

EFFECT OF HEATING ON PALYGORSKITE AND ACID TREATED PLYGORSKITE PROPERTIES

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Introduction

Palygorskite has fibrous structure consisting of talc-like ribbons parallel to the fibre axis, assembled in such way that the tetrahedral sheet is continuous throughout but inverts apical directions in adjacent ribbons, each ribbon alternating with channels along the fibrous axis. Octahedral cations present at the edges of the ribbons, complete their coordination with water molecules (coordination water). Additional water molecules are hydrogen bonded to the water of coordination both at the external surfaces and within the channels (zeolitic water) [1].

Important characteristics relating to palygorskite applications are particle size, particle shape, surface area, porosity, acidity and surface chemistry, together with other physical and chemical properties specific to a particular application. All of these mineral properties are affected by thermal and chemical treatment such acid activation.

Since the diffusion mechanism in solids depends on the pore size distribution, knowledge of its surface, texture and porosity is necessary to determine the sorptive response to the molecule of different size and shape.

The dehydration of palygorskite has been studied by many authors [2-7] showed that water is present in three different structural positions: Adsorbed and zeolitic water, bound water or crystal water and hydroxyl water. The bound and hydroxyl water are more strongly held in the palygorskite structure and require a higher temperature for their expulsion. All these studies were concerned with the structural changes taking place above 300°C, which are due to the loss of bound and hydroxyl water, because loss of zeolitic water was considered to have no affect on the structure.

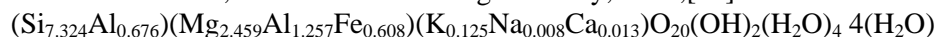
The temperature at which bound water begins to be expelled varies from sample to sample and is probably dependent on the number of factors, one of which is Al/Mg ratio, sample rich in Mg generally lose their bound water at higher temperatures [8].

Acid activation of sepiolite and subsequent heat treatment were investigated by several authors. Study of specific surface area and determination of surface acid centres during thermal treatment of acid pre-activated samples were established respectively by Lopez Gonzalez et al., 1981, [9] and Bonilla et al., 1981, [10]. Changes in pore structure were investigated by Rodriguez et al., 1981, [11] and Balci, 1996 and 1999, [12,13]. However, similar studies for palygorskite are missing.

The aim of this research is to study, by the technique ATG-ATD, DRX and adsorption isotherms of N₂, the textural and textural changes caused by thermal treatment of palygorskite and acid activated palygorskite. In order to prove such changes we first, verified the temperatures at which there is mass loss by thermal analysis and then every sample was subjected to thermal treatment at the fixed temperature for four hours. The effects of thermal treatment on the pore structure of palygorskite and acid treated palygorskite were investigated.

Material and methods

Red palygorskite from south Tunisia was used as starting material. Its chemical composition is (SiO₂ 53.5%, Al₂O₃ 11.98%, MgO 12.05%, Fe₂O₃ 5.9%, K₂O 0.72%, Na₂O 0.03%, CaO 0.09% and 16% of lost weight) and its structural formula, established according to Bailey, 1980,[14] is as follows:



The purified palygorskite sample was subjected to an acid treatment. The acid activation of the fibrous clay was obtained by contacting the clay with 2M solution of chlorhydric acid (solid/liquid ratio was 10/100 (w/w)) at boiling temperature under reflux for different periods. After the treatments, the resulting solids were washed with distilled water until no chloride anions could be detected and no increasing pH was observed. Chemical compositions of untreated and acid treated samples in octahedral and tetrahedral cations expressed in oxide form/100g of calcined sample were given in table 1.

