N. Frini- Srasra[1,2,*]E.Srasra[1]

DETERMINATION OF ACID–BASE PROPERTIES OF HCL ACID ACTIVATED PALYGORSKITE BY POTENTIOMETRIE TITRATION

[1]Unité de recherche sur les matériaux,CRTE,
Technopole Borj Cedria ,B.P.95-2050 Hammam-Lif Tunisia, nfrini@gmail.com
[2]Département de Chimie, Faculté de Sciences de Tunis, 1060 Tunis, Tunisia

Introduction

Clay minerals have many applications related to adsorption and catalysis, which use the acidic-basic properties of the clay mineral surface. Their textural and structural properties may lead to a wide range of applications especially if activation is able to increase the number and strength of its surface acidic sites. There are some studies on the acid activation of palygorskite: [1] investigated the effect of magnesium on structural alteration and on specific surface area and porosity, and proposed ([2]) a mechanism of acid activation of magnesic palygorskite. [3] studied the structural and textural modification of palygorskite under acid treatment in comparison with a Spanish sepiolite treated under the same experimental conditions. [4] studied the influence of octahedral sheet composition on the kinetics of acid leaching of palygorskite [5, 6], showed that $Tb^{3+}$and La^{3+} increase acid sites number and improve catalytic properties of acid activated palygorskite. Activated palygorskite presents an excellent catalytic activity in the rearrangement of chalcone epoxide reaction ([7]). The rearrangement of α-epoxyketone (chalcone epoxide) was found to yield E(-) enolic form of 1,3-diphenyl-1,3-propanedione indicating that the proton migration has taken place from the less favoured direction of the epoxy ring. It was observed, that acid activated palygorskite give higher yield (90%) of the compound; while, raw palygorskite, kaolinite as well as zeolite 4A have no effect in the rearrangement of chalcone epoxyde.

Although, the properties of acid activated palygorskite has been studied from different point of view, no attempt has been made to study the charge characteristics and especially the point of zero charge (PZC) and the acidic surface constant (pK_a). The determination of PZC based on potentiometric titrations or by mass titration has been the subject of many studies on oxide minerals as well as on layer clay minerals [8–13]. However similar studies for fibrous clay are missing. The PZC of palygorskite and sepiolite was evaluated, until now, only by electrophoretic mobility measurements in dilute suspensions in order to determine the isoelectric point [14, 15].

In this study, we determined the acid base properties on a series of acid activated palygorskite samples. The total surface site and the surface site density were calculated from Gran plots [16]. The acidic surface constants were estimated with three surface protonation models at a specific ionic strength. The point of zero charge was evaluated using the common crossing point of Z vs pH curves performed at different ionic strengths. The effect of activation period on acid-basic properties of palygorskite was investigated.

Material and Methods

Red palygorskite from south Tunisia was used as starting material. The crude sample contains impurities mainly dolomite (8%, measured by calcimetry) and less than 5% of quartz. Crude palygorskite was firstly treated with diluted HCl solution in order to remove carbonate. Then, it was washed with distilled water by centrifugation and dialysis to remove excess chloride. After sedimentation, the purified fraction was dried and grinding. The average size of the grains is <60 µm. Referring to ASTM file (Reference code: 21-0957), Tunisian palygorskite has monoclinic structure (Figure 2). Chemical composition of purified sample is (SiO_2 53.5%, Al_2O_3 11.98%, MgO 12.05%, Fe_2O_3 5.9%, K_2O 0.72%, Na_2O 0.03%, CaO 0.09%, LOI 16% of lost weight) and its structural formula, calculated according to [17], is as follows: $(Si_{7.324}Al_{0.676})(Mg_{2.459}Al_{1.257}Fe_{0.608})(K_{0.125}Na_{0.008}Ca_{0.013})O_{20}(OH)_2(H_2O)_4\ 4(H_2O)$. The cation exchange capacity (CEC) carried out by Kjeldahl method is 23 meq/100g and its specific surface area is 59.7 m^2g^{-1}.

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The purified palygorskite sample was subjected to acid treatment with 2M hydrochloric acid using solid/liquid ratio of 10/100 (w/w) at boiling temperature under reflux for different periods. The resulting solids were washed with distilled water until chloride free and pH was constant.

That Activated and raw palygorskite were characterised by X ray diffraction (Pan analytical X'Pert High Score Plus diffractometer equipped with a Cu anticathode), chemical analysis [18] and specific surface area (Micrometric Autosorb 2050 Analyser), from the nitrogen adsorption isotherms at 77 K by the BET method and after degassing the samples at 150°C with the residual pressure of 10^{-5} mm Hg.

Acid-base properties of palygorskite suspensions were determined using Potentiometric titration. Measurements were performed with a micro burette containing the titrant (NaOH $5.13 \cdot 10^{-2}$M) and a HI 9321 microprocessor pH meter (HANNA Instruments) combination electrode, calibrated with two commercial pH buffers at ambient temperature and in an aerated medium.

