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Thermal Behaviour of Titanium in Host Matrix Clay

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Titanium in hosted by a clay matrix has important applications in a variety of catalysts. However, there is insufficient information about of textural and structural characteristics of the titanium in matrix clay at room temperature and after thermal treatment. In this study, titanium in host matrix clay was obtained by treating montmorillonite clay minerals with different OH-Ti solutions. The titanium-solutions containing partially hydrolyzed titanium were obtained using a $TiCl_4$ solution with and without the addition of glycerol. The amount of Ti added to the solid was 20 mmol Ti per gram of clay. Thermal treatments were carried out at 500 and 1,000 °C in an air atmosphere. The solids were characterized by X ray diffraction, thermal analyses, infrared spectroscopy, N_2 adsorption-desorption isotherms. The products presented different structural and textural characteristics and, after calcination at 1,000 °C, anatase and rutile in different proportions were present in the samples.

Keywords: *titanium, clay, thermal treatment, montmorillonite*

1. Introduction

Titanium, as dioxide, presents interesting properties because it is an inert and nontoxic solid. It may be used as white pigment, for water and air purification[1], remediation, in catalysts, as an adsorbent, as compounds in bioceramic materials, etc. Different methods are applied to improve the surface area, size particles, porosity, grain size, and morphology properties.

The titanium in a host matrix solid can be used in appropriate applications: for example, photocatalytic properties can be improved by using TiO_2[2] as a pillar in clay[3], and visible light photocatalytic activity[4] could be improved by preparing mesoporous carbon-doped TiO_2.

Studies related to titanium-clay were started around 20 year ago by Sterte[5], thereafter solids were analyzed for catalytic uses: butanol hydroxylation[6], hydroxylation of phenol[7], dehydration of pentanol[8]; decomposition of propanol[9], selective catalytic reduction of NO by Ti-pillared clays[10,11].

More recently, clay with a titanium compound can be use as a catalyst to produce polyester (for example, polyethylene terephthalate, PET), where the catalyst is used to catalyze the esterification, transesterificaton and/or polycondensation[12].

The titanium-clays may be obtained by first using cation exchange of polynuclear hydroxy-titanium species to introduce the titanium ions between the interlayers of the clay. Then, upon heating, a stable metal oxide cluster of molecular dimensions is formed[5,13,14].

The clays are fine grained phyllosilicate minerals constituted by sheets of aluminum in octahedral coordination and sheets of silica in tetrahedral coordination. The montmorillonite is one of the smectite clay classification species constituted by 2:1 layer type (one sheet of aluminum in octahedral coordination is between two sheets of silica in tetrahedral coordination, triple-sheet-layer). Isomorphic substitution results in negative charges on the three-sheet-layer. These charges are balanced by adsorbed cations (Na^+, Ca^{2+}, K^+, Mg^{2+}) in interlayer position, which are easily exchangeable[15]. Clays are solids which structure may undergo important changes after thermal treatment, mainly from 500 °C, due to removing of the OH^- constituent of the clay from structure[16].

The aim of the manuscript was to analyze the structural and textural changes of the titanium in host matrix clay at room temperature and after thermal treatment.

2. Materials and Methods

A montmorillonite supplied by Georgia Kaolin Co. was used in this study and referred to as E. The E sample is a clay mineral with high montmorillonite as clay composition. Quartz and α-cristobalite impurities in low proportions were detected in the sample. The montmorillonite has a cation-exchange capacity (CEC) of 110 meq/100g and the following structural formula: $(Na_{0.32}\ K_{0.12}\ Ca_{0.25})(Si_{7.95}\ Al_{0.05})(Al_{2.95}\ Fe_{0.18}\ Ti_{0.03}\ Mg_{0.80})\ O_{20}\ (OH)_4$ was obtained by using a <2 μm size fraction[17].

2.1. Titanium-solutions

The titanium-solutions (containing partially hydrolyzed titanium cations) were obtained by different methods: a) using a $TiCl_4$ solution and 6.0 M HCl[5], where the final Ti concentration was 0.80 M, and the HCl/Ti ratio was 1.22. The solution was aged for 3 hours at 20 °C before use (TiT-solution); b) a $TiCl_4$ solution was slowly added to absolute alcohol (ethanol), this solution was then added to glycerol (50% $v.v^{-1}$ in water) following Lin et al.[18] and Bovey et al.[8]. This was named as TiG solution.