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

Samples	SiO ₂	Fe ₂ O ₃	MgO	Al ₂ O ₃
Paly	63.69	7.023	14.34	14.26
Paly2M2h	69.72	6.11	12.54	11.96
Paly2M17h	71.4	5.96	11.89	11.09
Paly2M40h	80.90	3.37	8.12	8.01

Resulting samples and the purified palygorskite were heated at required temperature (150°C, 350°C, 550°C and 750 after each water lost for 4 hours. The DTA and ATG curves were recorded simultaneously at an average heating rate of 10°C/mn with simultaneous thermobalance analyser (type Setaram 92).

Activated and no activated palygorskite before and after heating at different temperature were characterised by Chemical analysis [15], X ray diffraction (using Pan analytical X'Pert High Score Plus diffractometer equipped with a Cu anticathode) and specific surface area (using Micrometric Autosorb 2050 Analyser). The latest was determined from the nitrogen adsorption isotherms at 77 K by the BET method and after out degassing the samples at 150°C with the residual pressure of 10⁻⁵ mm Hg.

Results and discussion

DTA curves

DTA curves of untreated and acid treated palygorskite were presented in Figure 1. The DTA curve of the untreated palygorskite shows three endothermic reactions with peak maxima at 130°C, 238°C and at 489°C. This maxima shift to low temperature with increasing acid treating time. DTA curve of Paly2M40h sample was different: peaks were board and appear at low temperature 100, 170 and 292°C respectively indicating at this stage of acid treatment the crystal structure undergoes drastic change.

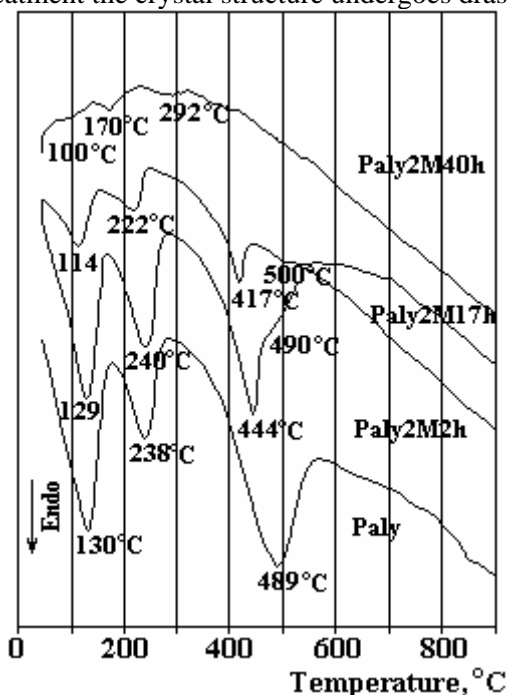


Fig. 1. DTA curves of untreated and acid treated palygorskite

TGA-DTGA curves

Figure 2 show the relative loss of weight of the original and acid treated palygorskite. The loss of weight was caused by the release of the different water molecules in palygorskite (hygroscopic water,

zeolitic water, bound water and structural water), all of which leave the mineral at different temperatures up thermal treatment. The dehydration was completed at about $\theta = 750^{\circ}\text{C}$. In the low temperature region ($<180^{\circ}\text{C}$) DTGA curve shows two clear peaks corresponding to the weight losses of 7.8 and 5.34 %. The two effects have been attributed to loss of Hygroscopic water and of some zeolitic water.

