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Effect of salt modification and acid activation on ethylene adsorption properties of sepiolite

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Abstract The adsorption of ethylene (C_2H_4) on sepiolite from Eskişehir, Turkey and on its salt modified forms (NaS, KS, CaS and MgS) and treated with 1, 3 and 5 M HCl solutions (SH, S3H and S5H) was investigated. The sepiolite samples were characterized using X-ray diffraction, X-ray fluorescence, thermogravimety, differential thermal analysis and N_2 adsorption methods. The C_2H_4 adsorption isotherms of all clay samples were obtained at 20 °C up to 37 kPa. The uptake of C_2H_4 decreased as HS $>$ CaS $>$ NaS $>$ S $>$ MgS $>$ KS $>$ H3S $>$ H5S for sepiolite samples. Capacity of sepiolites for C_2H_4 ranged from 0.478 to 0.622 mmol/g. It was found that the adsorbed amount of C_2H_4 on sepiolite samples decreased with increasing acid concentrations.

Keywords Adsorption · Ethylene · Sepiolite · XRD · TG–DTA

1 Introduction

Ethylene gas (C_2H_4) is an important plant hormone that is naturally produced in confined fruit or vegetable storage. It stimulates ripening of fruits, leading to maturity and senescence and opening of flowers (Yang and Hoffman 1984; Abeles et al. 1992; Salveit 1999; Knee 2002; Chow and McCourt 2006). Furthermore, accumulating of trace amounts of C_2H_4 during the storage period may result in a number of specific postharvest disorders and shorten the harvest shelf life. For example, the premature ripening and softening of agricultural products, the loss of green colour and the fading and wilting flowers are common problems when C_2H_4 concentrations have not been carefully controlled and maintained at an acceptable level. Controlling C_2H_4 accumulation in the storage will extend the shelf life of fruit and vegetables and maintain their freshness for a much longer period of time (Vermeiren et al. 1999; Bower et al. 2003). Therefore, excessive amounts of C_2H_4 should be removed from the storage room.

Sepiolite $Si_{12}O_{30}Mg_8(OH)_4(H_2O)_4 \cdot 8H_2O$, is a hydrated magnesium-silicate of fibrous morphology, with fine microporous channels of dimensions 3.7×10.6 Å^2 running parallel to the fibre axis (Brauner and Preisinger 1956). The presence of microporous and channels in sepiolite are responsible for its absorption and adsorption properties. Sepiolite has a high adsorptive capacity for many gases and vapours, especially when dimensions of the sorbate molecules allow them to penetrate into channels of the sepiolite (Molina-Sabio et al. 2001; Matsuda and Ikeya 2002; Erdoğan Alver et al. 2008, 2012; Sakızcı et al. 2011) Adsorption is due to the presence of active adsorption centres on sepiolite surfaces (oxygen ions on the tetrahedral sheet of the ribbons, water molecules coordinated to the Mg ions at the edges of the structural ribbons, and SiOH groups along the fibre axis). Isomorphic substitutions of Si^{4+} in the tetrahedral sheet of the mineral lattice with Al^{3+} constitute negatively charged adsorption sites. These sites are occupied by exchangeable cations, which compensate the electrical charge. The predominant exchangeable cation is Mg^{2+} (Galan 1996).

Acid treatment of clay minerals is a useful method for enhancing the structural and adsorption properties. This process changes their surface area and the number of acid centers by disaggregation clay particles, elimination of metal-exchange cations and proton exchange. In the

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activation process of the sepiolite by acid treatment, dissolution of the Mg^{2+} cations from structure takes place and then sepiolite transform into amorphous fibrous silica. The loss of octahedral cations due to acid treatment produces new acid cites in the clay structure, thus increasing the specific surface area and porosity. The activation of natural clay surfaces by acid treatment has been studied extensively (Abdul-Latif and Weaver 1969; Jimenez Lopez et al. 1978; Bonilla et al. 1981; Corma et al. 1984; Gonzalez et al. 1984; Campelo et al. 1989; Çetişli and Gedikbey 1990; Vicente Rodriguez et al. 1994; Balcı 1996, 1999; Myriam et al. 1998; Dekany et al. 1999; Yebra-Rodríguez et al. 2003).