2.2. Preparation of titanium-clays

Natural montmorillonite clay (E) and acid treated montmorillonite clay (AE) were used as clays to prepare OH-Ti-clay. The acid activated montmorillonite (AE) was prepared by treating the montmorillonite with a 6 NH_2SO_4 solution at boiling temperature for 30 minutes with a solid/acid ratio of 5%$w.v^{-1}$.

The OH-Ti-clays were obtained by adding OH-Ti-solution addition drop wise to a stirred suspension of montmorillonite clay in water. After 4 hours in continuous stirring, the solid was separated by centrifugation, and washed several times with distilled water until being chloride free. The amount of Ti added to the solid was

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20 mmol Ti per gram of clay. The solids were named TiT-E, TiG-E and TiG-AE.

The thermal treatment at 500 and 1000 °C of the Ti-clays were obtained in an electrically heated furnace by using a Pt crucible in air for one hour (TiT-E5, TiG-E5 and TiG-AE5; and TiT-E10, TiG-E10 and TiG-AE10).

2.3. Characterization methods

Energy Dispersive Analysis of X ray (EDAX) was obtained by EDAX DX PRIME and Philips® SEM505 microscopy. X ray diffractions (XRD) of the samples were obtained with a Philips® 3020 Goniometer with PW 3710 Controller using Cu Kα radiation at 40 kV and 20 mA and Ni filter. The solids were conditioned at 55% HR.

The infrared spectra (IR) were obtained by using Spectrum One Perkin-Elmer® equipment. The samples were diluted in KBr and compacted in the form of thin pellets.

Diagrams of differential thermal analyses (DTA) were carried out with a Netzsch® 409 apparatus using α-Al_2O_3 as a reference at a heating rate of 10 °C/min. All samples were carried to similar relative humidity previous to the analysis.

The adsorption isotherms were obtained at liquid nitrogen temperature with N_2 in Micromeritics® ASAP 2020 equipment. Samples were outgassed at 100 °C and 10^{-3} torr before nitrogen treatment for 12 hours. The BET surface area (S_{BET}) was calculated from the first part of the isotherms ($P/Po < 0.3$) using 0.162 nm^2 as the molecular area of adsorbed nitrogen molecule. The t-plot was made according to Lippens and De Boer[19].

3. Results and Discussion

The chemical analyses of the samples by EDAX are shown in Table 1. The chemical analysis of the E sample corresponds to a typical montmorillonite clay in which, in this type of analysis, the water content was not taken into account. The Si^{4+}, Al^{3+}, $Fe^{2/3+}$, Ti^{4+} are elements situated in tetrahedral (Si^{4+}, Al^{3+}) and octahedral (Al^{3+}, $Fe^{2/3+}$, Ti^{4+}) sheets of the clay. The Mg^{2+} can be situated in octahedral and/or interlamellar position, whereas Na^+, K^+ and Ca^{2+} are typical cations in interlamellar position.

After treatment of the montmorilllonite with OH-Ti solutions, the interlayer Ca^{2+}, Na^+ and part of K^+ were exchanged by OH-Ti cation species. Einaga[20] proposed the existence of the polynuclear cations species $((TiO)_8(OH)_{12})^{+4}$ in solutions prepared in similar conditions. The amount of titanium in montmorillonites after OH-Ti-solution treatments expressed as oxide were 15.88, 13.01 and 9.22% for TIT-E, TIG-E and TIG-AE samples, respectively. The reduction of aluminum, iron, and magnesium of the montmorillonite structure after OH-Ti treatment can be attributed to pH conditions mainly due to treatment with $TiCl_4$ solutions (pH: 4). The acid treatment on the clay reduces the cation exchange capacity of montmorillonite[21] and also may release the elements from the octahedral sheet of the clay, depending on acid concentration, treatment time, etc.[22]. A reduced amount of Ti was observed in TiG-AE (9.22% TiO_2) compared to TiG-E (13.01%) where TiG-AE was prepared from acid clay (AE) and TiG-E from natural clay (E). The increase of the Si/(Al + Fe) ratio of the clays from 2.50 to 4.02-4.19, Table 1, is indicative of the released cations from octahedral sheets due to treatment with OH-Ti solutions, attributed to the low pH of the solution used for treating montmorillonites. In the same Table the amount of Al and Fe released due to OH-Ti treatment were in the range of 42-51 and 3.3-15 mol, respectively.