For all acid-base titrations, 0,1 g palygorskite was added to a 15 ml water flask and stirred for 24 hours in order to attain equilibrium. Palygorskite suspensions were firstly acidified by HCl 10^{-2}M at pH ca 2 and then titrated with hydroxide solution to an alkaline pH (pH =11). NaCl solution was used to stabilize the system at a fixed ionic strength. Distilled water was added to bring the total initial volume of the suspension to 50 ml. The temperature was held constant at 25 ± 0.5°C. Afterwards, $5.13.10^{-2}$ M NaOH in 0.2 ml increments was used to titrate the suspension up to a pH approximately 11. The equilibrium criterion for each addition of the titrant was the stability of pH value measured. The NaCl electrolyte concentration was adjusted to 0.1, 0.01 and 0.001 mol·L^{-1}. Before each potentiometric titration the aqueous suspensions were equilibrated for about 10 min to each equilibrium pH value.

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For each studied system, Gran plots for the hydroxide titration are made from the experimental data and the two equivalence points Ve_1 and Ve_2 values was determined by linear regression as shown in Figure 1. The Ve_1 values obtained in the acidic region are used to calculate the amount of total protons added to the system. In fact, before the Ve_1 point the added NaOH reacted with the excess of HCl put initially in the system and so we can consider the Ve_1 point as the zero titration point of the palygorskite surface. Therefore, for each titration point, the concentration of total protons added is determined by:

$$H_{TOT} = \frac{-(V_b - V_{e_1})C_b}{(V_0 + V_b)} \quad (\text{molL}^{-1}) \qquad (1)$$

Where V_b is the volume of NaOH added, V_0 is the initial volume of the system and C_b is the concentration of NaOH.

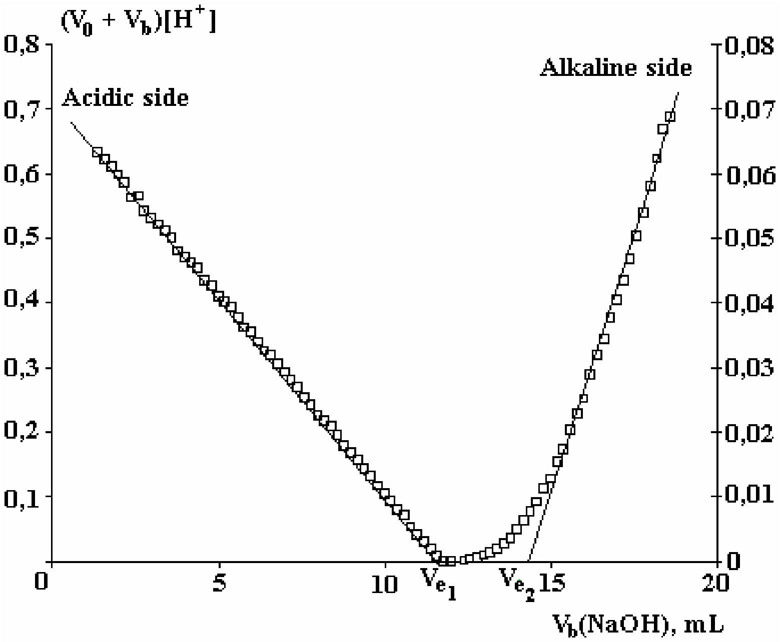

Figure 1. Gran plot of Paly2M25h suspension in 0.1M NaCl

The total surface site per solid weight (Hs) calculated from the two equivalence points in the Gran plot Ve_1 and Ve_2 and the average number of protons reacted per surface site (Z) were defined by the following formula:

$$H_s = \frac{(Ve_2 \text{ -} Ve_1)C_b}{m_s} \quad (\text{mol g}^{-1}) \qquad [2]$$

$$Z = \frac{(H_{TOT} - 10^{-pH} + 10^{(pH-pK_w)}) \times (V_0 + V_b)}{H_s \times m_s} \qquad [3]$$

Where m_s is the solid weight used in the titration system.

The surface acidic constants were determined graphically. Three surface protonation models were considered in this study. The one site-one pK_a model (model I), the two sites-two pk_as model (model II) and the one site-two pK_a model (model III).

