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The synthesis of MCM-41 nanomaterial from Algerian Bentonite: The effect of the mineral phase contents of clay on the structure properties of MCM-41

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ABSTRACT

This study focuses on the MCM-41 material (Mobil Composition of Matter). The MCM-41 nanomaterial presents higher physical properties such as pore sizes, surface areas and pore volumes. This material is usually synthesized by using laboratory reagents as silicate sources and aluminium source. These laboratory reagents are still expensive and toxic for large scale production. The main aim of this work is to resolve this problem and to replace these expensive laboratory reagents by more cost effective ones. The volclay and Algerian bentonite low-cost mass clay materials are used as silicate and aluminate sources separately by adopting an alkaline fusion process to extract both silicon and aluminium (1 kg of silicium and aluminium from volclay and Algerian bentonite cost around 0.03 and 0.01 € whereas the same amount of silicon from ludox and aluminium from sodium aluminates cost around 350 €). The synthesis of MCM-41 from bentonite was carried out by the hydrothermal method using the supernatants of bentonite (in the form of sodium silicate and sodium aluminate). On the basis of the data obtained from powder X-ray diffraction (XRD), transmission electron microscopy (TEM) and N₂ adsorption and desorption, the results revealed that the properties of MCM-41 synthesized from Algerian bentonite and volclay separately depend on both elemental composition and mineral phase contents of the used bentonite. Pure and highly ordered hexagonal mesoporous MCM-41 with uniform pore sizes and a high specific surface area have been successfully synthesized without any phases which exist in natural bentonite. The Algerian bentonite was chosen because of its low cost compared to volclay, another commercial clay source.

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1. Introduction

The mesoporous molecular sieves, widely known as M41S, are a fascinating class of solids with uniform channels 2–10 nm in diameter [1–3] and a highly specific surface area of up to 1000 m²/g. These characteristics, as well as their extraordinary high surface and distinct adsorption

properties, open up a high application potential of those materials, e.g. in the field of catalysis [4]. The open pore structure, high porosity and large surface area (implying large storage capacity) make an aerogel an ideal starting medium for a host–guest system, allowing small organic molecules to be deposited, encapsulated or doped [5,6]. These materials, of which MCM-41 is a well studied member, knew a limited production and used on a large scale for both environmental and economical reasons (the cost and toxicity of both template and silicon source). Recently, much attention has been given to the use of waste products

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as source of silicon and aluminium. Few of them treat the use of clay, cheaper natural source, as of silicon and aluminium for the large industrial scale production of mesoporous materials. The extraction of silicon and aluminium from clay is possible by alkaline fusion at mild temperature, although the mesoporous materials synthesized from waste products or clay exhibit slight inferior structural parameters compared to those synthesized from commercial reagents. Singer et al. [7] proposed to convert the coal fly ash by hydrothermal activation methods to zeolites using alkaline solutions (mainly NaOH and KOH solution), which are analogue to the formation of natural zeolites from volcanic deposits. In 1999, Chang et al. [8] have studied the conversion of the coal fly ash to a mesoporous aluminosilicate material in the hexagonal phase type MCM-41 with a very important incorporation of aluminium (Si/Al = 13.4). Kumar et al. [9] synthesized MCM-41 and Santa Barbara amorphous-15 (SBA-15) with a specific surface area of 842 m²/g and 483 m²/g, respectively, from coal fly ash by using the fusion method. Wakihara et al. [10] introduced for the first time an alkaline fusion to synthesize the conventional zeolites similar to chabazite or mordenite. This method improved the conversion rate of aluminium-silicate phases and resulted in very interesting types of zeolites. Kang et al. [11] reported the synthesis of Al-MCM-41 by using water glass (or silicate sodium) as Si source and metakaolin as only Al sources. Recently in our previous work in 2009, we have synthesized an Al-MCM-41 by using volclay as aluminosilicate source with a high specific surface area about ca. 1060 m²/g. So is it possible to use bentonite as a source of aluminium and silicon for the synthesis of nanomaterials, and what is the effect of its mineral phase contents on the physical properties of MCM-41 compared to the MCM-14 synthesized from volclay?