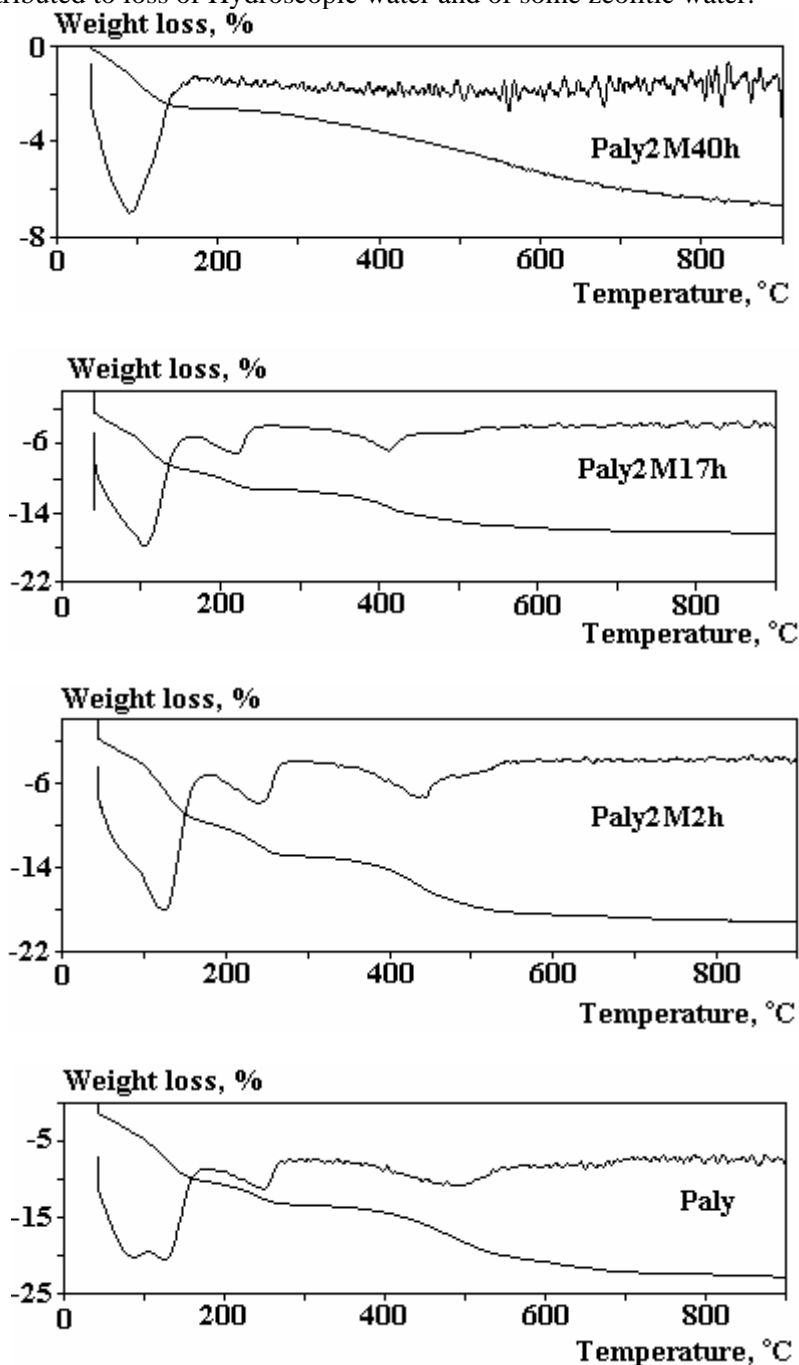


Fig. 2. TGA and DTGA curves of palygorskite before and after acid activation

Theoretically palygorskite contains four zeolitic water molecules, four bound water molecules and two hydroxyl groups owing the loss of one molecule of water. On the other hand, according to chemical formula one molecule of water presents 2.6% of the weight of calcined sample. Experimental data (Table 2) show an overlapping of different losses. Determination of the water molecule number released at different stage shows that more than half of the zeolitic water is lost by 180°C . The rest of zeolitic water is lost between $180\text{-}300^{\circ}\text{C}$. The loss of structural water occurred at higher temperature. The corresponding weight loss on the TGA curve amount (12.4%) has been assigned to the release of 3.77 molecules of bound water together with water from hydroxyl groups.