Adsorbents such as potassium permanganate ($KMnO_4$) (Jin et al. 2000; Alvarez and Garcia 1990; Shy et al. 2005; Liu et al. 2006) and activated carbon (Reich et al. 1980; Choi et al. 2003; Zhu and Groen 2005; Jeong et al. 2007) have been widely used to control accumulation of C_2H_4. $KMnO_4$ can contaminate food products while activated carbon is not selective to C_2H_4 adsorption (Faubion and Kader 1996; Suslow 1997; Peiser and Suslow 1998; Smith et al. 2009). Nevertheless, a limited number of studies have been carried out on the adsorption of C_2H_4 by clay-based samples and other natural adsorbent materials. Choudary et al. (2002) reported that the amounts of C_2H_4 adsorbed on Ag^+-impregnated clay-based adsorbent olesorb-1 at 30 and 60 °C at 760 Torr were 1.17 and 0.85 mmol/g, respectively. The separation of C_2H_4/ethane was studied on an $AgNO_3$ dispersed clay adsorbent (Park et al. 2004). Cho et al. (2005) prepared π-complexation adsorbents by dispersing $AgNO_3$ on clay and aluminosilica substrate, respectively. They reported that the capacities of C_2H_4 adsorption of $AgNO_3$/ALSG and $AgNO_3$/clay at 25 °C and 760 Torr were 1.81 and 1.26 mmol/g, respectively. Erdoğan et al. (2008) investigated the C_2H_4 adsorption properties of natural clinoptilolites modified with K^+, Na^+ and Ca^{2+} ions and reported that the natural clinoptilolites adsorbed more C_2H_4 than their modified forms. Saini et al. (2011) found that adsorption capacities of clay-based adsorbents PCH1 and PCH2 for C_2H_4 at 25 °C were 2.32 and 2.37 mmol/g, respectively. Erdoğan Alver et al. (2012) studied the C_2H_4 adsorption properties of natural sepiolite, kaolinite and bentonite samples treated with 1 M HCl solution at 4 and 20 °C up to 37 kPa. They reported that the retention of C_2H_4 by natural and acid-treated sepiolites (0.424–0.859 mmol/g) was greater than that exhibited by natural and acid-treated bentonites (0.068–0.144 mmol/g) and by kaolinites (0.014–0.061 mmol/g) at both temperatures.

There are large sepiolite reserves in different regions of Turkey. However, there has not been enough study about the thermal, structural and C_2H_4 adsorption properties of natural sepiolite and those of salt modified and acid-treated forms. Therefore, the novelty of this study is the investigation of the chemical compositions, thermal and structural properties of natural sepiolites after salt modified and acid-treated and to evaluate their capacities for C_2H_4 removal.

2 Experimental

2.1 Materials and methods

The sepiolite sample was obtained from Eskişehir, Turkey. The clay samples were air dried at room temperature and ground to pass through a ≤53 µm sieve. Na^+, K^+, Ca^{2+} and Mg^{2+} ionic forms of sepiolite were prepared by the Batch method, using 1 M solutions at 80 °C for 6 h. After the salt modified process, the treated samples were rinsed with de-ionized water and then dried at room temperature. Before the experimental procedure, all samples were dried in an oven at 110 °C for 16 h and stored in a desiccator.

Acid treated forms were prepared by treating 5 g of sepiolite with 100 ml of 1, 3 and 5 M HCl solutions in a shaker at 80 °C for 6 h. After the acid-treatment, samples were separated and washed with hot distilled water several times until the filtrate was Cl^- free and then dried at room temperature. Before the experimental procedure, all samples were dried in an oven at 110 °C for 16 h and stored in a desiccator. The resulting acid-activated samples are referred to below as SH, S3H and S5H, respectively, denoting their 1, 3 and 5 M HCl treatments. Inorganic chemicals such as HCl, KNO_3, $NaNO_3$, $Mg(NO_3)_2$ and $Ca(NO_3)_2$ were supplied by Merck (Darmstadt, Germany) and all solutions were prepared by using de-ionized water.