2. Experimental

2.1. Origin and chemical composition of Algerian bentonite

The natural bentonite used in this study was extracted from Maghnia mine (Hammam Boughrara, 600 km west of the capital Algiers); its chemical composition is listed in Table 1. The main components of bentonite sample are silicon and aluminium, with fewer amounts of other elements including Fe, Ca, and Na.

2.2. Synthesis of MCM-41 from Algerian bentonite

For the synthesis of mesoporous materials, we adopted the alkaline fusion, which consists of the extraction of the Si and Al species by mixing the Algerian bentonite with sodium hydroxide powder in a weight ratio of bentonite to NaOH of 1:1.2 and heated at 823 K for 1 h in air. The fused mass obtained was cooled to room temperature and milled

overnight. The fused bentonite was then mixed with water in a weight ratio of 1:4 and stirred for 1 day at room temperature. The resultant suspension was separated by centrifugation to obtain the supernatant. In a typical MCM-41, 0.867 g of hexadecyltrimethylammonium bromide (C₁₆TMABr), 15 ml water and 0.75 g aqueous NH₄OH were combined with 40 ml of the supernatant and stirred at room temperature during 1 h at pH 9.5. The crystallization procedure was done at a temperature of 373 K. 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.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were carried out using a Bruker AXS diffractometer using Cu K α (wavelength = 0.15404 nm) radiation, with scanning step 0.035° 2 θ between 2° and 80° 2 θ . The chemical composition was analyzed by X-ray fluorescence (XRF) (Philips PW2400). The approximate crystallite sizes of the sample were calculated using the Debye–Scherrer equation based on (100) diffraction peak ($2\theta \approx 2^\circ\text{--}3^\circ$). The structure, size morphology and local chemical composition of the mesoporous aluminosilicates were examined by analytical transmission electron microscopy (TEM) combined with an energy dispersive analysis by X-ray spectroscopy (EDXS) using a Philips CM20. N₂ and water vapour adsorption–desorption isotherms were obtained in an automatic adsorbometer conceived and realized in LEM-GRES. For the N₂ adsorption–desorption, the sample was outgassed at 473 K over 24 h prior to adsorption. The specific surface area was determined by the BET formula from data in the relative pressure range from 0.04 to 0.2.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 summarizes the XRD patterns of the bentonite (a) and the fused bentonite (b) at 823 K. It is deduced from XRD that the major mineralogical compositions that exist in bentonite are montmorillonite, quartz, illite and kaolinite (Table 2). The silica (SiO₂) content in the bentonite is predominant, and is about 60.49% followed by alumina (Al₂O₃), that is 18.59%. Haematite (Fe₂O₃) was found to be the third in abundance with an average of 2.29%. The two clay minerals, illite and kaolinite, were dominant and non-clay minerals, referred as “impurities” were found, including quartz (Fig. 1a).

3.2. Structural discussion

The disappearance of the reflections that characterize montmorillonite, quartz, illite and kaolinite confirms that

Table 1
Chemical composition of volclay and Algerian bentonite.

| Wt.% | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | TiO ₂ | CaO | MgO | Na ₂ O | K ₂ O | LOI |
|--------------------|------------------|--------------------------------|--------------------------------|------------------|-----|-----|-------------------|------------------|------|
| Volclay | 56.5 | 18.6 | 3.6 | 0.1 | 1.1 | 2.3 | 1.8 | 0.5 | 15.4 |
| Algerian bentonite | 60.5 | 18.6 | 2.3 | 0.1 | 1.0 | 3.8 | 1.2 | 0.9 | 12.1 |

