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Procedia Materials Science 1 (2012) 164 – 171

Procedia
Materials Sciencewww.elsevier.com/locate/procedia11th International Congress on Metallurgy & Materials SAM/CONAMET 2011.

High Temperature Structural Modifications of Intercalated Montmorillonite Clay Mineral with OH-Al Polymers

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Abstract

Two montmorillonitic clays were put into contact with a solution containing inorganic OH-Al polymers and subsequently washed and dried. The obtained solid (i.e. the clays with the OH-Al species in the montmorillonite interlayer) which was called the precursor, was subjected to a thermal treatment up to 1000 °C using DTA-TG for analysis at low temperature. Additionally, the structural changes of the precursor by heating at 1030, 1100 and 1200 °C for 2 hours and that of the natural clays were examined. The crystallinity and formation of new phases was followed by x-ray diffraction analysis. Mullite and cordierite were originated depending on the different contents of aluminium and magnesium in the structure of natural montmorillonite, respectively, accompanied with other phases. The intercalated OH-Al species in both clays favored the increase in the mullite content in the final products. However, the transformation to this phase was directly related to the octahedral aluminium of the natural clay and thus mullite was found to be the dominant phase from montmorillonite containing higher octahedral Al.

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Keywords: montmorillonite; OH-Al polymers; high temperature; mullite; cordierite

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1. Introduction

Generally, the pillared interlayer clays (PILCs) are prepared by calcination of precursors composed by intercalated clays with inorganic polymeric species of polyhydroxycations of Al, Fe, Zr, Ti., Cr, etc (Vaughan and Lussier, 1980; Pinnavaia et al., 1985; Volzone, 1995; Volzone and Hipedinger, 1999; Volzone, 2001; Volzone and Garrido, 2008; Volzone and Cesio, 2009). The thermal treatment of the precursors takes place in the range of 350 - 750 ° C depending on the type of clay mineral and the intercalating species. These products are suitable materials for catalysis and as adsorbents. Due to the natural origin of the clays, various factors such as the chemical and mineralogical composition of the clay mineral, the presence of structural defects and impurities, the synthesis procedure of the precursor determine the formation of crystalline and liquid phases at elevated temperatures. The composition of the precursor is enriched with the metal of the intercalated species modifying the phases that can be developed by calcination which in turn influence the microstructure and properties of the resulting product. Thus, the thermal behavior and constituent phases at high temperature determine their possible industrial use.

In a previous study on the effectiveness of the intercalation, the characterization of the precursor as well as the evolution of the phases formed from natural clays and resultant precursors with the temperature have been investigated by different techniques. Usually the structural characterization of the PILC involves the use of X-ray diffraction, and infrared and mossbauer spectroscopies for the examination, including the application of other specific techniques such as NMR, SEM-EDX, etc. The thermal performance of the precursor is examined by thermo analysis DTA-TG up to 800 ° C. At these moderate temperatures, the transformation of metal-hydroxylated species to metal oxide occurs and the reactions of formation of bonds between species and structural sheets of clay results.

Although most studies are mainly concerned with the thermal behavior, and textural and adsorption properties up to 800 °C, the available information about the thermal behavior of OH-Al precursor at elevated temperatures is scarce.

In this study, the phases developed from two montmorillonite clays intercalated with OH-Al polymeric species by calcinations up to 1200 °C were examined and a comparative study with the natural clay is presented. The influence of the different structural composition of montmorillonites and the thermal cycle on the crystalline phases present were determined by X ray diffraction (XRD).

2. Experimental

Two montmorillonitic clays (Wyoming and Cheto types) having different aluminium content in their structure, called W (17.6 wt% Al₂O₃) and Ch (14.79 wt% Al₂O₃) were previously characterized (Volzone and Garrido, 2011). Both clays contain quartz as impurity, and also low feldspar content was found in the Ch. The structural formulae of the montmorillonite clay mineral for the two clays are: [(Si_{3,94}Al^{IV}_{0,06})(Al^{VI}_{1,36}Fe_{0,06}Mg_{0,60})O₁₀(OH)₂] and [(Si_{3,91}Al^{IV}_{0,09})(Al^{VI}_{1,61}Fe_{0,13}Mg_{0,26})O₁₀(OH)₂] for the Ch and W, respectively (Volzone and Garrido, 2001). The first bracket of the formula indicates the composition of the tetrahedral layer, while the second parenthesis corresponds to the octahedral layer of montmorillonite.

