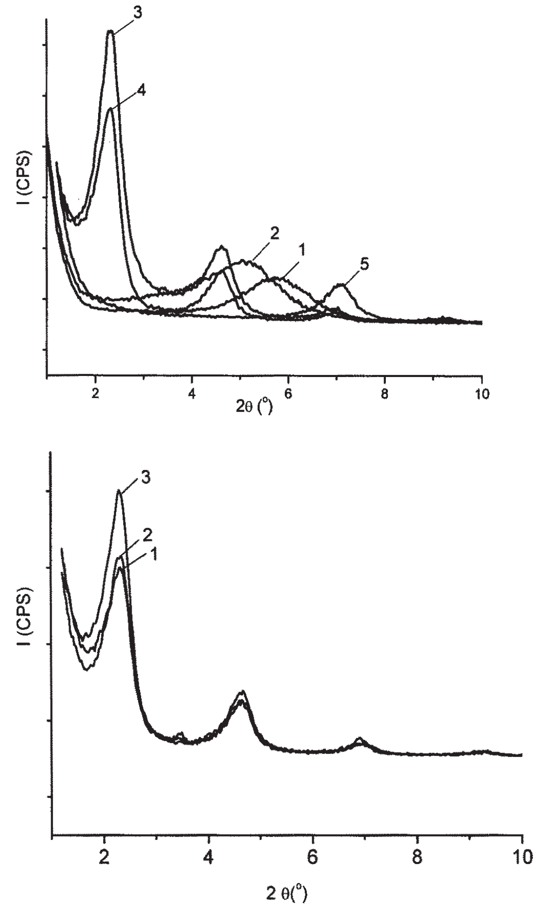

Fig. 5. XRD curves of a: 1-MMT-HDTMA-0.25, 2-MMT-HDTMA-0.5, 3-MMT-HDTMA-1; 4-MMT-HDTMA-2; 5-MMT-Na and b: 1-MMT-HDTMA-3, 2-MMT-HDTMA-4, 3-MMT-HDTMA-5

XRD Analysis

The influence of HDTMA concentration on the cationic exchange reaction was also highlighted by XRD analysis (table 1). The XRD curves of unmodified and modified MMT (MMT-HDTMA) with various HDTMA amounts are shown in figure 5-a, b.

As one may observe from figure 5-a, b and table 1, the HDTMA concentration used for MMT organophylization significantly influenced the basal distance of natural clay. In case of modified MMT with lower HDTMA amounts (0.25, 0.5 g) the basal distance of clay increased with only 1A^{o}. These results are in agreement with FTIR conclusions. For the modified montmorillonites with low HDTMA concentration, the cations are parallel to the silicate layers and therefore a small increase of basal distance was recorded.

The presence of a surfactant (HDTMA) excess ensures a significant increase of basal distance. The XRD results confirm that the surfactant orientation within silicate gallery depends on the HDTMA concentration.

The influence of MMT-HDTMA hydration degree

FTIR Analysis

FTIR spectra of PCH precursors and PCH synthesized using various water amounts are shown in figure 6.

Significant changes were detected in FTIR spectra of both PCH precursors (before thermal treatment) and PCH (after calcination)-fig.6-a,b. The formation of three dimensional silica network was highlighted by the change of peak position from 1067 to 1079 cm^{-1} for non-calcinated samples and from 1067 to 1084 cm^{-1} for PCH.

Table 1

XRD RESULTS FOR MODIFIED MONTMORILLONITE WITH DIFFERENT HDTMA AMOUNTS

Samples	**Basal distance** **d_{001}(Å)**
MMT-Na	12.5
MMT-HDTMA-0.25	13.3
MMT-HDTMA-0.5	13.6
MMT-HDTMA-1	**38.1; 19.1**; 12.7
MMT-HDTMA-2	**38.1; 19.1**; 12.6
MMT-HDTMA-3	**37.9; 19.1**; 12.6
MMT-HDTMA-4	**38.0**; 18.9; 12.8
MMT-HDTMA-5	**38.15; 19.1**; 12.8
MMT-HDTMA-6	**39.8; 20.2**; 12.9

XRD analysis

Also the XRD results indicate that the water content influence the PCH synthesis. This analysis was performed for PCH precursors and also for PCH. The XRD analysis results are summarized in table 2.