Figure 1 shows the differential thermal analysis diagrams for montmorillonite before and after titanium solution treatments. The temperature of the first endothermic peak in the range of 20-200 °C corresponds to the loss of interlamellar water (free and hydrated cations) and the positions of these peaks are related to the type of exchangeable cation, Na^+, K^+ and Ca^{2+}, being present in this case[17]. The temperature of the first peak of the original sample (E), 154 °C, shifted to lower after titanium intercalation: 103-133; 152 and 114-148 °C for TiT-E; TiG-E and TiG-AE treated motmorillonites, respectively, showing a broad peak with doublet peaks in TiT-E and TiG-AE samples. The minor intensities of the peaks for montmorillonite after treatment with a titanium $TiCl_4$ - solution (TiT-E) and for acid clays treated with $TiCl_4$ - glycerol (TiG-AE) may be attributed to a slight modification of the structural sample due to the acid condition of the treatment. The second endothermic peak at 679 °C, corresponding to a loss of hydroxyl groups, confirmed the presence of montmorillonite as the smectite specie of clay in sample E[23]. The presence of titanium in interlamellar spacing shifted the peak at a lower temperature (628, 673 and 646 °C for TiT-E; TiG-E and TiG-AE, respectively). This kind of peak may depend on the perfection of the stacking of the layers influenced by the presence of titanium.

The montmorillonite treated with Ti, using glycerol in the preparation (TiG-E), showed an important exothermic peak which appeared at around 294 °C with a shoulder at 455 °C indicating the loss of organic substance due to the presence of glycerol. The sample TiG-AE presented similar behavior with less pronounced peaks at minor temperature attributed to an altered structure due to the acid activated montmorillonite (AE) used for preparing TiG-AE.

Table 1. Chemical analyses of the samples.

Sample	E	TiT-E	TiG-E	TiG-AE
SiO_2	67.77	67.00	68.67	74.04
SiO_2	21.10	12.00	12.46	11.29
Al_2O_3	2.12	2.02	1.99	1.80
Fe_2O_3	0.26	15.88	13.01	9.22
TiO_2	4.40	2.95	2.90	2.81
MgO	1.40	0.00	0.00	0.00
Na_2O	0.88	0.49	0.50	0.20
K_2O	1.98	0.00	0.00	0.00
CaO	-	-	-	-
Si/(Al + Fe)	2.50	4.03	4.02	4.19
Al released	-	42.00	43.00	51.00
Fe released	-	3.30	5.90	15.00

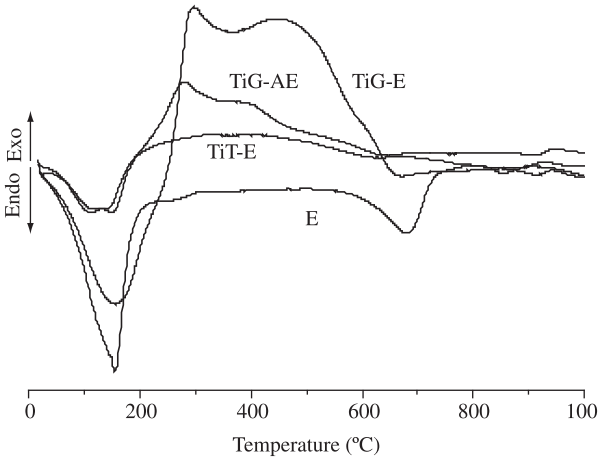


Figure 1. DTA diagrams of the montmorillonite clay E with and without OH-Ti treatments.

The endothermic-exothermic peaks of the montmorillonites at around 850-930 °C correspond to the destruction of the lattice and its recrystallization into new phases[16]. The third endothermic peak, situated at 854 °C of sample E, shifted at higher temperature after Ti treatments, Figure 1, showing that TiT-E, TiG-E and TiG-AE samples have a higher thermal resistance to structural changes for to originate new phases.