Table 2. Thermal weight loss (%) at various stages of thermal analysis of untreated and acid treated palygorskite

	$\theta_1 = 25-180^\circ\text{C}$		$\theta_2 = 180-300^\circ\text{C}$	$\theta_3 = 300-750^\circ\text{C}$
	$\theta < 120^\circ\text{C}$	$120 < \theta < 180^\circ\text{C}$	4	12.4
<i>Paly</i>	7,8 3 H ₂ O H ₂ O _{Zeol} ↘ 2.36H ₂ O _{Hyg} + 0.74H ₂ O _{Zeol}	5,34 2.05	1.54 H ₂ O 0.33 H ₂ O _B + 1.21 H ₂ O _{Zeol}	4.77 H ₂ O 3.77 H ₂ O _B + H ₂ O _{Hyd}
<i>Paly2M2h</i>		11.76	3.92	6.86
<i>Paly2M17h</i>		10.87	3.08	5.52
<i>Paly2M40h</i>		2.75	4.33	

H₂O_{Hyg} : Hygroscopic water; H₂O_{Zeol} : zeolitic water; H₂O_B: Bound water and H₂O_{Hyd}: Hydroxyl water

Acid-treated samples showed different thermal behaviour due to their rearranged crystal structure and their chemical composition. Acid activation caused the removal of some parts of hygroscopic and zeolitic water before heat treatment. Consequently, the observed weight loss up to 300°C was about 14% instead of 17.14%. Moreover, acid treatment causes the removal of Mg and Al during which some of the bound water and structural water associated with the Mg and Al coordinate may be taken away before thermal dehydration. The weight loss observed between 300-900°C was approximately half of the value observed for the untreated mineral over the same temperature range. Similar behaviour was observed for sepiolite [12, 13, 16, and 17].

The water content in the fully amorphized sample (*Paly2M40h*) is lower than in the original and no total destroyed samples. In this case, TGA curve show only two weight losses (corresponding to 7.08%) and DTGA curve enabling the detailed determination of the dehydration and dehydroxylation steps.

X ray diffraction

The X ray diffractograms of purified and acid treated samples heated at different temperature are presented in figure 3. The untreated palygorskite has sharp strong reflexions at 10.5, 6.4, 5.4, 4.5, 3.68 and 3.23Å. With increasing acid treating time, the crystallinity of palygorskite decreased, with a concomitant formation of amorphous matter. The latter can be observed by the appearance and increase of broad humps at 16-30° 2θ. After 40h treatment only this hump is observed indicating the complete destruction of the clay. When the untreated material was heated at 350°C for 4 hours, the 10.5Å reflection decreased and the new reflections at 9.05 and 4.49Å appeared. These reflections were considered to be due the presence of palygorskite anhydride [18]. The presence of both sets of reflections in the diffraction pattern implies that dehydration is nonuniform, part of the structure being dehydrated, while part remains intact. The 10.5 and the 9.05Å reflections disappeared at 550°C. After treatment at 750°C the structure was broken into amorphous phase. The diffractograms of both *Paly2M2h* and *Paly2M17h* samples show the presence of palygorskite anhydride, only after heating at 550°C while *Paly2M40h* isn't affected by thermal treatment.

Specific surface

The change in the pore structure and properties resulting from treatment with HCl 2M solution for various periods of time were investigated. Nitrogen adsorption-desorption isotherms of the original and acid treated samples are shown in figure 4-a. Data resulting from the adsorption isotherms concerning the textural characteristics are given in table 3. Nitrogen adsorption-desorption isotherms for natural and activated palygorskite correspond to type II in IUPAC classification with small hysteresis loops. The type of these isotherms is the same in palygorskite and activated solids and persists even in the 2M40H sample, which is mainly formed by the silica generated during acid attack. The value of surface area (calculated by application of the BET equation) increases as treatment progresses. Natural palygorskite has a surface area of 67.4 m²g⁻¹. The increase in the surface area from natural palygorskite to sample treated 2M at different time is mainly related to the elimination octahedral cations and generation of silica. No creation of microporosity is observed but activation increases the total pore volume from 0.0662 to 0.2902 cm³g⁻¹ due to development of mesoporosity.