The intercalation of OH-Al polymeric species in montmorillonite was made from an intercalating OH-Al polymer solution that was prepared by partial neutralization of solution 0.1M AlCl₃ by 0.1M Na(OH) and aged at room temperature for 4 days (Hsu, 1989). The obtained intercalating solution consists mainly of OH-Al polyhydroxycations with Al₁₃⁺⁷ structure and a low proportion (<5%) of Al ions as monomers.

Briefly, the synthesis of precursor started with the intercalation stage (by an ion exchange reaction). The clay was dispersed in water (2 wt%) and subsequently the polymeric solution OH-Al was slowly added to this suspension maintaining a constant stirring. The added Al amount was 3.25 mmol of Al/ g of clay. After 24

hours in contact, the solid was separated by centrifugation and washed several times to remove the electrolyte excess. Finally, the dried solid (precursor) was heated in an electric furnace at a heating rate of 5 °C/min to 1030, 1100 and 1200 °C for 2 h.

The identification of crystalline phases and the structural characterization of the precursor and natural clays were carried out by x-ray diffraction XRD by using a diffractometer Philips with goniometer 3020 and PW3710 controller with radiation of Cu-K α and Ni filter in the range of 3-70 °(2 θ). After calcinations crystalline phases present were identified on the powdered sample. Gravimetric and differential thermal analysis (TG-DTA) prior to 1000 °C was made on a Netzsch 409 using α -Al₂O₃ as reference at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Characterization of the precursor

Figure 1 shows the interlaminar space for natural clays and the precursor obtained by X-ray diffraction. The expansion of the basal spacing of 13.9 and 15.6 Å to 17.7 and 17.4 Å for W and Ch, respectively, confirmed the substitution of the exchangeable cations and the location of the OH-Al species in interlaminar space of montmorillonite. The interlayer spacing depends on the nature and charge of the pillaring species as it was found in previous investigations (Volzone and Hipedinger, 1999; Volzone, 2001), and the distribution and charge of the clay layer as well as type of clay minerals are also important factors. Thus, the basal spacings of the precursors were similar to those reported for the used Al13 as a pillaring species (Vaughan and Lussier, 1980; Volzone and Garrido, 2001).

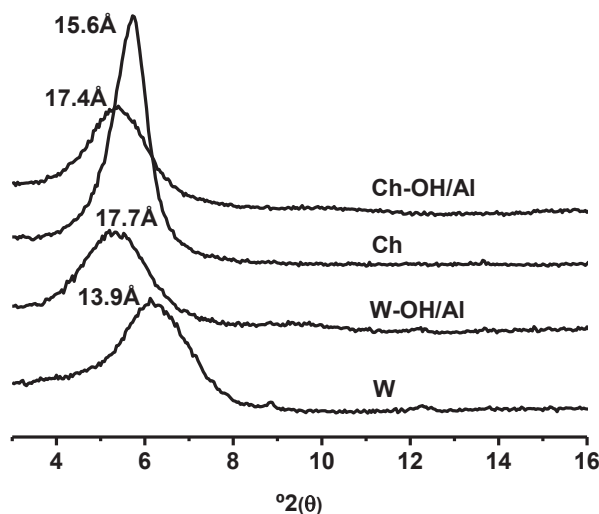


Fig. 1. Interlayer spacing of montmorillonites before and after intercalation of OH-Al species

The chemical analysis of the precursor corroborated that the Al₂O₃ content was 27.9 wt % for W, and 26.9 for the Ch.

Table 1 shows the temperature of endothermic and exothermic peaks determined by the differential thermal analysis for original and the precursors of W and Ch montmorillonites.

Table 1. Temperatures of endo-, exo-peaks of montmorillonites and precursors

Sample	Endo-peak Dehydration (°C)	Endo-peak Dehydration OH-Al species (°C)	Endo-peak Dehydroxylation of montmorillonite (°C)	Endo-peak Structure collapse (°C)	Exo-peak Restructuring (°C)
Ch	174	---	653	881	905
ChA	171	411	650	907	951
W	142	----	712	916	951
WA	152	399	678	890	936

The first endothermic peak corresponding to the loss of interlaminar water of clay mineral appeared at 174 and 142 °C for Ch and W, respectively. The different temperature value is related to the type of dominant exchangeable cation present in the interlayer (Volzone and Garrido, 2001). Thus, the intercalation with OH-Al species shifted the respective temperatures due to the incorporation of aluminum. The second endothermic peak centered at 653 and 712 °C for the original Ch and W montmorillonitic clays, is associated with the dehydroxylation of the clay mineral structure and shifted to slightly lower temperatures for the precursors indicating a new ordering of structure.