Models I and II

For the two models I and II, we assume that the amphoteric surface hydroxyl groups (≡SOH) only release protons to form negatively charged surface sites ($\equiv SO^-$) as shown in the following equation.

$$\equiv SOH \quad \leftrightarrows \quad \equiv SO^- \quad + H^+ \qquad K_a$$

$$K_a = \frac{[\equiv SO^-][H^+]}{[\equiv SOH]} \qquad \text{and from this} \qquad pH = pK_a + \log\frac{[\equiv SO^-]}{[\equiv SOH]}$$

If we consider the dissociation coefficient of (≡SOH) (α) and the electrostatic effects the pH formula becomes:

$$pH = pK_a + n\log\frac{\alpha}{1-\alpha} \qquad [4]$$

Where n is the Henderson-Hasselbach empiric constant and α is expressed by: $\alpha = \frac{[\equiv SO^-]}{[\equiv SOH]+[\equiv SO^-]}$. To determine the $\equiv SO^-$ concentration we considered the charge balance equation and the Gran plot data.

$$[H^+] + [Na^+] = [Cl^-] + [OH^-] + [\equiv SO^-]$$

$$[Na^+] = \frac{C_b V_b}{(V_0 + V_b)} \qquad \text{and} \qquad [Cl^-] = \frac{C_b V_{e_1}}{(V_0 + V_b)}$$

$$\text{Hence, } [\equiv SO^-] = \frac{(V_b - V_{e_1})C_b}{(V_0 + V_b)} + [H^+] \text{ - } [OH^-] \qquad [5]$$

By substituting Eq [1] into Eq [6], [$\equiv SO^-$] can be expressed by:

$$[\equiv SO^-] = -H_{TOT} + 10^{-pH} - 10^{(pH-pKw)} \qquad [6]$$

By using the Z formula (Eq [3]) the $\equiv SO^-$ concentration can be rewritten as follows:

$$[\equiv SO^-] = -\frac{Z \times H_s \times m_s}{(V_0 + V_b)} \qquad [7]$$

The determination of the total surface site ([$\equiv SO^-$] + [≡SOH]) differs from the surface protonation model.

➢ *For the one site-one pK_a model*, we assume that amphoteric surface hydroxyl groups (≡SOH) are homogeneous;

$$[\equiv SOH] + [\equiv SO^-] = \frac{H_s \times m_s}{(V_0 + V_b)} \quad [8] \qquad \Rightarrow \qquad \alpha = \frac{[\equiv SO^-] \times (V_0 + V_b)}{H_s \times m_s} \qquad [9]$$

and by substituting Eq [7] into Eq [9] we obtain

$$\alpha = \text{-}Z \qquad [10]$$

➢ *For the two sites-two pK_as model*, we assume the existence of two types of sites a) weak acidic sites with a concentration of sites [W_a] which dissociate at pH<7, and b) weak basic sites with [W_b] site concentration which dissociate at pH >7.

$$\equiv S_IOH \quad \leftrightarrows \quad \equiv S_IO^- \quad + H^+ \qquad K_{a1}$$

$$\equiv S_{II}OH \quad \leftrightarrows \quad \equiv S_{II}O^- \quad + H^+ \qquad K_{a2}$$

Moreover, when the interface between clay mineral and water has different acidic sites, the successive dissociation of these sites can be defined by their dissociation coefficients α_1 and α_2 corresponding to pK_{a1} and pK_{a2} respectively:

$$\alpha_1 = \frac{[\equiv SO^-]}{[W_a]} \qquad \alpha_2 = \frac{[\equiv SO^-] - [W_a]}{[W_b] + [W_a]}$$

where [W_a] is the concentration of weakly acidic sites between pH 5-7, determined by:

$$\left[W_a\right] = \frac{(V_e - V_{e_1})C_b}{(V_0 + V_b)} \qquad [11]$$

$[W_b]$ is the concentration of weakly basic sites at pH > 7, determined by: $\left[W_b\right] = \frac{(V_{e_2} - V_e)C_b}{(V_0 + V_b)}$ [12]

Ve is the equivalence point determined by the maximum of the differential curve dpH / dV. From Eqs [7] [11] and [12] α_1 and α_2 can be calculated.

Finally, by extrapolating the linear regression curve pH vs. $\log\frac{\alpha}{1-\alpha}$ to zero $\log\frac{\alpha}{1-\alpha}$, we can estimate the pK_a value.

Model III

For model III or the One site amphoteric surfaces model, reasoning and assumptions will be different. An amphoteric site is bifunctional, it can serve both as an acidic and as a basic functional group. It can undergo protonation and deprotonation

$$\equiv SOH + H^+ \leftrightarrows \equiv SOH_2^+ \qquad K_{a1}$$

$$\equiv SOH \leftrightarrows \equiv SO^- + H^+ \qquad K_{a2}$$

The corresponding equilibrium constants are

$$K_{a_1} = \frac{\left[\equiv SOH\right]\left[H^+\right]}{\left[\equiv SOH_2^+\right]} \qquad K_{a_2} = \frac{\left[\equiv SO^-\right]\left[H^+\right]}{\left[\equiv SOH\right]}$$

A mass balance on the surface sites can be written as:

$$[\equiv SOH]_{TOT} = [\equiv SOH] + [\equiv SO^-] + [\equiv SOH_2^+] \qquad [13]$$

The charge balance equation is : $[H^+] + [Na^+] + [\equiv SOH_2^+] = [Cl^-] + [OH^-] + [\equiv SO^-]$ [14]

The surface charge Q is defined by the difference between the positively and negatively charged sites

$$Q = [\equiv SOH_2^+] - [\equiv SO^-] = [Cl^-] - [Na^+] + [OH^-] - [H^+]$$

$$Q = H_{TOT} + [OH^-] - [H^+]$$

$$Q = \frac{Z \times H_s \times m_s}{(V_0 + V_b)} \qquad [15]$$

At pH<< pH_{PZC}, we can neglect the deprotonation (the solid surface is positively charged) and equation [13] becomes $[\equiv SOH]_{TOT} = [\equiv SOH] + [\equiv SOH_2^+]$ and $Q = [\equiv SOH_2^+]$.