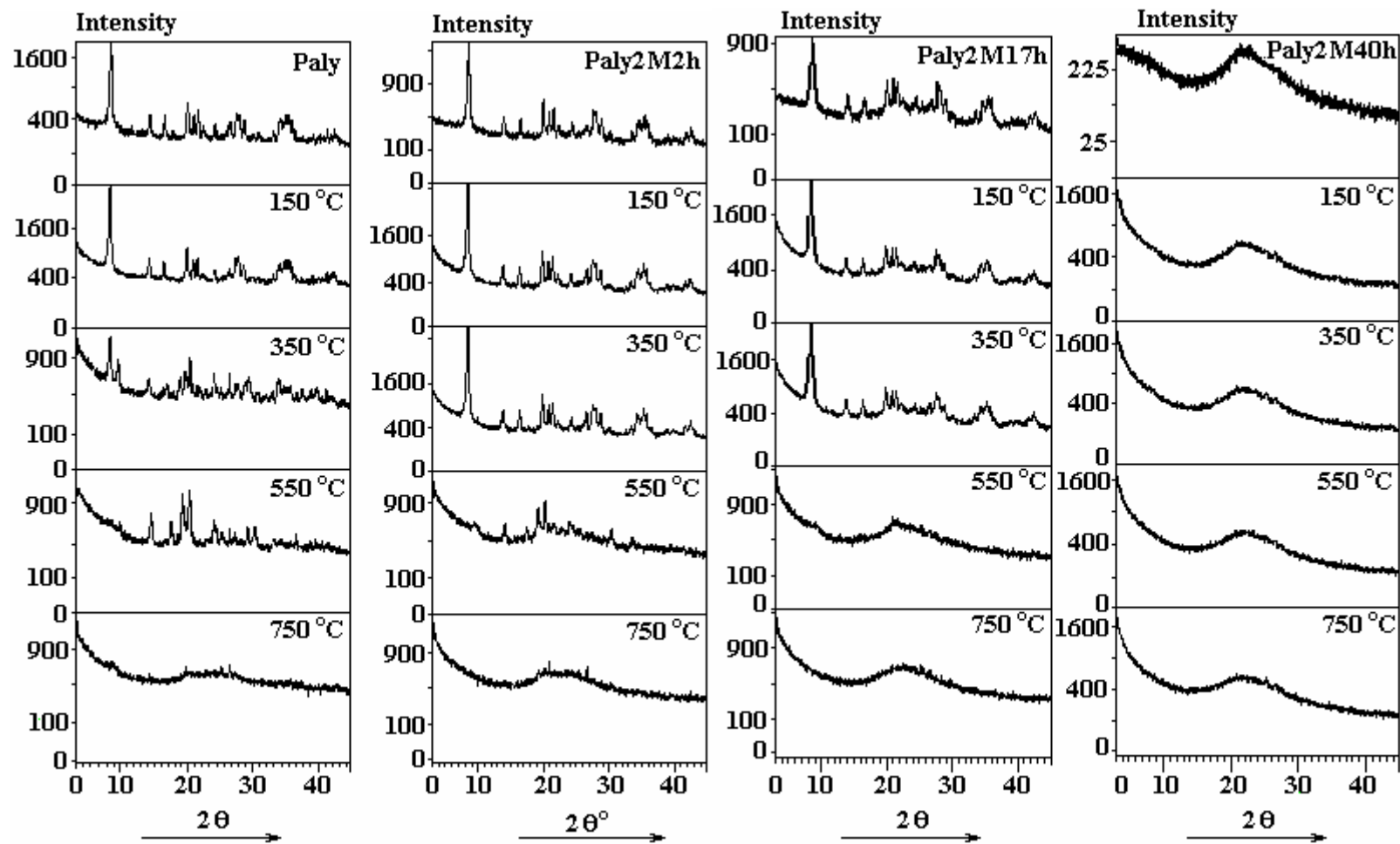


Fig 3. X-ray diffractograms of different samples as function of temperature of thermal treatment