Third endothermic peak that developed at 881 and 916 °C is ascribed to the collapse of the montmorillonite structure (Mackenzie and Caillere, 1979), whereas the exothermic peak close to 900-950°C indicates the appearance of new phases.

Mass losses determined by the thermogravimetric analysis are shown in Table 2. The high mass loss between 300 - 800 °C occurred for the precursor and this increase corresponds to the dehydroxylation of intercalated Al species. There are no significant changes above 800 °C.

Table 2. Mass loss of natural montmorillonites and precursors

sample	Temperature range 25-300 °C (%)	Temperature range 301-800 °C (%)	Temperature range 801-1000 °C (%)	Total mass loss (%)
Ch	20.8	3.6	--	24.4
ChA	18.0	6.8	--	24.8
W	10.6	4.6	--	15.2
WA	15.3	5.7	--	21.0

3.2. Evolution of the crystalline phases with temperature for the original clay and the precursor

The crystalline phases developed by heating of natural clay at high temperatures were identified by XRD. Figures 2 (a) and (b) mainly show the presence of cristobalite, mullite, cordierite and quartz being the relative proportion of these phases variable according to the temperature and type of clay.

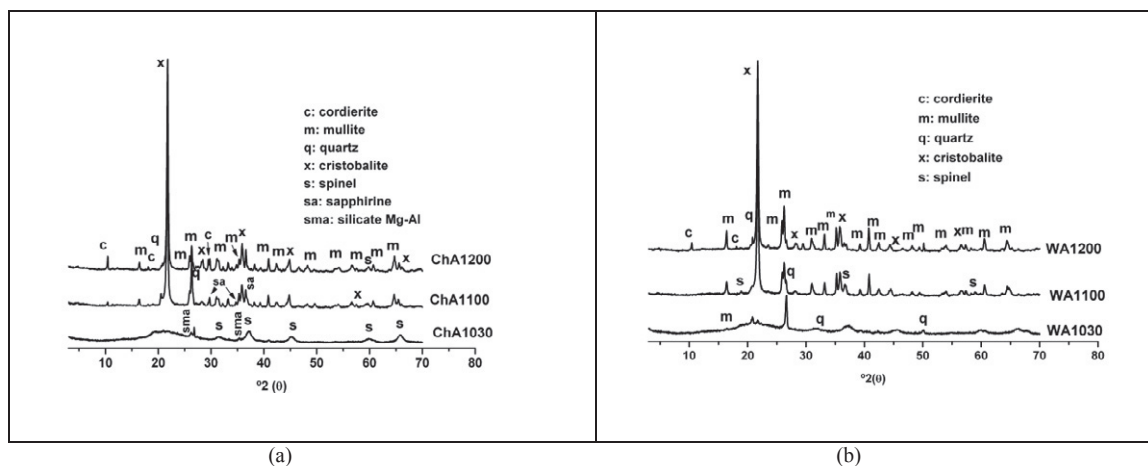


Fig. 2. XRD of natural clays after calcination: (a) Ch; (b) W

The natural Ch is mainly composed by montmorillonite clay mineral, with low feldspar and quartz contents as impurities (Volzone and Garrido, 2001). For Ch calcined at 1030 °C, the absence of characteristic reflections of montmorillonite demonstrated the structural collapse of such clay mineral which occurs at temperatures above 850 °C (Table 2). In addition, the new originated silicate of Mg-Al phase was accompanied with scarce cristobalite, traces of spinel and residual feldspar (Fig. 2a). With increasing the temperature at 1100 °C, the transformation to cordierite occurred, and it probably was formed from the silicate of Mg-Al whose content and that of feldspar decreased, whereas the proportion of cristobalite increased. At 1200 °C a relative increase of the cordierite formed was observed accompanied with cristobalite and unreacted feldspar.