Figure 2 shows the thermal weight loss of the samples. The total loss for natural montmorillonite, E, was 13.87% (Table 2), corresponding to two marked zones of weight loss, up to 200 °C (10%) and the second zone from 200 to 680 °C (3.87%), corresponding to water intercalated and the OH^- structural loss, respectively, typical of montmorillonite clays[16]. The total weight losses of OH-Ti-montmorillonites were different depending on the Ti treatment, nevertheless, in all treated samples the loss was continuous in all temperature ranges up to around 700 °C, Figure 2. The total loss of TiT-E was 15.20%. TiG-E and TiG-AE showed three differentiate losses with higher amount for the first (17.35 and 13.95%, respectively). The different values are related to the presence of organic or previous acid-treated montmorillonite (AE). In Table 2 the values of the loss at different temperature ranges are shown. The higher loss of TiT-E regarding E up to 200 °C may be due to the loss of the OH^- water of the Ti species intercalated in interlayer spacing. The similar loss of weight for TiG-E and TiG-AE (8.6 and 8.8%, respectively) in respect of TiT-E (11.2 %) suggests different Ti species formation with less OH-contribution. Assuming that weight loss up to 200 °C corresponds to hydroxyl of OH-Ti species situated in interlayer position, and taking into account the amount of titanium retained (Table 1), it was possible to calculate the OH/Ti for each sample. The OH/Ti values: 3.08, 3.00 and 4.24 of TiT-E; TiG-E and TiG-AE, respectively, are indicative that the species in interlayer for the two first samples were similar and higher for TiG-AE, indicating that the last sample has more a higher rate of OH in titanium species. The TiG-E sample needs a slightly higher temperature (152 °C) in respect of the TIG-AE (148 °C) for to lose the same value at low temperature (Figure 2). Finally, according to Table 2, the different total loss of each sample is related to different loss contributions.

The total loss for E sample was 13.87% and corresponds to the losses of: the free/hydration-cations water, and OH^- of the structure. In TiT-E the increase in loss weight (15,20%) is due to the loss of OH^- of Ti species. Nevertheless, the total loss for TiG-E is higher due to the contribution of organic compounds that contribute with 6.48%. The lower value for TiG-AE may be due to a less organic retention because the content of structural montmorillonite was reduced for a previous acid treatment. The less total weight for TiG-AE may be also attributed to the loss of structural montmorillonite. The loss of weight up to about 500 °C is continuous for the three Ti-montmorillonites, probably due to the dehydroxylation of OH^- groups associated with the interlayer titanium complex (Figure 2).

The clays treated with Ti solutions showed a higher basal spacing (19-22 Å) than the one in the original sample (15 Å), Table 3, due to the replacement of Na^+, K^+, Ca^{2+} cations in interlayer positions by OH-Ti species. The different values may be attributed to the arrangement of OH-Ti-species present in each hydrolyzed Ti-solution as a different OH/Ti ratio was calculated in the above paragraph.

The heating of montmorillonite, E, at 500 °C originated an interlayer spacing of 9.3 Å, corresponding to a collapsed distance between 2:1 layer. Nevertheless, the interlayer spacing after calcinations of the Ti-montmorillonite reached values from 16 to 19 Å (Table 3) showing that, at 500 °C, the 2:1 layer of the clay presents separated interlayer, in a similar form to the pilarization processed[6].

Figure 3a and 3b show N_2 adsorption-desorption isotherms of the Ti-samples before and after treatment at 500 °C, respectively.