2.2 Instrumentation

Chemical compositions were determined on powdered samples fused with lithium tetraborate using X-ray fluorescence analysis (XRF—Rigaku ZSX Primus instrument). The X-ray diffraction (XRD) diffractograms were obtained with D8 Advance, BRUKER AXS instrument, using CuK_α radiation ($\lambda = 1.54$ Å) at 40 kV and 20 mA, in the range 5–50° 2θ. The samples were scanned with a 2θ step of 0.02°. Thermal analysis was carried out using a Setsys Evolution Setaram TG/DTA apparatus (range: 30–1000 °C) under flowing nitrogen (20 ml/min) at a heating rate of 10 °C/min using ~30 mg samples in alumina crucibles. An empty alumina crucible (100 µl) was used as reference and heat flow between the sample and the reference was recorded.

The specific BET surface areas of the samples were measured with automated Autosorb 1-C volumetric equipment (Quantachrome Instruments, Boynton Beach, FL, U.S.A.) using nitrogen gas adsorption at −195,8 °C. Before each measurement the samples were degassed at 125 °C for

Table 1 Chemical analyses in oxides % for of natural and salt modified and acid-activated sepiolite samples

Component (%)	S	KS	NaS	CaS	MgS	HS	H3S	H5S
SiO_2	65.734	64.283	64.668	64.363	65.675	90.836	96.185	96.722
Al_2O_3	5.337	4.963	5.229	5.180	5.228	3.799	1.878	1.725
Fe_2O_3	3.204	3.196	3.104	3.121	3.362	1.907	0.514	0.399
MgO	22.500	24.209	23.955	23.718	23.122	2.306	0.547	0.240
CaO	1.812	1.326	1.379	2.479	1.186	0.143	0.164	0.120
Na_2O	–	0.125	0.396	–	–	–	–	0.145
K_2O	0.610	1.301	0.493	0.554	0.553	0.523	0.301	0.255
P_2O_5	0.018	0.017	0.012	0.018	–	–	–	–
TiO_2	0.208	0.213	0.243	0.215	0.265	0.282	0.265	0.246
SO_3	0.013	0.032	–	0.029	0.023	0.025	–	–
Others	0.564	0.335	0.521	0.323	0.586	0.179	0.146	0.148

7 h. High-purity (99.99 %) nitrogen was used as the adsorbate. Retention values of C_2H_4 by clay samples were determined using automated Autosorb 1-C volumetric equipment (Quantachrome Instruments, Boynton Beach, FL, U.S.A.) at 20 °C up to 37 kPa. About 0.1 g of the sample was outgassed in vacuum at 125 °C for 7 h before C_2H_4 adsorption.

3 Results and discussion

3.1 Chemical analysis

The chemical composition of the natural and salt modified and acid-treated sepiolite samples are given in Table 1. The acid treatment caused a gradual decrease in Al, Mg and Fe (octahedral cations) and an enrichment in SiO_2 coming from the tetrahedral layer of sepiolite. When the concentration of hydrochloric acid was further increased the amount of metal cations extracted was increased (Bonilla et al. 1981; Vicente Rodriguez et al. 1994). The results are consistent with those obtained by XRD showing evidence of a clear amorphization of the structure in the acid-treated samples (Fig. 1).

3.2 X-ray analysis

The XRD patterns of the natural and salt modified and acid-treated sepiolite samples are presented in Fig. 1. XRD analysis of the sepiolites exhibited the positions and intensities of the reflections correspond to the literature data for sepiolite (Moore and Reynolds 1997). The presence of other peaks arises from some impurities in the sepiolite sample. The X-ray pattern of natural sample showed the natural sepiolite characteristic reflection peaks (d = 12.10 Å; d = 4.50 Å; d = 4.30 Å and d = 2.57 Å) and also quartz (d = 3.34 Å), dolomite (d = 2.89 Å) and calcite (d = 3.04 Å) characteristic reflection peaks. There was no any appreciable change of the XRD patterns of natural sepiolite after salt solution treatment which indicates no any structural change with the incorporation of exchangeable ions to the natural sepiolite.