On the other hand, When $[H^+]$ is very low (at pH>> pH_{PZC}) the surface acquires a net negative charge and equation [13] becomes $[\equiv SOH]_{TOT} = [\equiv SOH] + [\equiv SO^-]$ and $Q = -[\equiv SO^-]$

Under these conditions, the Ka_1 and Ka_2 approximate to:

$$K_{a_1} = \frac{\left(\left[\equiv SOH\right]_{TOT} - Q\right)\left[H^+\right]}{Q} \qquad K_{a_2} = \frac{-Q\left[H^+\right]}{\left[\equiv SOH\right]_{TOT} + Q}$$

By using Eq. [8] and [15] we obtain:

$$K_{a_1} = \frac{(1-Z)\left[H^+\right]}{Z} \quad \text{and} \quad K_{a_2} = \frac{-Z\left[H^+\right]}{1+Z}$$

And from these

$$pH = pK_{a_1} + n\log\left(\frac{1-Z}{Z}\right) \quad pH = pK_{a_2} - n\log\left(\frac{1+Z}{-Z}\right)$$

By extrapolating the linear regression curves of pH versus $\log\left(\frac{1-Z}{Z}\right)$ and versus $\log\left(\frac{1+Z}{-Z}\right)$, we can estimated the pKa_1 and pKa_2 values.

$$K_{a_1}K_{a_2} = \frac{\left[\equiv SO^-\right]\left[H^+\right]^2}{\left[\equiv SOH_2^+\right]} \quad pH = \frac{pK_{a_1} + pK_{a_2}}{2} + \frac{n}{2}\log\frac{\left[\equiv SO^-\right]}{\left[\equiv SOH_2^+\right]}$$

Near pH_{PZC}, $[\equiv SOH]$ is negligible in comparison with $[\equiv SO^-] + [\equiv SOH_2^+]$.

From this approximation, we obtain

$$pH = \frac{pK_{a_1} + pK_{a_2}}{2} + \frac{n}{2}\log\frac{1-Z}{1+Z} \qquad [16]$$

Results and Discussion

Acid activation

The X ray diffractograms of purified and acid treated samples are presented in Figure 2. The untreated palygorskite has sharp strong reflexions at 10.5, 6.4, 5.4, 4.5, 3.68 and 3.23Å. With increasing treating time, the crystallinity of palygorskite decreased, with a concomitant formation of amorphous utter. The latter can be observed by the appearance and increase of a broad hams at 16-30° 2θ. After 35h treatment only this hams is observed indicating the complete destruction of the clay.

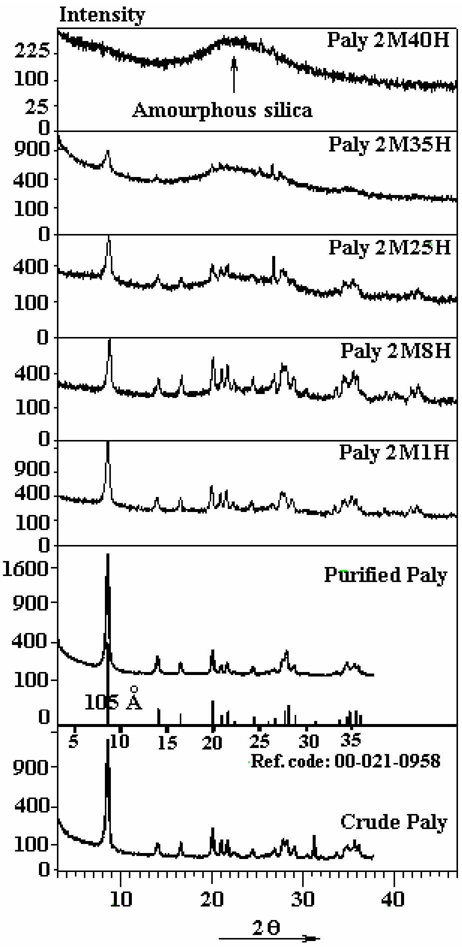

Figure 2. XRD diffractograms of treated and untreated palygorskite

Acid treatment caused a progressive decrease in octahedral cations (Al, Mg and Fe) and a residual enrichment in SiO_2 (Table 1). In the beginning of acid treatment, the decrease in octahedral cations is limited showing the resistance of palygorskite structure and the difficulties of the opening of the channels. Once the H^+ access becomes easy throughout the structure is facilitated, the dissolution becomes rapid and reaches its maximum at 35h. For greater activation times, we note an increase in the octahedral cations, which can be attributed to coprecipitation.