Natural W consists mainly of montmorillonite clay mineral with quartz and feldspar as accessory minerals (Volzone and Garrido, 2001). The diffractogram of the sample heated at 1030 °C (W1030 in Figure 2b), shows a broad band nearly 20 °(2θ) indicating a high content of an amorphous phase. Besides the characteristics reflections of residual quartz and feldspar, cristobalite and spinel existed. By calcination at 1100 °C, cristobalite and mullite mainly formed while the reflections of spinel disappeared. Some quartz and traces of feldspar remained unreacted. At 1200 °C cristobalite and mullite increased with the presence of low contents of cordierite, being the relative proportion of cristobalite less than that observed at 1100 °C.

The contribution of amorphous phase appeared at all temperatures for the W (Fig 2b) suggesting the formation of liquid at these temperatures. Contrarily, the sample Ch (Fig. 2a) presented an increase in the degree of crystallinity with temperature.

Figures 3 (a) and (b) show the diffractograms of the ChA and WA precursors, respectively, heated up to 1200 °C. Unlike the original Ch that showed ordered layered structures when heated at 1030 °C, the precursor ChA exhibited a low structural ordering. Nevertheless, low intensity reflections of spinel were detected for ChA heated at 1030 °C. Therefore, the intercalated OH-Al polymers inhibited the formation to silicate of Mg -Al and delayed the appearance of cristobalite. This may be explained by strong interactions established between the polycation and the sheet of clay. Although previous studies reported different pillaring mechanisms between the pillaring agent Al13 and the montmorillonite layers, the transformation of the polycations during heating may include a cross-linking reaction, with the formation of bonds between the pillars and the tetrahedral sheets of the clay minerals, as Vicente et al.(2001)found by using a saponite clay mineral.

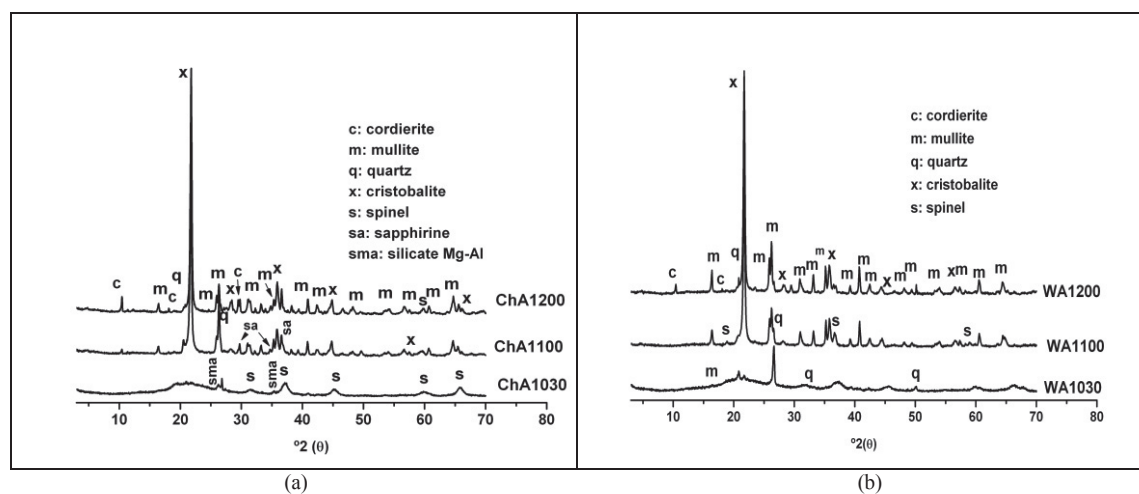


Fig. 3. XRD of precursors after calcination: (a) ChA; (b) WA

For ChA calcined at 1100 °C, the formation of cristobalite and mullite significantly increased whose presence were not detected in the original Ch. Furthermore a Mg-compound of spinel type, identified as sapphire, scarce cordierite and residual quartz was also found. Intercalated OH-Al species favored the transformation to mullite even at this relatively low temperature and also prevented the development of cordierite with regard to the natural Ch. Reaction to cordierite and mullite were enhanced by heating at 1200 °C; there was no significant change in the proportion of cristobalite, whereas sapphire and quartz contents were reduced with respect to ChA calcined at 1100 °C. A comparative study of the resulting phases by heating at 1200 °C showed that an important development of cordierite occurred for the natural Ch, whereas for ChA the presence of this phase was reduced and additionally mullite originated.