Significant structural modification of the sepiolite sample occurred during acid treatment which can also be seen in Fig. 1. The X-ray patterns of sepiolite samples after acid treatments showed a larger amount of amorphous phase as a consequence of the partial leaching of the octahedral sheet (Gonzalez et al. 1984). The broad characteristic band of free silica situated between 2θ = 18–30° indicated transformation of the sepiolite into amorphous phase. With progressive acid attack, the crystallinity of the samples decreased, as can be seen in intensity of the characteristic XRD peaks. After the acid treatment with 1 M HCl, the characteristic sepiolite reflections (d = 4.50 Å, d = 4.30 Å and d = 2.57 Å) were still present but their intensities were very weak (Fig. 1). The peaks (d = 12.10 Å; d = 4.50 Å and d = 2.57 Å) corresponding to sepiolite disappeared in the H3S and H5S samples and only reflection on corresponding to quartz was observed when the severity of the attack was increased. After the acid treatment with 5 M HCl, the sepiolite reflection (d = 4.30 Å) was still present but its intensity decreased considerably. Similar results were reported by other workers (Belzunce et al. 1998; Myriam et al. 1998).

3.3 Specific surface area

The specific surface areas of all sepiolite samples were determined from nitrogen adsorption isotherms by using data range $P/P_o = 0.05–0.30$ (Brunauer et al. 1932; Gregg and Sing 1991). BET surface area values of the samples dehydrated at 125 °C for 7 h under vacuum were summarized in Table 3. It was found that the areas of sepiolite

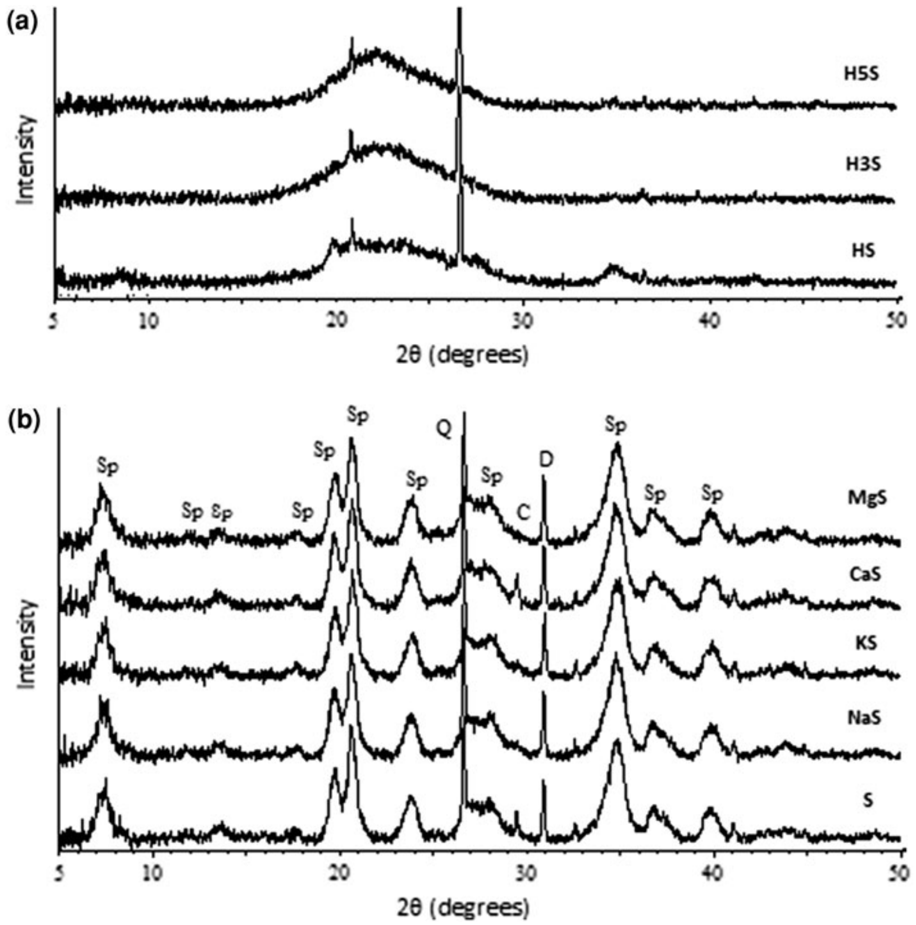

Fig. 1 XRD patterns of **a** natural and salt modified and **b** acid-activated sepiolite samples (*Sp* sepiolite, *D* dolomite, *Q* quartz, *C* calcite)