As one may observe from table 2 the increase of basal distance was influenced by the MMT-HDTMA hydration degree. High water amount favours the hydrolysis of TEOS and thus the formation of three dimensional silica network between the silicate layers occurred. Using this strategy a PCH with a basal distance of 34.8A^{o} was obtained.

We concluded that the ratio between water and TEOS significantly influenced the PCH precursors basal distance. A precise water amount is required in order to achieve a complete hydrolysis of TEOS.

The influence of reaction times

The PCH synthesis was done using various reaction times in order to identify the optimal reaction time. The PCH precursors and PCH were characterized by FTIR and XRD analyses.

FTIR analysis

For this study the FTIR analysis results did not indicate a significant influence of the reaction time on the PCH synthesis. The FTIR spectra of PCH precursors showed the same peaks at similar wavenumbers position regardless the reaction times. Similar results were obtained for PCH.

XRD analysis

The XRD results showed that the silica network formation within the modified montmorillonite occurred in the first three hours. After this reaction time there was no significant change in the XRD results. The PCH precursor synthesized at a reaction time of 3 h exhibits a high value

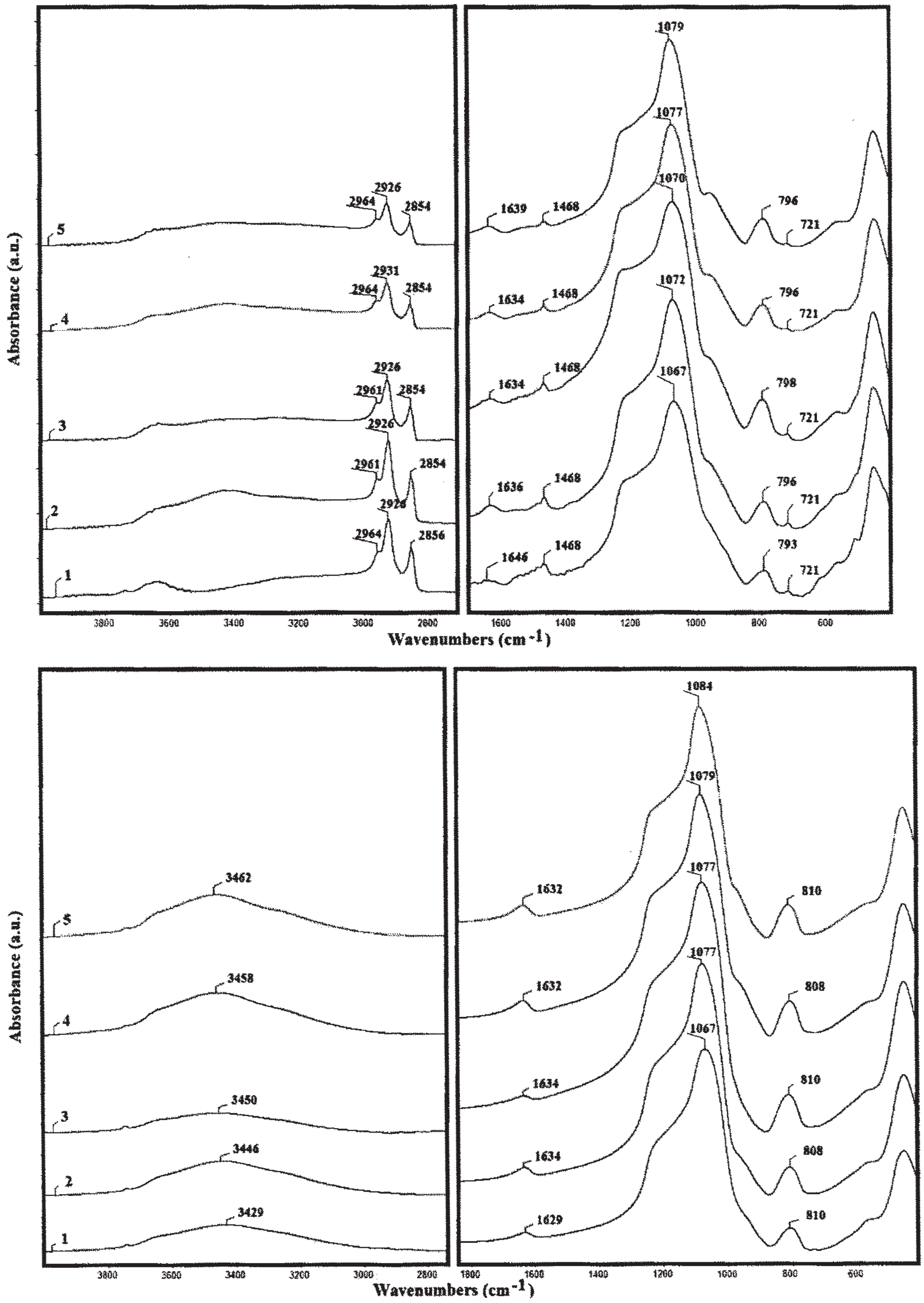

Fig. 6. FTIR spectra of a: PCH precursors (before thermal treatment): 1-PCH-1w-n, 2-PCH-2w-n, 3- PCH-3w-n, 4- PCH-4w-n, 5- PCH-5w-n and b: PCH (after calcination): 1-PCH-1w-c, 2-PCH-2w-c, 3- PCH-3w-c, 4- PCH-4w-c, 5- PCH-5w-c