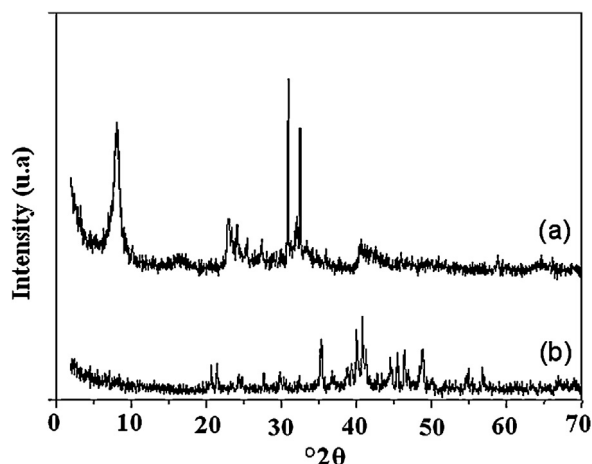
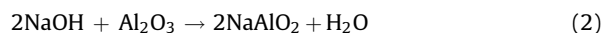
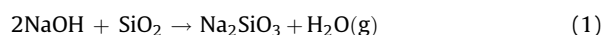


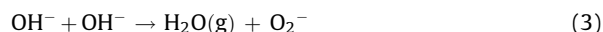
Fig. 1. XRD patterns of the bentonite (a) and the fused bentonite (b) at 823 K.

the alkaline fusion of bentonite dissolves the totality of this species (Fig. 1b) and leads to deduce that the alkaline fusion process by intermediary of sodium hydroxide at low temperature generates new phases called sodium silicate (Na_2SiO_3) (Eq. (1)) and sodium aluminate (NaAlO_2) (Eq. (2)).

The chemical equation describing this process is:



The alkaline fusion causes structural disturbances through the breaking of unstable bonds, it is considered as a combination between the dehydroxylation process, which is temperature dependent, and sodium hydroxide effect. These two phenomena led to the decomposition of Algerian bentonite at mild temperature; similar results were obtained by Adjdir et al. [12]. Adams [13] found that the heating of montmorillonite with small monovalent cations much above 100 °C leads to a decrease of the interlayer spacing (collapse of the clay layers). During the dehydroxylation process, water is formed by a reaction between adjacent OH^- groups and migrates through the crystal. Water is lost from the octahedral sheets by chemical dehydroxylation (Eq. (3)).



This causes a large disruption of the crystal lattice. The tetrahedral layer is left but octahedral layer is destroyed and the distance between these layers decreases. Every crystal

Table 2
Mineral phase content of Algerian bentonite.

| Nature | Clay minerals | | | Non-clay minerals |
|--------------------|---------------|--------|--------|-------------------|
| | Mont (A°) | I (A°) | K (A°) | Q (A°) |
| Samples | | | | |
| Algerian bentonite | 12,65 | 10 | 7,16 | 4,25 |
| | 4,43 | 5 | 3,57 | 3,34 |
| | 2,95 | - | 2,37 | 2,45 |
| | 2,52 | - | - | 2,28 |

cell loses one molecule H_2O , which is created by the jump of H^+ between two neighbouring OH^- groups (Eq. (4)).

The generally accepted concept for the dehydroxylation of kaolinite, according to Frost and Vassallo [14], is based upon the interaction of two hydroxyl groups in a two-step process to form a water molecule by proton transfer leaving chemically bonded oxygen, as a superoxide anion. These steps require proton delocalization at specific hydroxyl sites to form H_2O , these protons must migrate to a second hydroxyl site. If two adjacent hydroxyls are involved in the two-step process, then this process will be homogenous (see Eq. (4) and Eq. (5) below).



Studies of individual pure clays [15–17] show that the dehydroxylation temperature depends on the mineralogy and in particular on the stereochemistry of the clays, trans-vacancy hydroxyl structures being more easily dehydrated than cis-vacancy configurations [18–20].

On the basis of the EDAX data expressed in percentages, there was a wide variation of chemical constituents of fused Algerian bentonite, where the silicon is around 41.01% much higher than aluminium, which is around 5.08%. This result indicates that a large amount of silicon remains in the fused bentonite (not extracted from it), unlike what was found in the case of volclay, where the amount of silicon extracted is greater than aluminium. This can be explained by the different components of clay. Volclay is constituted from montmorillonite, muscovite, quartz and feldspar, whereas Algerian bentonite is formed from montmorillonite, kaolinite, illite, calcite and quartz. Based on the results obtained, the decomposition of the various constituents of the clay depends on the temperature and time required for fusion.