Table 2 BET surface areas and C_2H_4 adsorptions of natural and salt modified and acid-activated sepiolite samples

Sample	BET surface area (m^2/g)	C_2H_4 adsorption (mmol/g) at 20 °C and 37 kPa)
S	408	0.590
KS	389	0.579
NaS	359	0.617
CaS	367	0.620
MgS	382	0.580
HS	607	0.622
H3S	470	0.528
H5S	419	0.478

samples treated with nitrate solutions were low compared to natural sample. The BET surface areas (obtained by N_2 adsorption isotherms at −195.8 °C) were: 359, 367, 382, 389 and 408 m^2/g for NaS, CaS, KS, MgS and S, respectively (Table 2).

The acid treatment causes a considerable increase in surface area. The most intense attacks entirely dissolve the fibrous clays and produce amorphous silica, whose specific surface area is bigger than that of the natural sample. An activated product of maximum surface area was obtained with an acid solution of 1 M HCl concentration. The specific surface area of natural sepiolite sample increased from 408 to 607 m^2/g after 1 M HCl treatment (see Table 2). The value of the surface area decreased from 607 m^2/g for the HS sample of 470 m^2/g for H3S sample. More intense condition of attack produced a decrease to 419 m^2/g for H5S sample. Similar results were also observed in previous papers where the sepiolites were treated with acid solutions (Gonzalez et al. 1984; Vicente Rodriguez et al. 1994; Myriam et al. 1998; Dekany et al. 1999). Vicente Rodriguez et al. (1994) observed that the specific surface area of sepiolite increased after acid treatment. Myriam et al. (1998) showed that activation of sepiolite increased the specific surface area from 213 to 340 m^2/g after 1 N HCl treatment. In addition, acid activation of natural sepiolite with 7 N HCl decreased the nitrogen BET surface area from 213 to 153 m^2/g.

3.4 Thermal properties

The thermogravimety (TG–DTG) and differential thermal analysis (DTA) curves of all forms of sepiolite samples are