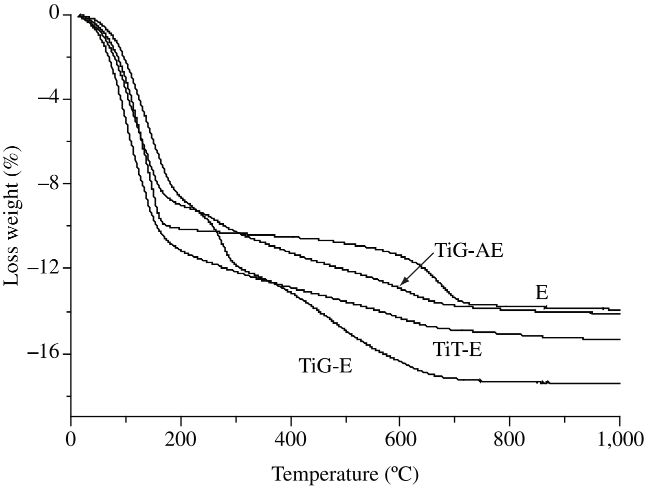
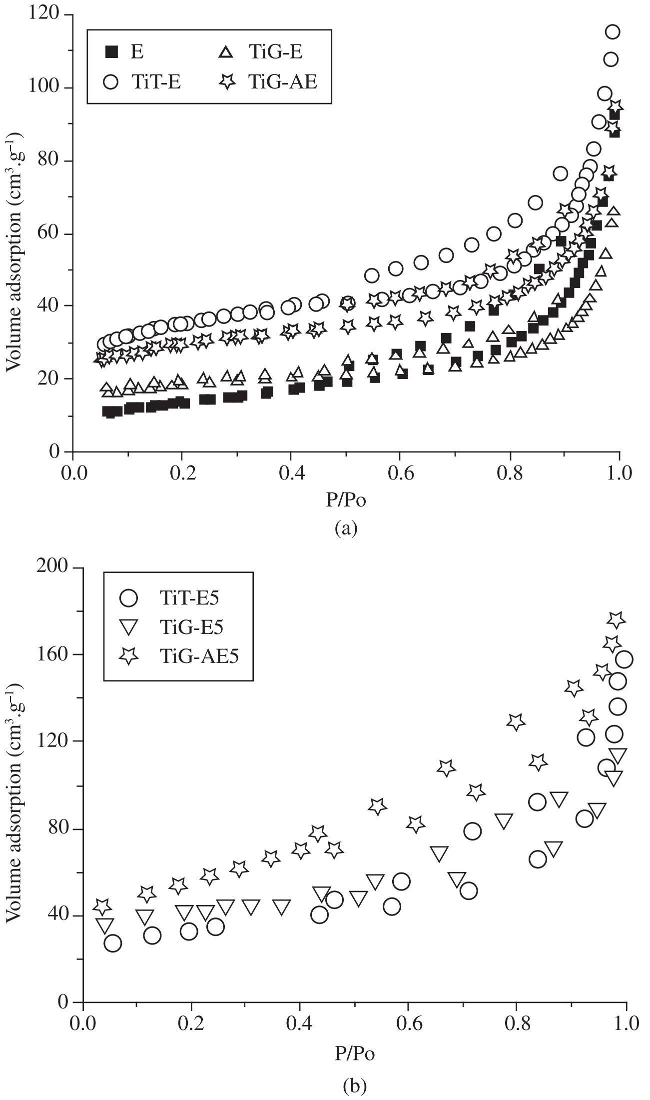


Figure 2. TG diagrams of the montmorillonite clay E with and without OH-Ti treatments.



(a)

(b)

Figure 3. N_2 adsorption-desorption isotherms of the montmorillonite clay E with and without OH-Ti treatments. a) in natural conditions; and b) after thermal treatmet at 500 °C.

The shape of the adsorption-desorption isotherm of the raw sample, E, was H3 type and corresponded to the system by slit-shaped pore according to Gregg and Sing[24], Figure 3a. The adsorption-desorption isotherms of intercalated titanium montmorillonites maintain a form similar to the one of the raw sample, indicating that the pore preserves a similar form, nevertheless, the higher volume adsorbed at low P/Po of the Ti-samples (TiT-E, TiG-E and TiG-AE) indicated a contribution of higher micropore volume. Figure 3b shows the prepared Ti-montmorillonites after 500 °C. The TiT-E5, TiG-E5 and TiG-AE5 isotherms showed a higher total volume adsorbed than without thermal treatment (Figure 3a, Table 4). The isotherms of samples were similar, although the TiG-AE5 showed a higher volume adsorbed in the intermediate zone of the P/Po, indicating a contribution with different mesopore size (Figure 3b). The textural parameters resulting from the analysis of the isotherms are given in Table 4. The BET surface increased after Ti treatment from 46 $m^2.g^{-1}$, original E, to 122, 63 and 102 $m^2.g^{-1}$ for TiT-E, TiG-A and TiG-AE, respectively. The thermal treatment at 500 °C preserved the BET surface for TiT-E (120 $m^2.g^{-1}$) and an increase was observed for montmorillonites treated with Ti and glycerol, TiG-E5 and TiG-AE5 samples that reached 139 and 193 $m^2.g^{-1}$, respectively.