Table 1. Chemical compositions of untreated and acid treated samples expressed in oxide form/100g of calcined sample

Samples	SiO_2	Fe_2O_3	MgO	Al_2O_3
Paly	63.69	7.023	14.34	14.26
Paly2M1h	69.72	6.11	12.54	11.96
Paly2M8h	71.4	5.96	11.89	11.09
Paly2M25h	75.37	4.27	11.18	9.55
Paly2M35h	88.08	0.66	4.60	7.08
Paly2M40h	80.90	3.37	8.12	8.01
Paly2M50h	79.58	3.79	5.76	8.57

BET specific surface area gradually increases with treating time up to 35h (from 59.7 m^2/g to 437 m^2/g) decreasing thereafter (Table 2). Such behaviour has been observed in the past [19, 20, 3]. The initial increase of S_{BET} is attributed to the opening of the structure channels following dissolution of the octahedral sheet and amorphous silica formation; whereas the decrease can be attributed to the condensation of the silanol groups [2]. This confirms that silica contributes to the total amount of the surface area. Moreover, activation increases the total pore volume from 0.3494 to 1.039 cm^3g^{-1} due to development of mesoporosity.

Acid-base properties of acid treated and untreated palygorskite

Determination of total surface site

Hs average values are listed in Table 2. The total surface site of Tunisian palygorskite determined by potentiometric method is 0.518 mmol g^{-1}, comparable to a Brazilian palygorskite (0.476 mmol g^{-1}) determined by N-butylamine thermodesorption [21].

As expected, Hs increases with time of acid activation to 1.53 $mmolg^{-1}$ at 35h, decreasing slightly thereafter.

The site density values (Ds) show that there is no correlation between the total surface site (Hs) and the surface site area S_{BET} (Table 2).

Surface charge

To determine the surface charge of our samples versus pH, we considered the average number of protons reacted per surface site (Z) determined by equation [3].

Figure 3 shows the evolution of Z versus pH for the different samples. Acid activation modifies the shape of the curves as well as the sign of surface charge. Moreover, the behaviour of Z vs pH curves is not the same for all treated samples. Potentiometric titration shows a negatively charged surface in all pH range (3-11) for the untreated palygorskite and for the samples treated for longer time (Paly2M35h Paly2M40h and Paly2M50h). Such behaviour is similar to that observed for illite [22] and for amorphous SiO_2 [23]. This means that within the entire pH range, deprotonation reaction is predominant. Furthermore, in the case of natural palygorskite the Z plots reach a plateau at Z (pH, I) approximately - 0.65, which indicated that more than half of the total surface sites have released their protons. This suggests that the surface is heterogeneous and there are mainly two kinds of surface sites with different hydroxide affinities at the solid/water interface. This plateau is not pronounced for the treated palygorskite samples. When the palygorskite is moderately treated, its surface shows a different behaviour. Depending on pH, its surface can bear net negative or positive or no charge. Therefore, the ≡SOH groups at external surfaces can be protonated and deprotonated under acidic and alkaline pH conditions respectively. The acid activation produces new surface sites having different acid-basic properties.

Determination of zero charge (PZC)

Curves of Z versus pH at different NaCl concentration plotted for different samples. The curves have a common intersection point, at a pH which is considered as a point of zero charge (PZC). As shown in Figure 3 and Table 2, the PZC decreases gradually from about 8.8 in the starting material to about 3.9 in the most heavily treated sample Paly 2M50h. The amount of this shift depended on the acid treatment period. We can conclude that acid treatment produces a shift of the PZC of the sample toward the PZC of the amorphous silica (at about 2-3) [24]. This result is consistent with the fact that Paly 2M50h sample contained 80% of amourphous silica and that no residual palygorskite is present.

Determination of the surface acidic constants

To explain the behaviour of the surface hydroxyl groups three surface protonation models was used. The choice of models is based on the surface charge results. Model I and II are applied when Z is always negative at the entire pH range. In the both models, we considered that only deprotonation reaction is occurring at the solid surface. Model III is used when surface sites can undergo protonation and deprotonation. Thus, we tested model I and II for natural palygorskite. Model I was tested for Paly2M35h, Paly2M40h and Paly2M50h and model III for Paly2M1h, Paly2M8h and Paly2M25h.

