Effect of organic modification on the thermal transformations of abentonite during sintering up to 1250°C

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Abstract. X-ray diffraction (XRD) and thermal analysis techniques were used to study the thermal transformations of raw (Maghnia bentonite) and modified bentonite (algae extract (ulvans) within clay). XRD data showed that the basal spacing (d_{001}) was gradually decreased from ~ 12.80 Å (6.90° (2θ)) at room temperature to about 9.97 Å (8.86° (2θ)) and 10.08 Å (8.74° (2θ)) after calcination at 200, 400 and 600°C for raw and modified bentonites, respectively. Such behaviour was assigned to the loss of physisorbed water molecules (200°C) and to the occurrence of a distorted octahedral metal (complex for modified bentonite) in the clay. Calcinations above 800°C gave rise to a complete distortion of this crystal lattice, leading to the disappearance of d_{001} XRD peak due to the dehydroxylation of bentonites. The occurrence of cordierite was enhanced at lower temperature (1100°C instead of 1250°C) in the modified bentonite.

Keywords. Bentonite and modified bentonite; algae extract (ulvans); phase transformations; X-ray diffraction; thermal analyses.

1. Introduction

Smectites, including bentonite, are 2:1 layered aluminosilicate clay minerals that are widely distributed in soils, sediments and prehistoric clay deposits.^{1,2} Due to isomorphic substitution in the tetrahedral Si and/or octahedral Al layers, smectites possess structural negative charges that are compensated by exchangeable cations in the interlayer regions. Because these cations are not structural, they can be easily replaced by other positively charged atoms or molecules.^{3,4} Ogloza and Malhotra⁵ demonstrate that the dehydroxylation temperature range is affected by the heating rates, particle size, compaction of the sample and the type of cation present in the interlayer.

The changes which take place on heating in the structures of silicates, including montmorillonite, have attracted the attention of some researchers.^{5–7} The identification of the as-obtained new phases is made difficult, in particular, because of the complexity of their X-ray diffraction (XRD) diagrams.^{8–15}

Clays intercalated with polymers (polyimide, nanocomposite, etc.) approached the subject of degradation and decomposition was reported by several researchers^{16–25} of these compounds with temperature. They revealed for example that the onsets of degradation temperatures of the nanocomposites increase with the organophilic clay content,

but did not specifically perform a discussion of the structural transformations during thermal treatment.

In the present study, interlayer cations of a raw bentonite were replaced by ulvans (algae extract). The presence of these organic polymers (ulvans) should affect significantly the thermal behaviour of the studied bentonite. Our investigation aimed to understand the effects of added/intercalated algae (ulvans) on the structural changes and thermal behaviours of related bentonite during a thermal treatment.

2. Materials and methods

2.1 Materials

Raw and modified bentonites from bentonite of Maghnia were used in the present work.

Commercial montmorillonitic clay, namely, bentonite of Maghnia supplied by BENTAL-ENOF Spa (Entreprise Nationale des Produits Miniers Non-Ferreux et des Substances Utiles, 31, Rue Mohamed Hattab-Belfort, Alger, Algérie – 73% Montmorillonite, 7% illite and 20% quartz, CEC = 91 meq per 100 g) from Algeria was used by OLMIX²⁶ (SA Olmix, ZA du Haut du Bois 56580 BREHAN) to obtain modified bentonite clay (intercalated compound, atomized at temperatures of about 200°C, comprising a montmorillonite clay and an algae extract (ulvans)).^{27,28}

The chemical analyses of bentonite of Maghnia (table 1) were given by Technical Fact Sheets provided by the

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suppliers and also estimated by X-ray fluorescence by Société Française de la Céramique (SFC). The mineralogical composition was estimated qualitatively by XRD and quantitatively by the chemical composition (table 1).

Bentonite clays were heated at $5^{\circ}\text{C min}^{-1}$ under air from room temperature up to 200, 400, 600, 800, 900, 1000, 1100 and 1250°C for 2 h.

2.2 Methods

The structural evolution of the various samples was determined by Brunauer, Emmett and Teller (BET) surface area, density, thermal analysis (DTA–TGA), X-ray diffraction (XRD) and scanning electron microscopy (SEM).