The powder XRD patterns of as-synthesized and calcined Al-MCM-41 samples are illustrated in Fig. 2. According to the large 2θ range scanned ($2\theta = 10\text{--}40^\circ$), no characteristic peaks of amorphous silicon phase and impurity, which are usually present in the naturally

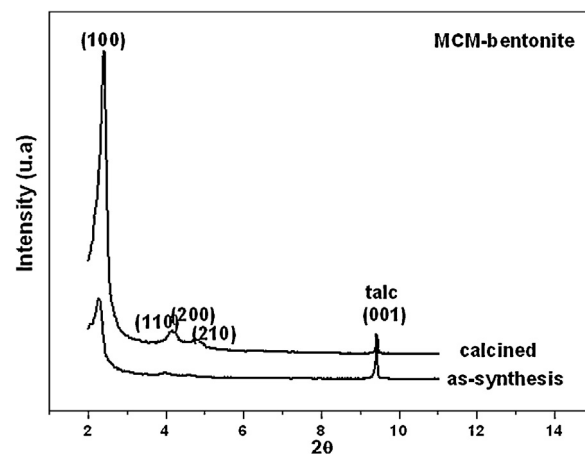


Fig. 2. XRD patterns of the MCM-bentonite as-synthesis and calcined samples prepared at pH = 9.5.

occurring clay, were observed. Therefore, major amounts of silicon and aluminium extracted from the Algerian bentonite were consumed to produce Al-MCM-41. The characteristic reflection (100) was observed in the low-angle X-ray patterns, which is characteristic of a hexagonal pore structure typical of Al-MCM-41 [21]. Moreover, more appreciable characteristic reflections (110), (200) and (210) were observed which show a better structuring of the hexagonal channels of Al-MCM-41 [1].

A high Na^+ ion concentration in the initial solution is known to favorize the formation of zeolites and hinder the formation of Algerian bentonite-MCM phase [22]. The adjustment of the pH during the synthesis is important due to the high concentration of Na^+ ions present in the supernatant of fused bentonite. The value of the synthesis pH influences strongly the quality of the obtained Algerian bentonite-MCM [23].

The diffraction peaks (100), (110) and (200) of the resultant sample of Algerian bentonite-MCM calcined become stronger after calcinations at 550°C than those obtained from the as-synthesized one, showing that the ordering of the sample was enhanced. The unit cell of calcined material decreases from 4.50 to 4.40 nm compared to the one of the as-synthesis one. This phenomenon was caused by the removal of the surfactant from the channels, by condensation of silanol groups on the walls and by the dehydroxylation phenomenon.

The powder XRD patterns of the Al-MCM-41 samples synthesized from volclay and Algerian bentonite calcined are depicted in Fig. 3. The XRD patterns of the calcined sample from volclay and of Algerian bentonite exhibit the same peaks and consist of one very strong peak and three weak peaks corresponding to (100), (110), (200) and (210) reflections at 2θ values ranging from 2 to 6. The diffraction peak (210) was detected by applying Bruker Topas 3.0 software. Referring to the XRD of both samples, it is deduced that the sample synthesized from Algerian bentonite presents a better crystallinity compared to that one from volclay. This can be attributed to the aluminium content in the volclay-MCM framework Si/Al ca. 17 and in MCM-bentonite Si/Al ca. 44. Adjdir et al. [24] found that when the aluminium content into the silicate framework

increases, the crystallinity of this sample decreases. On the other hand, bentonite contains less aluminium compared to volclay; consequently the extraction of aluminium from Algerian bentonite could be less and hence, the aluminium content is less. This approach is confirmed by the full width at half maximum (FWHM) of both samples; in the case of MCM-volclay, the FWHM has a value of 0.295° , however the FWHM of MCM-bentonite is 0.216° . The fusion, or more precisely speaking the dehydroxylation, is a decomposition of crystals to a disordered structure. This change is followed by collapse of the structure and formation of sodium silicate instead.