of basal distance (36 A°) (table 2). After this reaction time the basal distance of PCH remains constant .

The removal of surfactant by thermal treatment does not affect the basal distance. Also for the calcinated samples the XRD results showed that the highest basal distance (37 A°) was achieved by the PCH-3h-c (fig.8).

The influence of reaction medium pH value

As one may notice from table 2 the PCH synthesis was also influenced by the *p*H value of reaction medium. The XRD analysis showed that the highest basal distance for PCH precursor (38.4 A°) and also for calcinated product (36.6 A°) was detected at a *p*H of 8. These results lead to the conclusion that the interactions between surfactant/ co-surfactant and silica precursor, TEOS hydrolysis and polycondensation reactions rate are influenced by the *p*H value of the reaction medium.

Table 2
XRD RESULTS OF PCH PRECURSORS (BEFORE THERMAL TREATMENT) AND PCH (AFTER CALCINATION)

Influence of hydration degree		**Influence of reaction time**		**Influence of pH value**	
Sample	**Basal distance (Å)**	**Sample**	**Basal distance (Å)**	**Sample**	**Basal distance (Å)**
PCH-1w-n	27.6	PCH-1h-n	34	PCH-pH1-n	38.0
PCH-1w-c	30.3	PCH-1h-c	35	PCH-pH1-c	35.3
PCH-2w-n	28.8	PCH-3h-n	**36**	PCH-pH2-n	38.3
PCH-2w-c	31.6	PCH-3h-c	**37**	PCH-pH2-c	35.2
PCH-3w-n	29.9	PCH-5h-n	36	PCH-pH3-n	37.5
PCH-3w-c	31.6	PCH-5h-c	35	PCH-pH3-c	34.7
PCH-4w-n	**32.5**	PCH-22h-n	35	PCH-pH7-n	36.5
PCH-4w-c	**33.1**	PCH-22h-c	36	PCH-pH7-c	34.5
PCH-5w-n	**32.6**	PCH-67h-n	36	PCH-pH8-n	38.4
PCH-5w-c	**34.8**	PCH-67h-c	36	PCH-pH8-c	36.6
-	-	-	-	PCH-pH 9-n	35.9
-	-	-	-	PCH-pH9-c	35.6