The BET surface areas were determined from N_2 adsorption experiments using a Micromeritics model Tristar[®] analyzer. Prior to the analysis, each clay sample (~ 1.5 g) was submitted to drying and degassing for 12 h at 110°C .

The densities of montmorillonite powders were estimated using an AccuPyc II 1330 Pycnometer.

The thermal behaviours were studied using a coupled DTA–TGA Setsys 2400 apparatus (Setaram) equipped with a DTA- 1500°C head system. The device was used in the temperature-scanning mode and all experiments were performed under dry air and argon atmospheres from room temperature to 1250°C with a heating rate of $5^{\circ}\text{C min}^{-1}$. Experiments were carried out in a Pt crucible with 40 mg of powder under ambient atmospheric pressure and a pure alumina powder, served as a reference material.

X-ray diagrams were obtained on powdered samples with a Bruker-AXS D 5000 powder diffractometer using $\text{K}\alpha_1$ radiation of Cu and a graphite back-monochromator. XRD experiments were achieved in step-scan mode from 2° to 35° (2θ) with a dwell time of 2 s per 0.02° (2θ) step. Crystalline phases were identified by comparison with powder diffraction files (PDF) standards from International Centre for Diffraction Data (ICDD).

Table 1. Chemicals (a) and mineralogical (b) compositions (wt.%) of bentonite of Maghnia.

	(a)								(b)		
	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	Montmorillonite	Quartz	Orthoclase
Technical fact sheet	55–65	12–18	—	0–2	1–5	2–3	0.76–1.75	1–3	$\sim 75\%$	$\sim 15\%$	$\sim 10\%$
X-ray fluorescence	64.86	17.96	0.29	2.85	0.51	3.58	1.62	1.56

Figure 1. TGA (dash lines)–DTA (strong lines) profiles of raw and modified montmorillonite powders measured under dry air (a) and (c), respectively; and obtained under argon gas atmosphere (b) and (d), respectively (heating rate of $5^{\circ}\text{C min}^{-1}$).

SEM observations of powders were performed under an acceleration voltage between 10 and 30 kV using a Hitachi S-260. Prior to their observation a metal layer (Pt) was deposited on the samples.

3. Results and discussion

3.1 Thermal analyses

The DTA–TGA curves of raw and modified montmorillonite are shown in figure 1. The first endothermic peaks in the DTA curves of the bentonite of Maghnia and modified bentonite are detected in the temperature ranges 50–250 and 50–230°C, respectively. These temperature ranges correspond to the elimination of solvating water²⁹ from the interlayer space of the clay. The related mass loss from TGA thermograms, is 3.5% and 2.8% for the raw and modified montmorillonite respectively. The difference may result from the processing of modified montmorillonite which has been previously dried by atomization (Olmix's process),^{27,28} and correspond to loss of water from the interlayer spacing.³⁰

In the second stage, the raw montmorillonite exhibits a multi-step dehydroxylation between 450 and 700°C associated to a total mass loss of about 2%. Two endothermic peaks (at 475 and 634°C) are noted on the DTA curve obtained under argon while an additional exothermic peak is noted under air at 312°C, probably due to residual organic matter in the raw clay. This dehydroxylation process of the raw bentonite is consistent with mixed trans-vacant and cis-vacant smectite according to literature.^{11,31} Above 800°C, no further mass loss is noted and a typical S-shape peak appears at 858–895°C under both atmospheres, mainly due to decomposition/recrystallization reactions.

For the modified bentonite, the 4% mass loss between 230 and 450°C are assigned to the oxidation and partial decomposition organic matter³⁰ resulting from the algae extracts used in the modification process. As expected, the related DTA peaks are exothermic under air atmosphere while they are endothermic under argon (inert conditions). The organic materials tend to undergo combustion and/or oxidation during thermal treatments under air due to the presence of dioxygen gas (O₂). Such transformations are exothermic in general. Conversely, when thermal analysis is performed under a neutral or reducing atmosphere (argon gas in our case), the decomposition of organic materials requires sufficient energy to arise, thus the observed endothermic phenomenon.³⁰ Between 450 and 700°C, a multi-step decomposition is also noted with a mass loss of 2.4% and 1.5% under air and argon atmospheres respectively. The latter transformations are related to the complete decomposition of the aromatic groups of the ulvan polymers together with the dehydroxylation of montmorillonite mineral contained in the bentonite.^{4,32,33} The mass loss occurs in a smooth and progressive evolution under argon atmosphere, suggesting a different decomposition mechanism compared to the behaviour under air. Furthermore, the DTA peaks