According to Taylor [25], in the absence of salts, the dehydroxylation of clays involves the migration of protons from inside the structure to surfaces or boundaries and their combination with OH groups present in these regions to form water. The reaction is facilitated by the volatilization of the water. In this process, the clay structure loses one positively and one negatively charged species, hence, no charge imbalance is produced. Only some vacant OH sites are produced. Natale and Helmy [26] found that dehydroxylation is different from the reaction that was apparently operative in the presence of NaOH; here, protons migrated and volatile products are formed. In this reaction, structural hydroxyls were not lost. Hence, a charge imbalance and a diffusion potential were created, which forced the movement of sodium ions into the crystal along the electric potential created by the movement of the protons in the opposite direction. Because of its size (it is much greater than a proton) and its 8- to 10-fold coordination with oxygen in silicates, the movement of sodium into the clay structure at fusion temperature requires drastic changes in the oxygen packing. The presence of sodium, therefore, produces a distortion of the clay structure and the loss of the crystallographic properties of the clay, namely, the production of a disordered structure and the disappearance of the XRD pattern of the mineral phases.

3.3. N_2 adsorption–desorption

Fig. 4. shows the N_2 adsorption–desorption isotherm for Al-MCM-41 from Algerian bentonite and Table 3

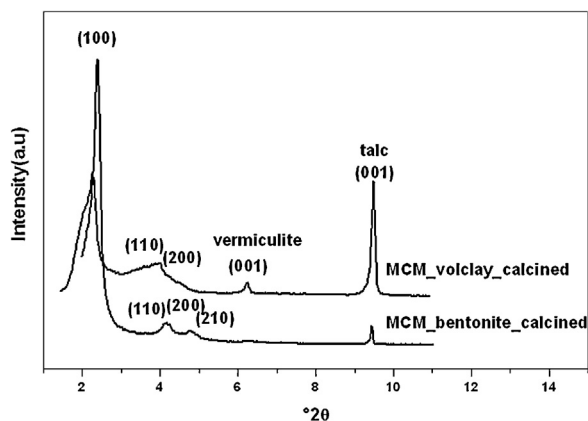


Fig. 3. XRD patterns of the Al-MCM-41 samples synthesized from volclay and Algerian bentonite calcined.

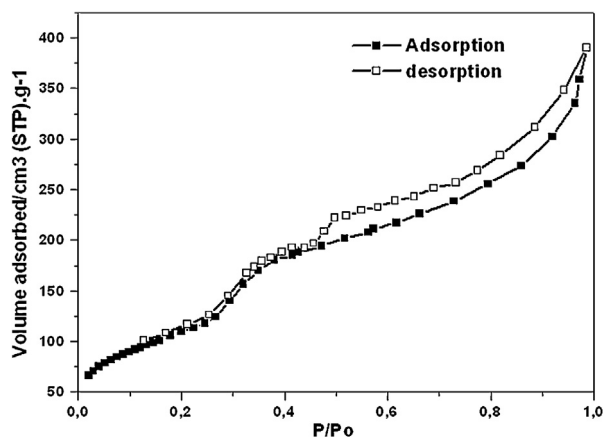


Fig. 4. N_2 adsorption–desorption isotherms for the calcined Al-MCM-41 sample prepared at $\text{pH} = 9.5$.

Table 3
Structural characteristics of the calcined Al-MCM-41 from volclay and Algerian bentonite.

| Sample | Si/Al | a_0 (nm) | FWHM 2θ | D_p (nm) ^a | S_{BET} (m ² /g) ^b | V_{meso} (m ³ /g) ^c | bp (nm) ^d |
|---------------|-------|------------|----------------|-------------------------|--|---|----------------------|
| MCM-volclay | 17 | 4.50 | 0.295 | 3.70 | 1060 | 0.77 | 0.75 |
| MCM-Bentonite | 44 | 4.40 | 0.216 | 3.80 | 494 | 0.72 | 0.60 |

FWHM: full width at half maximum.