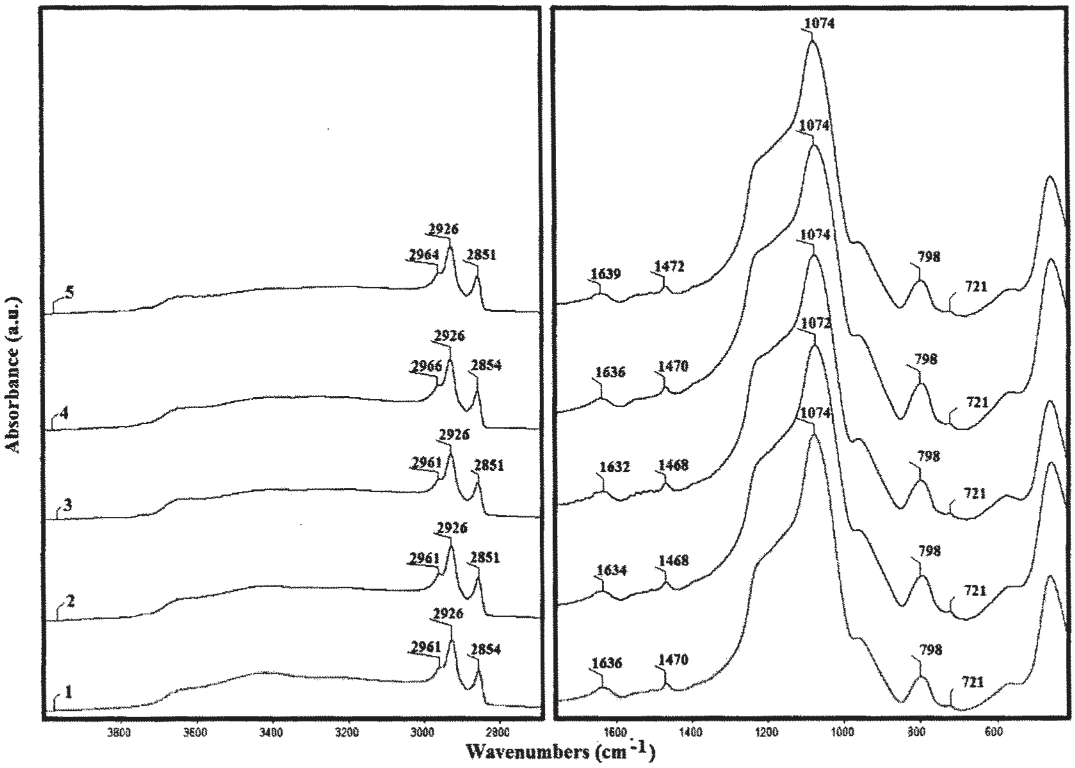

Fig.7.FTIR spectra of a: PCHprecursors synthesized at different times: a: 1-PCH-1h-n, 2-PCH-3h-n, 3- PCH-5h-n, 4- PCH-22h-n, 5- PCH-67h-n;