associated to the polymer oxidation is highly exothermic under air and roughly endothermic under argon. Above 800°C, all DTA peaks are endothermic and are located at 860 and 1139°C under air, 883 and 1113°C under argon. Moreover there is a mass loss of 0.2% associated to the endothermic peak near to 860°C while under argon the mass loss is almost 1% and is in the range 883–1100°C. This is due to the decomposition of carbonates and sulphates included into the natural polymer within the modified bentonite.

3.2 Specific surface area, density

Raw and modified bentonites show significant changes in density and BET surface area values with heating from room temperature to 1250°C. Figure 2 shows that the BET surface area values of raw bentonite are almost stable up to 600°C with a mean value of 75 m² g⁻¹. At temperatures above 800°C, the BET surface area values are highly decreased and approach <1 m² g⁻¹. This trends indicate that the dehydration process (DTA–TGA results in figure 1) has little effect on the specific surface area of the studied clay but it significantly increases the density. The dehydroxylation reaction appears to have a strong impact onto the

Figure 2. Specific BET surface area (a) and density (b) of raw and modified montmorillonite plotted against temperature.

Figure 3. Colour changes of raw montmorillonite (R.M.) and modified montmorillonite (M.M.).

Figure 4. X-ray diagrams of the raw (a) and modified (b) montmorillonites at room temperature and after heating at 200, 400, 600, 800, 900, 1000, 1100 and 1250°C for 2 h. *M* = montmorillonite; *M'* = dehydrated montmorillonite; *Mu* = mullite; *Mo* = monticellite; *F* = forsterite; *D* = diopside; *I* = illite; *In* = indialite; *Q* = quartz; *C* = cordierite; ? = undetermined.

specific surface area after the elimination of cis-vacant hydroxyl groups (above 600°C)^{11,31} while the density undergoes a slight decrease. Finally, a slight increase appears due to structural reorganization of montmorillonite mineral around 900–1000°C. Further calcinations up to 1250°C give rise to very little variations, probably due to progressive occurrence of high temperature phases.

For the modified bentonite, the specific surface area value is initially 1 m² g⁻¹ (from room temperature to 200°C) and is increased after calcinations at 400 and 600°C to a value

Figure 5. Net area of $d_{(001)}$ peak of the raw and modified montmorillonites plotted against temperature.

of 30 m² g⁻¹. The latter behavior can be explained by the degradation of the organic film (from ulvans) which was surrounding the clay particles. Therefore, the external clay platelets surfaces are likely to be more accessible for nitrogen adsorption, giving rise to the observed high specific surface area. The aforementioned comments are in agreement with color changes observed in the modified montmorillonite due to the presence of organic matter (figure 3). For calcination above 800°C, the BET surface area of the modified bentonite is decreased and remains lower than 1 m² g⁻¹. The density is increased after calcinations above room temperature, except for 800°C where a strong decrease of the density is noted. Such behavior may indicate the occurrence of great pore content within modified bentonite samples compared to the case of raw bentonite samples. In the latter, the density increases simultaneously with the elimination of solvating water as noted, but after the dehydroxylation, a slight decrease is observed due to residual voids caused by structural water loss.

3.3 Structural changes

The XRD diagrams of raw and modified montmorillonite treated at different temperature are shown in figure 4. At room temperature (25°C), the basal spacing (d_{001}) of the raw bentonite (12.80 Å) is very close to that of the modified bentonite (12.84 Å) despite the apparent difference in their intensities (figure 5). In both cases, the basal spacing is

higher than in the case of a solvating water-free montmorillonite (9.99–9.96 Å).^{13,34,35} According to the latter literature and regarding the aforementioned thermal analyses and BET surface area results, the high basal spacing of montmorillonite in the raw bentonite is due to a water monolayer in the interlayer space (solvating water). The high *d*-spacing of montmorillonite in the modified bentonite may result from the intercalation of ulvan polymers in the interlayer space associated with less amount of solvating water. This assumption is supported by the lower dehydration mass loss (DTA–TGA thermograms (figure 1c and d) and the very low specific surface area of this modified bentonite.