^a Pore diameter is given by: $D = C \times d_{100} \times [\rho \times V_p / (1 + (*V_p))]^{1/2}$, where V_p is the pore volume, ρ is the density of the pores walls, 2.2 cm³ g⁻¹ for silica materials, d_{100} is the interplanar spacing and C is a constant depending on the pore geometry ($C = 1.213$ for a cylindrical geometry) [1].

^b Specific surface area.

^c Mesoporous volume.

^d Wall thickness, $a_0 - D_{DRX}$.

summarizes the textural proprieties of this sample. The obtained isotherm is typical for Al-MCM-41 phase. The corresponding isotherm is of type IV, characteristic of the mesoporous solids according to the IUPAC nomenclature [27]. The type IV isotherm is defined by three stages: at low relative pressures, a slow increase of nitrogen corresponding to monolayer-multilayer adsorption on the pore walls. At intermediate relative pressures, a sharp step indicative of capillary condensation within mesopores. In the last stage, at high relative pressures, a final plate with a slight inclination associated with multilayer adsorption on external surface of the particles.

The isotherm presents the sharp capillary condensation step at p/p_0 0.3, typical of a uniform mesoporous material with a pore size at around 3.8 nm. The specific surface area of Al-MCM-41 was ca. 494 m²/g with a pore volume of 0.72 cm³/g calculated at 0.42 p/p_0 . This p/p_0 value was chosen to eliminate the adsorbate volume which can occur between the platy particles (Table 2).

The lower specific surface area obtained is probably due to particle size. The particle size of MCM-volclay is ca. 19.8 nm, whereas the particle size of MCM-bentonite is 28 nm, calculated by the Debye–Scherrer equation. A similar result was found by Kumar et al. [9] and Adjdir et al. [24].