The total volume of the montmorillonite, 0.117 $cm^3.g^{-1}$ (at P/Po = 0.983), in general, also increased after treatment (Table 4). After thermal treatment at 500 °C of the Ti-montmorillonites values duplicated from 0.083 to 0.159 $cm^3.g^{-1}$ for TiG-E and from 0.122 to 0.237 cm3.g^{-1} for TiG-AE, respectively, except for TiT-E that only increased a third, from 0.150 to 0.194 $cm^3.g^{-1}$. The micropore volumes (Vmic) obtained by the high-pressure branch extrapolated to the adsorption axis in t-plots[24] are shown in Table 4. These values increased between 3-6 times after titanium treatments from original montmorillonite. The percentage in micropore volume to total volume contributions were the same (15%) for Ti-montmorillonites. This percentage was maintained after 500 °C thermal treatment for TiT-E. Nevertheless, it was twofold and threefold in samples treated with glycerol, reaching 29 and 36%. Then, the increase in total volume was due to micropore contribution.

The infrared absorption band of the montmorillonite at 3,624 cm^{-1} is attributed to the stretching vibrations of the OH^- groups of Mg-Al-OH and, at 3,454 cm^{-1}, it is related to the presence of H-O-H. The amount of adsorbed water in clays is related to the deformation vibrations of the H-O-H group (1661 cm^{-1}). The bands at 1042 and 798 cm^{-1} are attributed to Si-O stretching vibrations. The bands at 518 and 465 cm^{-1} correspond to deformation vibrations of Si-O-Al^{IV} and Si-O-Si, respectively. The main modification in the IR spectra after titanium treatments can be seen at two different zones as shown in Figure 4. The band at 3,624 cm^{-1} was reduced in intensity and may be attributed to the release of octahedral cations from the structure and to the replacement of interlayers cations by titanium in interlayer spacing, as it was confirmed by chemical analyses (Table 1). The band at 3,454 cm^{-1} attributed H-O-H (Figure 4) was shifted to less wavelength, 3,418, 3,429 cm^{-1}, indicating a high bond of OH- of the titanium species in interlayer spacing.

The slight reduction of the intensity band at 518 cm^{-1} in respect of the intensity band at 465 cm^{-1} (Figure 4) after titanium treatment was indicative that the bond of Si-O-Al^{IV} was modified after Ti treatment, which is attributed to the effect of the pH treatment.

The samples heated at 1,000 °C were analyzed by X ray diffraction and infrared.

The montmorillonite clay is destroyed at 800-900 °C and, generally at 1,000 °C, new phases are starting to form depending on

Table 2. Loss of weight from thermal gravimetric analysis.

	25-200 °C	200-650 °C	650-1000 °C	Total
E	10.0	-	3.87	13.87
TiT-E	11.2	-	4.00	15.20
TiG-E	8.6	6.48	5.27	17.35
TiG-AE	8.8	1.48	3.63	13.95

Table 3. Interlayer spacing of the samples in natural and after heating at 500 °C.

Sample	d (001) Å	Sample	d (001) Å
E	15.0	E-500 °C	09.3
TiT-E	22.0	PTiT-E	18.8
TiG-E	22.0	PTiG-E	19.0
TiG-AE	19.0	PTiG-AE	16.0

Table 4. Textural characteristics. Vtot: total volume; Vmic: micropore volume.