The calcinations of samples up to 600°C induce a shift of the basal spacing value from 12.80 Å (6.90° (2 θ)) to 9.97 Å (8.86° (2 θ)) and from 12.84 Å (6.88° (2 θ)) to 10.08 Å (8.76° (2 θ)), respectively, for the raw and the modified bentonite. The occurrence of a distorted octahedral metal (complex for modified bentonite) may arise in the clay after calcination at 200°C. A fine study of the evolution of the montmorillonite (*d*₀₀₁) peak intensity indicates that the major differences are located at room temperature and after calcination at 400°C. The latter behaviour is in agreement with thermal analyses whereby it has been shown that the ulvan polymers undergo several steps of decomposition (in the range 350–550°C) and are completely transformed above 400°C. It can thus be assumed that the residual interlayer polymers ensure the stacking of montmorillonite platelets.

For temperatures above 800°C, the interlayer *d*-spacing vanishes due to high temperature phase occurrence, amorphous as well as crystalline phases. In fact, the new crystalline phases such as mullite and cordierite are formed at lower temperature (1100°C) within modified-bentonite samples in comparison to raw bentonite samples. The dominant XRD peaks after heating at 900°C belongs to quartz, opal (tridymite, cristobalite, etc.). The increasing intensity of SiO₂ peak may also be due to the creation of a new opal-like material from the decomposition of the montmorillonite after 900°C.³⁶ It is likely that the presence of intercalated natural polymers ensures a better ordering of clay platelets, giving rise to the improvement of surface exchanges which promotes early structural reorganizations.

Moreover, the microstructural evolution of the various samples after calcinations and sintering have been checked and the resulting SEM images are presented in figure 6. The raw bentonite is constituted with clay aggregates with irregular shapes (figure 6a) while the modified bentonite has typical cenospheric-like particles (figure 6a') due to the atomization process. With increasing heating temperature, the non-modified bentonite particles exhibit little variations up to 800°C (figure 6b–e) and above this temperature, they become larger with rounded morphology (figure 6f–h). The latter is consistent with the occurrence of a viscous flux above 800°C as expected from the common thermal transformation of such clays. In the case of the modified bentonite, the cenospheric-shape is kept up to 1000°C (figure 6b'–f'). Moreover, the clay granules exhibit surface modification characterized with multiple cracks formation

Figure 6. Scanning electron microscopy view of raw (a, b, c, d, e, f, g, h) and modified montmorillonite (a', b', c', d', e', f', g', h') at 25, 200, 400, 600, 800, 1000, 1100 and 1250°C, respectively.

Figure 7. Typical images of calcined montmorillonite samples. As-received montmorillonite (top images) and modified montmorillonite (bottom images).

between 400 and 600°C. This may be related to the internal stresses due to the ulvans transformations in this temperature range. Above 1000°C, the spherodized shape is lost and residual large pores are observed together with the occurrence of a glassy phase (figure 6g' and h'). Figure 7 shows some typical micrographs and images of both bentonites after sintering at 1000, 1100 and 1250°C. The differences in colour are due to the additional metal ions provided by the natural polymer within the modified bentonite. Furthermore, the modified montmorillonite samples exhibit a strong swelling between 1000 and 1250°C in comparison to non-modified bentonite samples. The total porosity of such products is around 65%.

4. Conclusion

The thermal transformations of a bentonite modified by intercalation of ulvans (algae extracts) have been studied up to 1250°C.

The solvating water content is lower in the case of modified bentonite whereby the natural polymers wrap the clay particles. The mixed cis-vacant and trans-vacant character of the studied smectite has been evidenced.

The basal spacing (d_{001}) appears to gradually decrease from ~ 12.8 Å (6.9° (2θ)) at room temperature to about 9.9 Å (8.9° (2θ)) and 10.1 Å (8.7° (2θ)) after calcination at 200, 400 and 600°C for raw and modified bentonites, respectively.

Above 800°C, the dehydroxylation of bentonites is achieved and results to a complete distortion of this crystal lattice, leading to the disappearance of d_{001} XRD peak. The formation of high-temperature crystalline phases, mullite and cordierite, is promoted at lower temperature (1100 instead of 1250°C) in the modified bentonite.

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