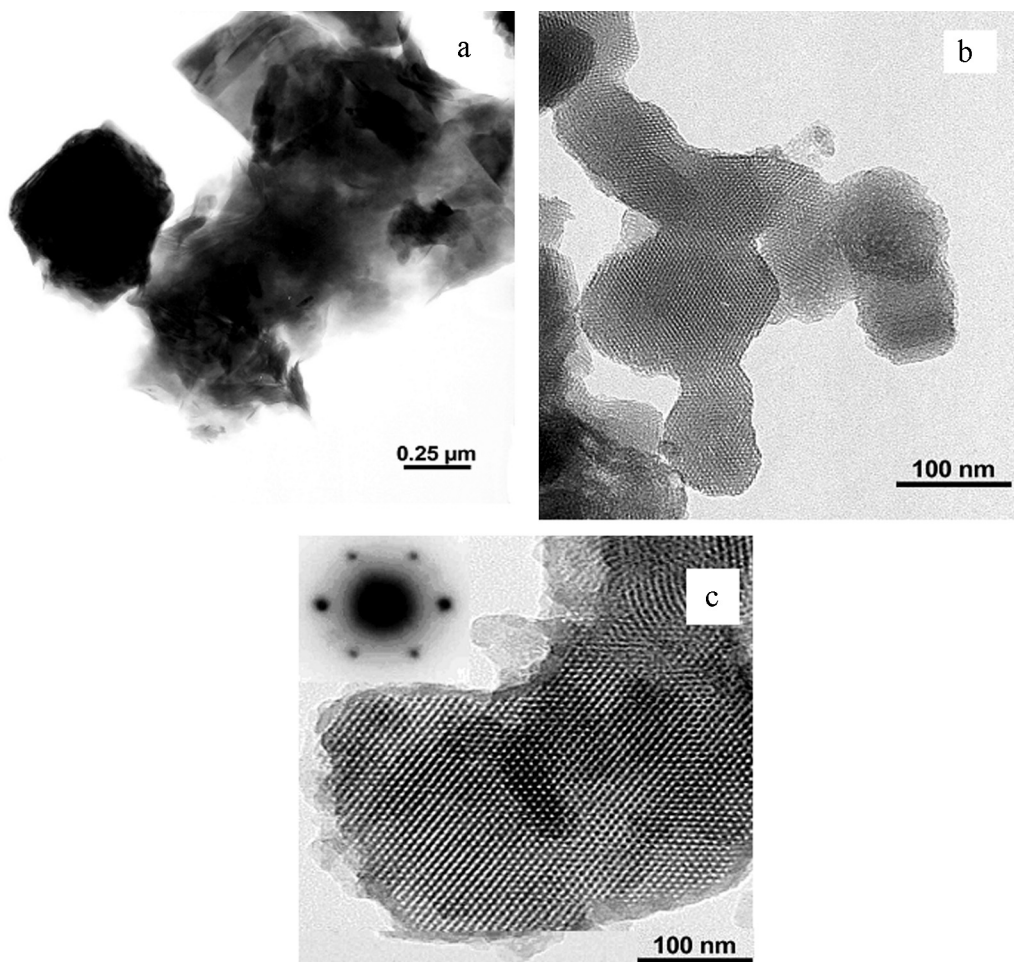


Fig. 5. TEM images of bentonite-fused (a). Images of MCM-bentonite calcined (b) and selected area electron diffraction patterns as inset in (c).

3.4. Transmission electron microscopy

The wall thickness in the case of MCM-volclay is around (0.75 nm) and higher than that found for MCM-bentonite (ca. 0.60 nm). This can be explained by the incorporation of aluminium species [28] where the Si/Al ratio of MCM-volclay is much higher than of MCM-bentonite, and by the length bond of Si–O (158 pm), which is weaker than that of Al–O (183.6 pm) in MCM-41.

The EDXS analysis for the crystalline phase of MCM-bentonite led to a Si/Al ratio of 44. This value confirms that only a part of aluminium reacted to produce an MCM-41.

In addition, MCM-bentonite calcined was studied by TEM. After the heat treatment at 550 °C of the Algerian bentonite with sodium hydroxide, the microstructural as well as the compositional uniformity are lost when compared to the untreated Algerian bentonite (Fig. 5a).

The TEM of the Al-MCM-41 synthesized from bentonite is presented on Fig. 5b. This image confirms that the material has a uniform pore system and clear hexagonal patterns of the pores or honeycomb-like structure. This result is well correlated with the XRD, and by the electronic diffraction, where the unit cell of Al-MCM-41 is well defined. The value of the unit cell is equal to 4.2 nm and agrees nicely with the one obtained by XRD with 4.4 nm.

3.5. Selected area electron diffraction pattern (SAED)

Fig. 5c inset shows a high symmetry along the two possible orientations of $p6mm$ plan group obtained for the sample, proving the hexagonal arrangement of the nanomaterials pores.

4. Conclusion

In conclusion, it is shown that the Algerian bentonite can be used as an aluminosilicate source for the synthesis of Al-MCM-41 which is affected in its aluminium content by the mineral phase content of both clays used.

A solid with a symmetrical hexagonal pore structure typical of Al-MCM-41 was observed for the sample synthesized from the Algerian bentonite at pH = 9.5. The adjustment of the pH of the mixture after addition of all reagents decreased Na^+ ion concentration in the solution and therefore increased the reactivity of the silicon and aluminium to obtain the final MCM product.

The N_2 -sorption isotherm was of type IV, characteristic of a mesoporous solid. The wall thickness and mesoporous volume of the MCM-41 from the Algerian bentonite are

typical for materials of MCM-41 type. TEM image confirms that the material has a uniform pore system with hexagonal patterns. EDXS revealed that the hexagonal phase had a Si/Al ratio of 44. This value is much higher than the Si/Al ratio of 4.7, which was measured for the Algerian bentonite. The purely mesoporous aluminosilicate was free from impurities such as quartz.

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