We should note that for all the previous calculation, a weakly acidic surface functional group (≡XH) accounting for ion exchange reactions, is neglected because palygorskite has a low cation exchange capacity. Moreover, total number of structural-charge sites which are accessible for Na/H exchange reactions do not exceed 2% of the total CEC [25].

pKa values estimated with different surface protonation models are summarised in Table 3 and fits of the experimental data to the models are shown in Figure 3. For the starting material we obtained a pK_a value between 6.47-6.85 with the one site-one pK_a model and pK_{a1}=5.26-5.9, pK_{a2} = 10.05 -10.64 respectively for the two surface acidic constants when we use the two sites-two pK_a model. If we compare the pK_a values obtained from the two models, we see clearly that the pK_a in model I is comparable to the pK_{a1} in model II. Model I simplifies the heterogeneous palygorskite surface as a system with uniform acid-base properties and simulates the surface acid-base characteristics with the behaviour of the stronger surface sites. However, model II gives better description of the experimental data than model I. Unlike the natural palygorskite, the model I is suitable for the samples treated for a long time (more than 25 hours). pKa values obtained from this model is 8.7–9.3. Application of model III in acid treated samples for a period less than 35 hours, yielded two pKa values: pKa$_1$ in the range 3–4 and pKa$_2$ at about 9.5. If we compare these results with the pKa values of silanol and aluminol groups found in the literature (Table 4), we can conclude that in the natural palygorskite there are two kinds of surface sites aluminol (pKa ≈ 5) and silanol sites (pKa ≈ 10). Acid treatment progress disrupts the 2:1 structure and produces incomplete tetrahedra and octahedra at the edges. Opening of channels allows the H$^+$ access to acidic basal AlOH sites (pKa ≈ 3.4) stronger than edges AlOH sites (pKa ≈ 6.5). Beyond 25 hours of acid treatment, acid activation palygorskite behaves as amorphous silica (pKa ≈ 9).

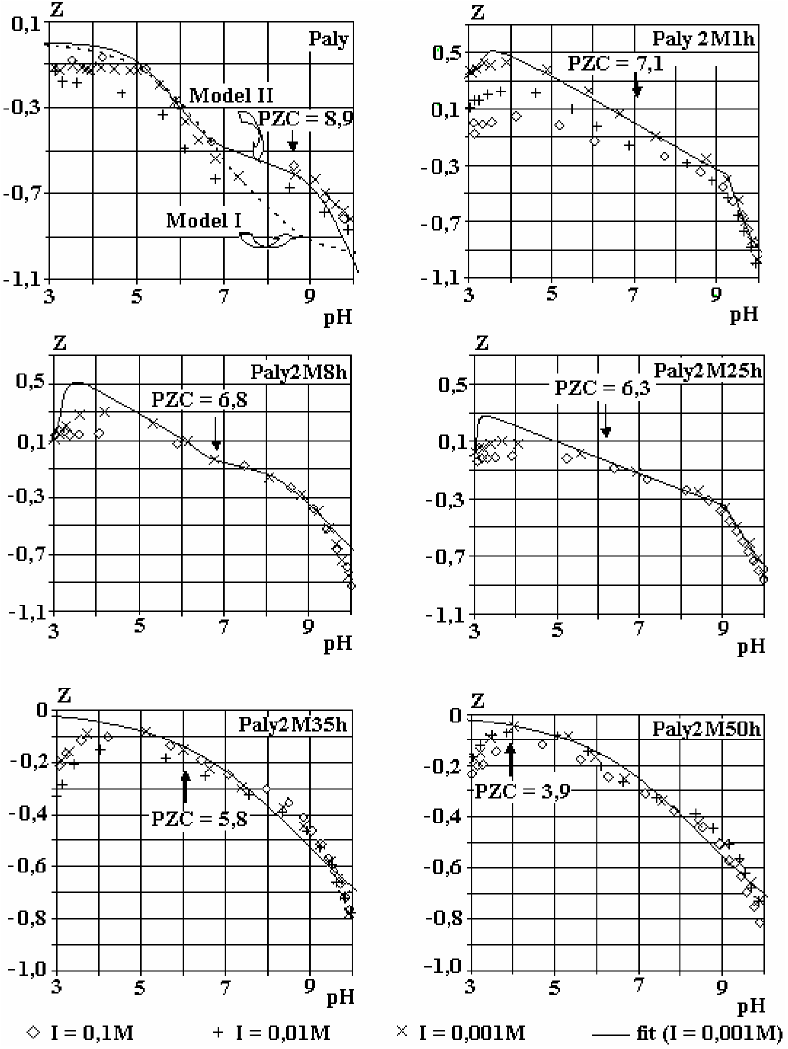

Figure 3. Potentiometric titration curves for different palygorskite samples for each ionic strength.Fits of the experimental data to the models are shown for suspension samples in 0.001M NaCl

Table 2. Surface area, Total surface site surface, site density and point of zero charge of different palygorskite samples

Time (h)	0	1	8	25	35	40	50
Hs (mmol g$^{-1)}$	0.518	0.758	1.003	1.029	1.527	1.435	1.425
S$_{BET}$ (m^{2}g^{-1})	59.7	127.5	161.6	307.2	437.0	325.3	138.3
Ds *(sites nm^{-2})	5.22	3.58	3.74	2.02	2.1	2.66	6.2
PZC	8.9	7.1	6.8	6.3	5.8	4.5	3.9

$* Ds = \dfrac{(H_s \times N_A)}{S_{BET} \times 10^{18}}$ (sites nm^{-2}); Where: N$_A$ is the Avogadro's number (6,02 .10^{23} mol^{-1}) and S$_{BET}$ the palygorskite N$_2$/ BET surface area expressed in m^{2}g^{-1}.