For the precursor WA, synthesized from W containing higher Al_2O_3 than Ch, the structural modifications produced at 1030 °C (i.e. the collapse of the structure of montmorillonite, minor formation of cristobalite and spinel with residual quartz and feldspar) were similar to those of the ChA. At 1100 °C and higher temperatures, there are differences in the final phase compositions. Cristobalite and mullite formation from WA enhanced as well as quartz and feldspar content were reduced (Fig. 3b). Transformation to mullite and cristobalite was favored by calcination to 1200 °C, and additionally less cordierite from spinel resulted.

There are notable differences in the nature of the new compounds formed for the two types of clay. For Ch, cordierite predominated and on the other hand, formation of mullite resulted from W. This result may be explained by different chemical composition of the montmorillonite types as evidenced by their structural formula (as showed above). Thus, the W clay shows an octahedral layer richer in Al while the corresponding for the Ch is characterized by the partial isomorphous substitution of Al by Mg. According to the mentioned results, the OH-Al precursor from smectite shows a reduction of the onset temperature for structural changes from that of original sample. This effect coincides with that reported by Vincente et al. (2001) on the transformation of a pillared saponite to enstatite and silica.

In relation to the phase transformations of the clay at high temperatures, previous studies demonstrated that there exists a good agreement with the sequence of destruction of the clay structure and recrystallization to new phases (Mackenzie and Caillere, 1979; Vincente et al, 2001), but in the cited literature there is some discrepancy with the mechanism of formation of the spinel type phase. For smectite (montmorillonite) and illite clays this takes place by separation of a Si rich liquid phase (from the tetrahedral layer) followed by the reorganization of the octahedral layer which is a constituent of the dehydroxylated structure of the clay.

Therefore both the Mg and Fe associated with the octahedral Al belonging to this layer would be part of the spinel. However, there is a controversy about the incorporation of Si at this stage. The constituents of the tetrahedral layer of montmorillonite and alkali probably recombine to form a silica-rich liquid phase. The crystallization to cristobalite and mullite start at 1000 and 1050 °C, respectively. As a result mullite can crystallize with a variable chemical composition even through incorporation of Fe in its structure.

In this work, the Al₂O₃ content of resultant mullite was estimated by the Ban and Okada method (Ban and Okada, 1992) using a graph that relates the ratio between the intensities of the 222 and 111 mullite reflections to the Al₂O₃ content. For ChA calcined at 1200 °C the ratio measured was 0.82 that corresponds to an Al₂O₃ content of approximately 62 wt%. For the WA, the respective ratio was relatively low (0.75) and it can be attributed to the high structural Fe content of the natural W, as its structural formulae evidenced. This result suggested that the Fe substitution by octahedral Al probably contributed to Fe incorporation to mullite.

4. Conclusions

Cheto and Wyoming montmorillonite clays were intercalated with OH-Al polymeric species to produce the ChA and WA precursors. As a result, the interlaminar spacing of such natural clay minerals increased from 15.6 and 13.9 Å to 17.4 and 17.7 Å, respectively, and caused an increase in the Al₂O₃ content from 14.8 and 17.7 % to 26.9 and 27.9 % for the Ch and W after intercalation, respectively.

Crystalline phases developed from W montmorillonite by heating treatment to 1030 °C were: cristobalite and spinel; with little residual feldspar and quartz. The presence of mullite was detected at 1100 °C, while the major phases formed at 1200 °C were cristobalite and mullite, and traces of quartz.

In the case of Ch calcined at 1030 °C, the formation of Mg-Al silicate with scarce cristobalite was observed with unreacted feldspar and quartz. At 1100 °C and 1200 °C significant cristobalite and cordierite developed with low feldspar and residual quartz contents.

The presence of the OH-Al species delayed structural changes to 1030 °C. The retention of aluminium favored the development of mullite from both precursors at 1100 °C.

Although aluminium contents of both precursors were similar, the transformation to mullite enhanced significantly for the WA. This result indicates that the reaction to new phases such as mullite is mainly controlled by the composition of the octahedral layer of montmorillonite being less important the role of the total aluminium content.

Acknowledgements

Financial support by CONICET is acknowledged.

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