	Total BET surface area $m^2.g^{-1}$	Vtot $cm^3.g^{-1}$	Vmic $cm^3.g^{-1}$	Vmic/Vtot (%)
E	46	0.117	0.004	3
TiT-E	122	0.150	0.023	15
TiG-E	63	0.083	0.013	15
TiG-AE	102	0.122	0.019	15
TiT-E5	120	0.194	0.024	12
TiG-E5	139	0.159	0.046	29
TiG-AE5	193	0.237	0.086	36

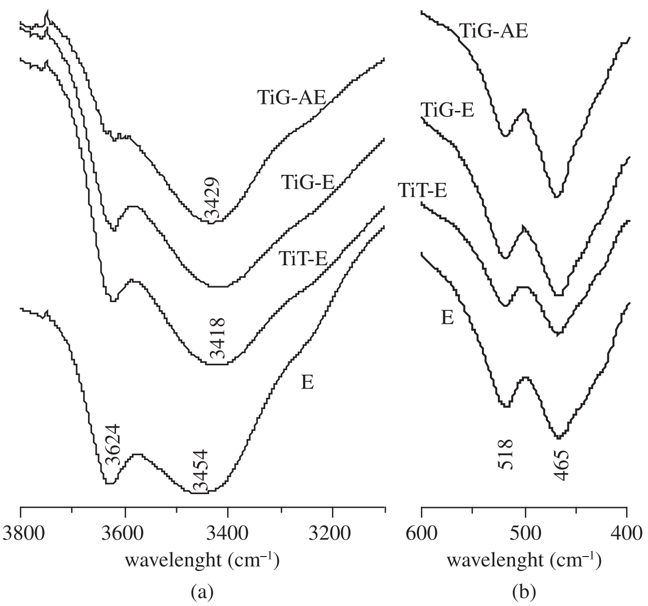


Figure 4. IR spectra of the montmorillonite clay E with and without OH-Ti treatments.

the initial chemical composition[16]. In Table 5 the phases found at 1,000 °C of all samples are shown. The original montmorillonite, E, developed µ-cordierite ($2MgO.2Al_2O_3.5SiO_2$), β-quartz (SiO_2), β-cristobalite (SiO_2) and anorthite ($Ca.Al_2Si_2O_8$) after heating at 1,000 °C, similar as it was found in a previous paper[26]. The β-quartz (SiO_2), β-cristobalite (SiO_2) were preserved in all Ti-samples. Nevertheless, due to the release of interlayer and octahedral cations from the structure after titanium treatment (Table 1), other phases were found. The presence of titanium as anatase in different proportion in the samples and rutile, mainly in TiT-E, are shown in Figure 5, and Table 5. Anatase, rutile and brookite are three phase structures of titanium dioxide and, as the anatase phase shows a higher photocatalytic activity than rutile, the sample TiT-E10 may be considered as better than the other samples obtained.

The IR spectra of samples heated at 1,000 °C are shown in Figure 6. Infrared spectra may be used to identify an oxide and to distinguish between different polymorphism forms[25].

The presence of anatase in TiT-E10, TIG-E10 and TiG-AE10 could be detected at near 695 cm^{-1}[25] and a smaller band at 400 cm^{-1}, attributed to rutile in TiT-E10 sample. The presence of chlorine in the TIT-E sample transforms to rutile at high temperature[27,28]. At 1,000 °C the Si-O stretching and Si-O bending bands shifted to 1,090 cm^{-1} and 470 cm^{-1}, respectively, implying changes in the structure of the tetrahedral sheets. The band at 790 cm^{-1}, attributed to quartz (β-quartz (SiO_2), β-cristobalite (SiO_2)), remained. The presence of a developed intensity broad band centered at 3,450 cm^{-1} of the Ti-samples at a high temperature treatment is attributed to silicate species, $M^{2+}(SiO_4^{=})$, Farmer[25], which is indicative of a new substance, in concordance with an X ray diffraction (Table 5).