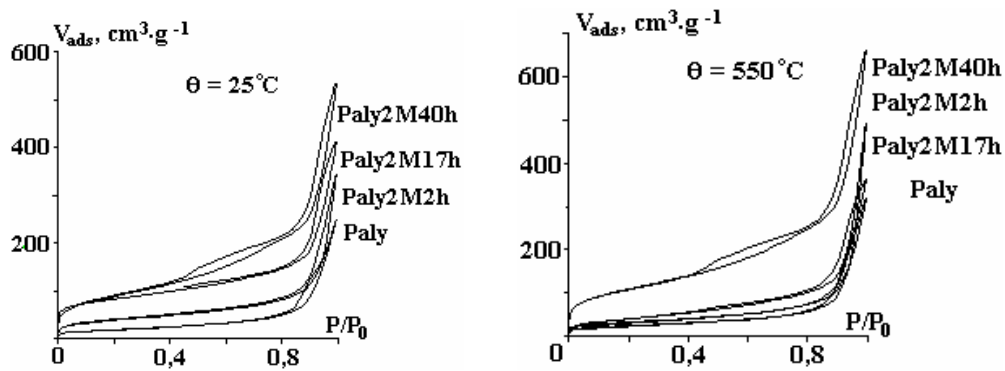


Fig. 4. Nitrogen adsorption-desorption isotherms of the original and acid treated samples at 25°C (a) and 500°C (b)

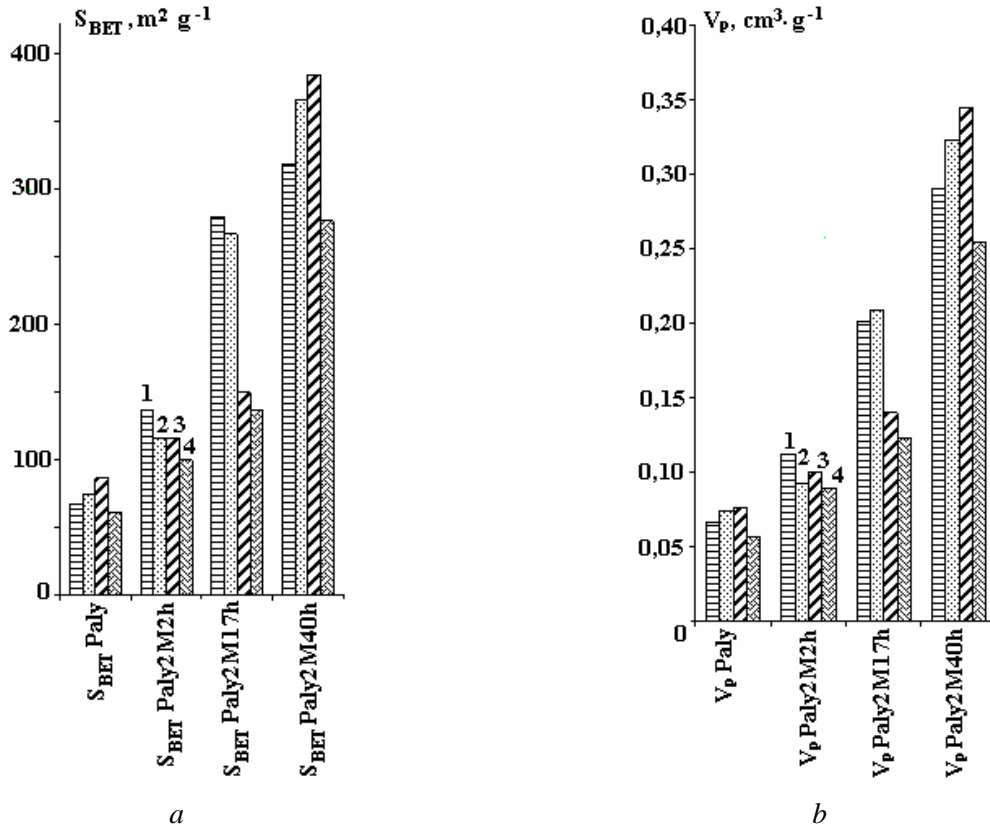


Fig.5. Specific surface area (a) and pore volume (b) evolution with thermal treatment. 1 – 25; 2 – 350; 3 – 550; 4 – 750 °C