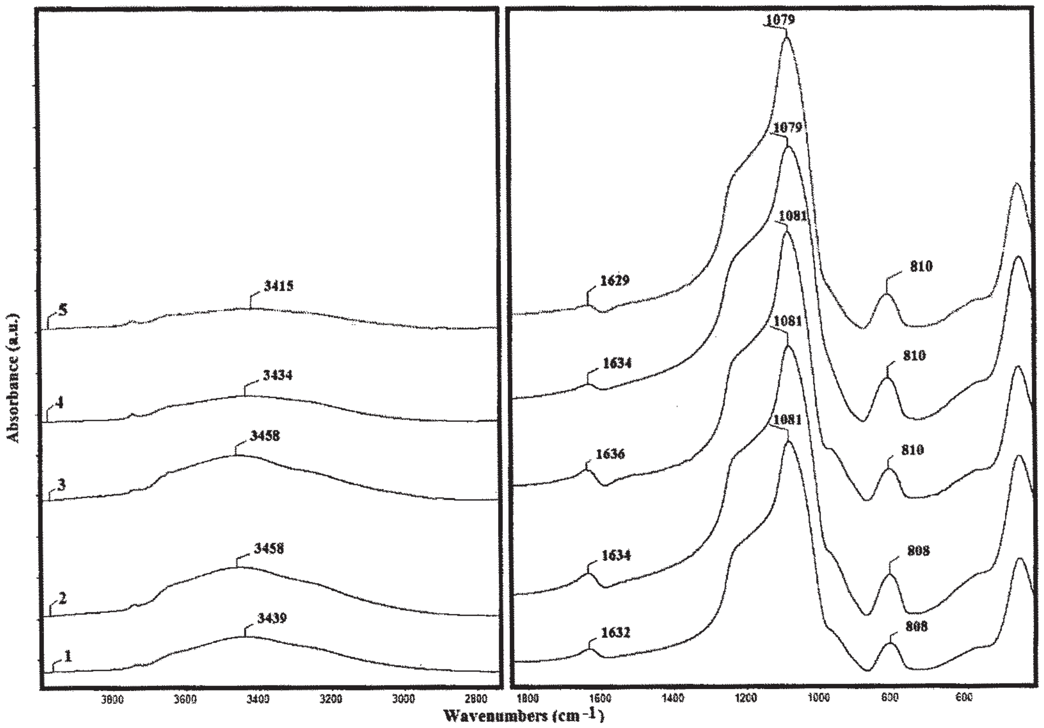

Fig.7.FTIR spectra of a: PCHprecursors synthesized at different times: b: PCH-1h-c, 2-PCH-3h-c, 3- PCH-5h-c, 4- PCH-22h-c, 5- PCH-67h-c

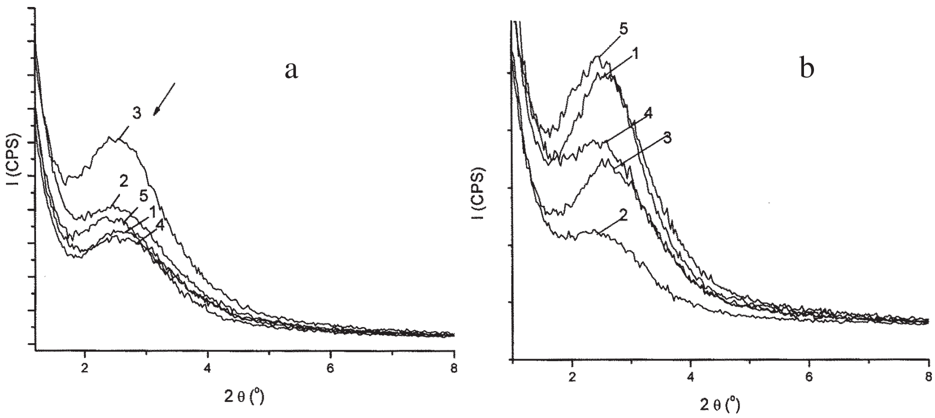

Fig. 8. XRD curves for PCH precursors (a): 1-PCH-1h-n, 2-PCH-3h-n, 3- PCH-5h-n, 4- PCH-22h-n, 5- PCH-67h-n and PCH (b): PCH-1h-c, 2-PCH-3h-c, 3- PCH-5h-c, 4- PCH-22h-c, 5- PCH-67h-c synthesized at different reaction times

Conclusions

Some PCH precursors and PCH products were synthesized using different reaction conditions (different water amounts, *p*H value of reaction medium and reaction times).

The FTIR and XRD analyses showed that the HDTMA concentration used for MMT organophylization influenced the cation conformational changes and therefore different basal distances of PCH were obtained.

The water amount used for MMT-HDTMA hydration influences the basal distance of PCH. High water amount ensures the synthesis of PCH characterized by a basal distance of 34.8 A°.

The optimal reaction time for synthesis of a PCH precursor characterized by a high basal distance (36 A°) is about 3 h. Using this precursor a PCH with a basal distance of 37 A°was obtained.

The *p*H value of reaction medium has a strong influence on the interactions between MMT-HDTMA/co-surfactant and silica precursor. Also the silica network formation between silicate layers is influenced by the variation of *p*H value.

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