Table 3. pKas values estimated with different surface protonation models

	pKa			**pKa$_1$ - pKa$_2$**			**pKa$_1$ - pKa$_2$ - (pKa$_1$ + pKa$_2$)/2**		
	Model I			Model II			Model III		
	0.1M	0.01M	10^{-3}M	0.1M	0.01M	10^{-3}M	0.1M	0.01M	10^{-3}M
Paly	6.68	6.47	6.85	5.26 10.13	5.46 10.64	5.89 10.05			
Paly2M1h							4.9 9.28 7.05 (6.88)	3.98 9.29 6.64 (6.05)	3.47 9.42 6.45 (7.00)
Paly2M8h							3.38 9.32 6.35 (6.70)		3.32 9.49 6.4 (6.59)
Paly2M25h								3.01 9.51 6.26 (6.90)	3.11 9.37 6.24 (5.87)
Paly2M35h	9.04	8.84	8.84						
Paly2M40h	9.18		9.30						
Paly2M50h	8.69	8.91	8.69						

$\frac{pK_{a_1} + pK_{a_2}}{2}$ Values between parentheses are obtained from Eq [16] by extrapolating the linear regression curves of pH versus $\log\left(\frac{1-Z}{1+Z}\right)$

Table 4. Surface dissociation constants for some aluminium and silica of kaolinite compounds found in the literature

	pka$_1$	pka$_2$	References
AlOH	2.9	9.84	Schindler et al., 1987
SiOH	1.0	4.0	Carroll-Webb and Walther, 1988
AlOH	7.9	9.1	Carroll-Webb and Walther, 1988
SiOH	2.4	6.5	Motta and Miranda, 1989
AlOH -Basal	3.4	8.4	Wieland and Stumm, 1992
AlOH- edges	6.5	8.5	Wieland and Stumm, 1992
SiOH		8.23	Brady and al., 1996
AlOH-edges	2.33	5.28	Brady and al., 1996

Conclusion

The potentiometric titration showed that acid treatment produced an increase in the total surface site number, a shift of the PZC of the sample toward the PZC of amorphous silica depending on the acid treatment period and changes on the surface charge properties. Thus, the modification of palygorskite by acid activation creates new active sites and increases its catalytic properties (such activity, selectivity and thermal stability) and adsorption capacity.

Application of the three surface protonation models leads to reasonable descriptions of the surface properties and their evolution with acid treatment.

REFERENCES

1. *Gonzalez, F., Pesquera, C., Blanco, C., Benito I., Mendioroz, S. and Pajares, J.A.,* (1989a) Structural and textural evolution of Al- and Mg-Rich palygorskites, I. Under acid treatment. *Applied Clay Science,* **4,** 373–388.

2. *Gonzalez, F., Pesquera, C., and Benito, I.,* (1989b) Mecanism of acid activation of magnesic palygorskite. *Clays and Clay Minerals,* **37,** N°3, 258–262.

3. *Myriam, M., Suarez, M., Martin-Pozas, J. M.,* (1998) Structural and textural modifications of palygorskite and sepiolite under acid treatment. *Clays and clay minerals,* **46,** N°3, 225–231.

4. *Corma, A., Mifsud, A., Sanz, E.,* (1990) Kinetics of the acid leaching of palygorskite influence of the octahedral sheet compositions. *Clay Miner.* , **25,** 197–205.

5. *Araujo Melo D.M., Ruiz J.A.C., Melo M.A.F., Sobrinho E.V., Schmall M.* (2000) Preparation and characterization of terbium palygorskite clay as acid catalyst. *Microporous and Mesoporous Materials*, **38**, 345–349.

6. *Araujo Melo D.M., Ruiz J.A.C., Melo M.A.F., Sobrinho E.V., Martinelli A.E.* (2002) Preparation and characterization of lanthanum palygorskite clays as acid catalysts. *Journal of Alloys and Compounds*, **344**, 352–355.

7. *Joy B., Ghosh S., Padmaja P., Lalithambika M.* (2005) A facile 1,2 proton migration of chalcone epoxyde using acid activated palygorskites. *Catralysis communications*, **6,** 573–577.

8. *Noh S. J., James Schwartz A.* (1989) Estimation of the point of zero charge of simple oxides by mass titration. *J. Colloid and Interface Sci.*, **130,** 157–164.