Table 3. Textural data of different samples as function of thermal treatment temperature

θ °C	Paly		Paly2M2h		Paly2M17h		Paly2M40h	
	S_{BET} $m^2 g^{-1}$	V_p $cm^3 g^{-1}$	S_{BET} $m^2 g^{-1}$	V_p $cm^3 g^{-1}$	S_{BET} $m^2 g^{-1}$	V_p $cm^3 g^{-1}$	S_{BET} $m^2 g^{-1}$	V_p $cm^3 g^{-1}$
25	67.4	0.0662	136.9	0.1123	279.1	0.0096	317.6	0.2902
350	74.2	0.074	114.9	0.0929	266.5	0.2090	365.9	0.3225
550	85.9	0.0763	116.2	0.1003	149.1	0.1398	384.2	0.3445
750	60.7	0.0566	99.4	0.0891	136	0.1232	276	0.2539

Thermal treatment doesn't affect type of adsorption-desorption isotherme (Figure 4-b). However, during dehydration, the pore structure and surface area of the mineral are affected due to changes in the crystal structure (Table 3). Evolution of specific surface area and pore volume given in figure 5, shows different behaviours with thermal treatment. In both samples natural and 2M40h the surface increases first as adsorbed and zeolitic water are eliminated, until a maximum is reached. Next, up to 550°C, a sudden drop occurs. For Paly 2M2H and Paly2M17h samples surface area and porosity decrease continually. The heat

treatment at 750°C produces a noticeable decrease of surface area caused by closure of mesoporosity for all the samples.

Comparing unheated samples to ones treated at 750°C we notice that Paly2M17h sample has the most altered structure its specific surface area decrease to 136 from 279 m²g⁻¹.

Conclusion

XRD study shows that deshydration is nonuniform. Thermal analysis shows an overlapping of different water losses. N₂ adsorption-desorption data reveal textural modifications either by chemical and thermal treatment. The removal of zeolitic water molecules from the channels of the mineral causes an increase both in the BET surface area and porosity. On the other hand, the acid treatment caused the leaching of some inorganic parts of the mineral other than the removal of water. This leaching might decrease the strength of the pore walls which results in the pore wall opening. Hence, acid pre-treatment might increase the amount of meso and macropore volumes. The presence of macropore and mesopore (pores with larger dimensions) play a significant role where adsorption and /or chemical reaction take place.

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Summary

The behaviour of palygorskite as an adsorbent or catalyst support is governed mainly by the magnitude of its surface areas and degree of surface activity. Most heterogeneous catalytic reactions take place at elevated temperature. It is important and necessary to know the possible changes in physico-chemical properties and hence the catalytic activity due to the thermal treatment. The present work investigates the effect of heat treatment on the surface and textural properties of palygorskite and acid activated palygorskite. Samples were heated at required temperature (150°C, 350°C, 550°C and 750°C) for four hours. Chemical analysis, X ray diffractions, thermal analysis and textural properties evaluated on the basis of nitrogen adsorption have been reported for different samples. Acid-treated samples showed a shift of DTA curves maxima to low temperature with increasing acid treating time. The weight loss observed between 300-900°C was approximately half of the value observed for the untreated mineral over the same temperature range. On heating, water molecules are removed causing changes in the BET surface area and the porosity. The modification as function of the temperature differs with sample. However, at 750°C noticeable decrease of surface area, attributed to closure of mesoporosity, was observed for all the samples.