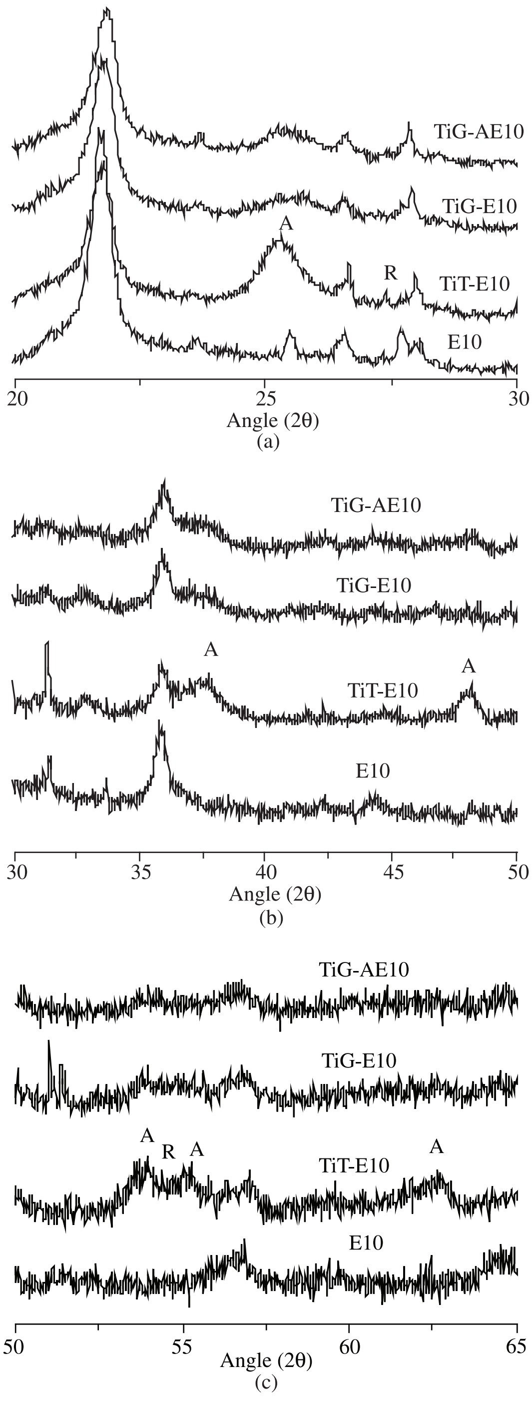


Figure 5. XRD diagrams of the montmorillonite clay E with and without OH-Ti treatments after thermal treatment at 1,000 °C.

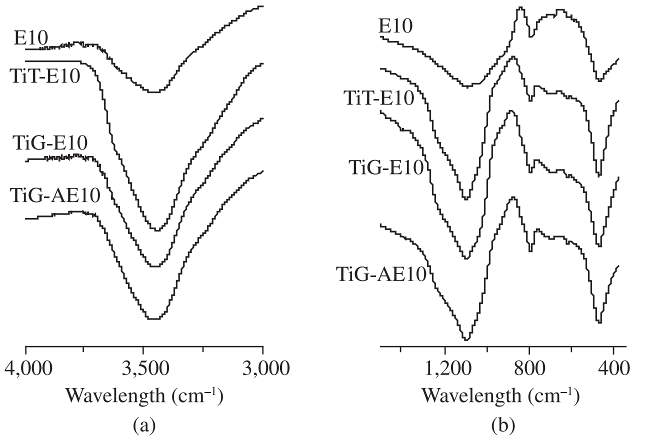


Figure 6. IR spectra of the montmorillonite clay E with and without OH-Ti treatments after thermal treatment at 1,000 °C.

Table 5. Phases at 1,000 °C of the original and Ti-samples.

E-10	TiT-E10	TiG-E10	TiG-AE10
µ-cordierite	β-cristobalite	β-cristobalite	β-cristobalite
β-quartz (impurity)	β-quartz (impurity)	β-quartz (impurity)	β-quartz (impurity)
β-cristobalite	anatase+++	anatase+	anatase++
anorthite	Rutile	-	-
	silicoaluminate	silicoaluminate	silicoaluminate

4. Conclusions

Treatment of montmorillonite clays with two different solutions containing the same amount of titanium addition resulted in a different uptake of titanium, which can be attributed mainly to the type of hydrolyzed OH-Ti solutions used for the treatments and the way OH-Ti species interact with clay.

The treatment of the clay with hydrolyzed OH-Ti solutions resulted in an increase in the interlayer spacing of the clay, and a higher surface area and the micropore volume on the solids. This may be due to the removal of exchangeable interlayer cations and part of structural cation of the clay. The thermal treatment at 500 °C improved the textural properties (surface area, pore volume) and the interlayer spacings slowly decreased but did not collapse (as it is typical in original montmorillonite clay). At 1,000 °C the structure of the clay was transformed to phases of calcined clay and the anatase was the principal compound found in the solid. Nevertheless, the rutile phase was also present in the product obtained without glycerol in the preparation of OH-Ti solutions.

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