9. *Hayes K. F., Redden G., Ela W. and Leckie J.O.* (1991) Surface complexation models: An evaluation of model parameter estimation using FITEQL and oxide mineral titration data. *J. Colloid Interface Sci.*, **142**, N°2 , 448–469.

10. *Zhuang J., Yu G.R.* (2002) Effects of surface coatings on electrochemical properties and contaminant sorption of clay minerals. *Chemosphere*, **49,** 619–628.

11. *Schroth B. K., Sposito G.* (1997) Surface charge properties of kaolinite. *Clays and Clay minerals*, **45,** N°1, 85–91.

12. *Avena M., de Pauli C.P.* (1998) Proton adsorption and electrokinetics of an Argentinean montmorillonite. *J. Colloid and Interface Sci.* , **202**,195–205.

13. *Kriaa A., Hamdi N., Srasra E.* (2005) Determintion of point of zero charge of Tunisian kaolinites by potentiometric and mass titration methods. *Analytical Chemistry: an Indian Journal*, **2,** Issue1.

14. *Neeman A. and Singer A.* (2000) Rheological Properties of aqueous Suspension of Palygorskite. *Soil. Sci. Soc. Am. J.*, **64,** 427–436.

15. *Alkan M., Demirbas O., Dogan M.* (2005) Electrokinetic properties of sepiolite suspensions in different electrolyte media. *J. Colloid Interface Sci.*, **281,** 240–248.

16. *Gran G.* (1952) Determination of the equivalence point in potentiometric titration. Part II. *Analyst*, **77**, 661.

17. *Bailey S.W.* Structures of layer silicates: in cristal structures of clay minerals and their X-ray identification, Brindley G. W. and Brown G., eds., Mineralogical Society, London, 1980, p. 2–123.

18. *Solgic Z. and Marjanovic-Krajovan Y.* (1968) Méthode rapide d'analyse de SiO_2, Fe_2O_3, Al_2O_3, TiO_2, CaO et MgO dans une bauxite: analyse rapide de calcaire et de dolomite. *Chimie Analytique*, **50,** 122–127.

19. *Vicente, M. A., Lopez-Gonzalez, J.D., Banares M. A.,* (1994) Acid activation of a spanish sepiolite : physicochemical characterization, free silica content and surface area of products obtained. *Clay Miner.*, **29,** 361–367.

20. *Suarez, M., Flores, L.V., Vicente M. A., Martin-Pozas, J. M.,* (1995). Acid activation of palygorskite with HCl : Development of physico–chemical, textural and surface properties. *Applied clay Sci.*, **10,** 247–258.

21. *Ruiz J. A. C., Melo D. M.A., Souza J. R. and alcazar L. O.* (2002) Determination of total acid in palygorskite chemically modified by n-butylamine thermodesorption. *Material research*, **5,** 173–178.

22. *Du Q., Sun Z., Forsling W.and Tang H.* (1997) Acid-base properties of aqueous illite surfaces. *J. Colloid Interface Sci.*, **187,** 221–231.
23. *Dove P. M. and Craven C.M.* (2005) Surface charge density on silica in alkali alkaline earth chloride electrolyte solutions. *Geochim. Cosmochim. Acta* , **69,** N°21, 4963–4970.
24. *Sverjensky D.A.* (2005) Prediction of surface charge on oxides in salt solutions: Revisions for 1:1 (M^+L^-) electrolytes, *Geochim. Cosmochim. Acta*, **69,** N°2, 225–257.
25. *Wanner H., Albinsson Y., Karnland O., Wieland E., Wersin P. and Charlet L.* (1994) The acid/base chemistry of montmorillonite. *Radiochimica Acta*, **66/67,** 157–162.

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Summary

The surface acidity of raw and acid activated palygorskite clay were studied by acid-base potentiometric titration. The Gran plot method was applied for the hydroxide titration and the total surface site (Hs) and the average number of protons reacted per surface site (Z) of palygorskite samples at a given ionic strength were calculated. Acid treatment increases the clay acidity and modifies its surface charge. The point of zero charge value, determined by the common crossing point of Z vs pH curves performed at different ionic strengths, decrease from 8.8 to 3.5 with acid treatment period. For illustrating the acidic characteristics of treated and untreated palygorskite surface, three surface protonation models are tested : a/ the one site-one pK_a model, $\equiv SOH \leftrightarrows \equiv SO^- + H^+$, b/ the two sites-two pK_as model, $\equiv S_IOH \leftrightarrows \equiv S_IO^- + H^+$ and $\equiv S_{II}OH \leftrightarrows \equiv S_{II}O^- + H^+$ and c/ the one site-two pK_a model, $\equiv SOH \leftrightarrows \equiv SO^- + H^+$ and $\equiv SOH + H^+ \leftrightarrows \equiv SOH_2^+$. The three surface protonation models describe sufficiently of the surface properties and their evolution with acid treatment.