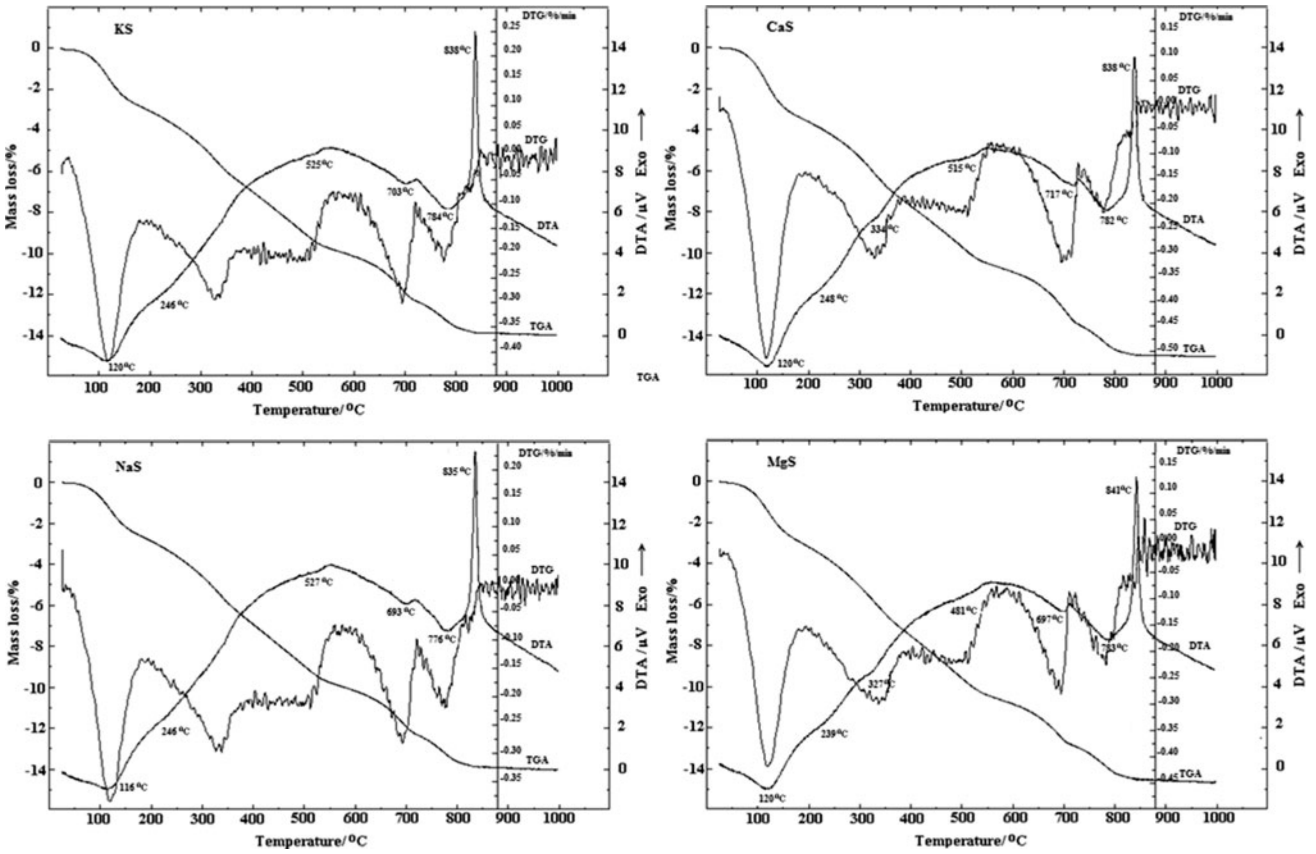

Fig. 2 TG–DTG and DTA curves for the salt modified sepiolite samples

presented in Figs. 2 and 3. In addition, related mass losses for natural, salt modified and acid-treated samples are given in Tables 3 and 4. As seen in Figs. 2 and 3, the curves of natural and salt modified samples are similar. The DTA curves of the MgS and CaS samples exhibited three endothermic peaks at 120, 239–248 and 327–334 °C in the temperature range of 30 and 400 °C. In comparison with those of these samples, the DTA curves of S, KS and NaS samples gave two endothermic peaks at 116–125 and 245–246 °C between 30 and 400 °C. These peaks corresponded to the loss of hydroscopic and zeolitic water, respectively (Figs. 2, 3). The removal of hydroscopic water from the external surface and zeolitic water from the voids of the structure was completed up to 245 °C with a weight loss a 3.53–4.27 % for the natural and salt modified sepiolite samples. This removal gave a high peak in the DTG curve (Figs. 2, 3). The DTA curves of natural and salt modified clays exhibited an endothermic peak at 481–527 °C between 400 and 550 °C due to the dehydration of the bound water. Bound water molecules are lost in two steps accompanied by structural changes (Nagata et al. 1974; Serna et al. 1975; Kiyohiro and Otsuka 1989). In this study, the first part of the bound water for S, NaS, KS, MgS and CaS was evolved from structure between 250 and 400 °C with 3.20–3.53 % weight loss. In this region, a smaller peak was seen in the DTG curve (Figs. 2, 3). The remaining part of the bound water for these samples began to leave the structure at higher temperatures. The removal of bound water was completed before 725 °C and was accompanied by a 5.38–5.73 % additional weight loss, which is in a good agreement with literature values (Figs. 2, 3) (Kiyohiro and Otsuka 1989; Balcı 1999). Two endothermic peaks after 550 up to 1000 °C with the maximum rates at 693–717 and 776–784 °C caused from both of the calcination of the dolomite and dehydroxylation of the sepiolite (Figs. 2, 3). The removal of hydroxyl groups for S, NaS, KS, MgS and CaS was completed at 1.41–1.45 % weight loss up to 825 °C. The removal of the second part of the bound water and hydroxyl groups was observed by a broad peak in the DTG curve (Figs. 2, 3). The DTA curves of the natural and salt modified clays displayed a sharp exothermic peak at 835–841 °C corresponding to the destruction of sepiolite and crystallization of high temperature phase (Figs. 2, 3) (Martin Vivaldi and Fenol Hach-Ali 1970; Nagata et al. 1974; Serna et al. 1975; Corma et al. 1984; Campelo et al. 1989; Balcı 1996, 1999; Frost et al. 2009). It was observed that the percent mass loss for natural and salt modified clays varied in the range from 13.95 to 15.06 %.

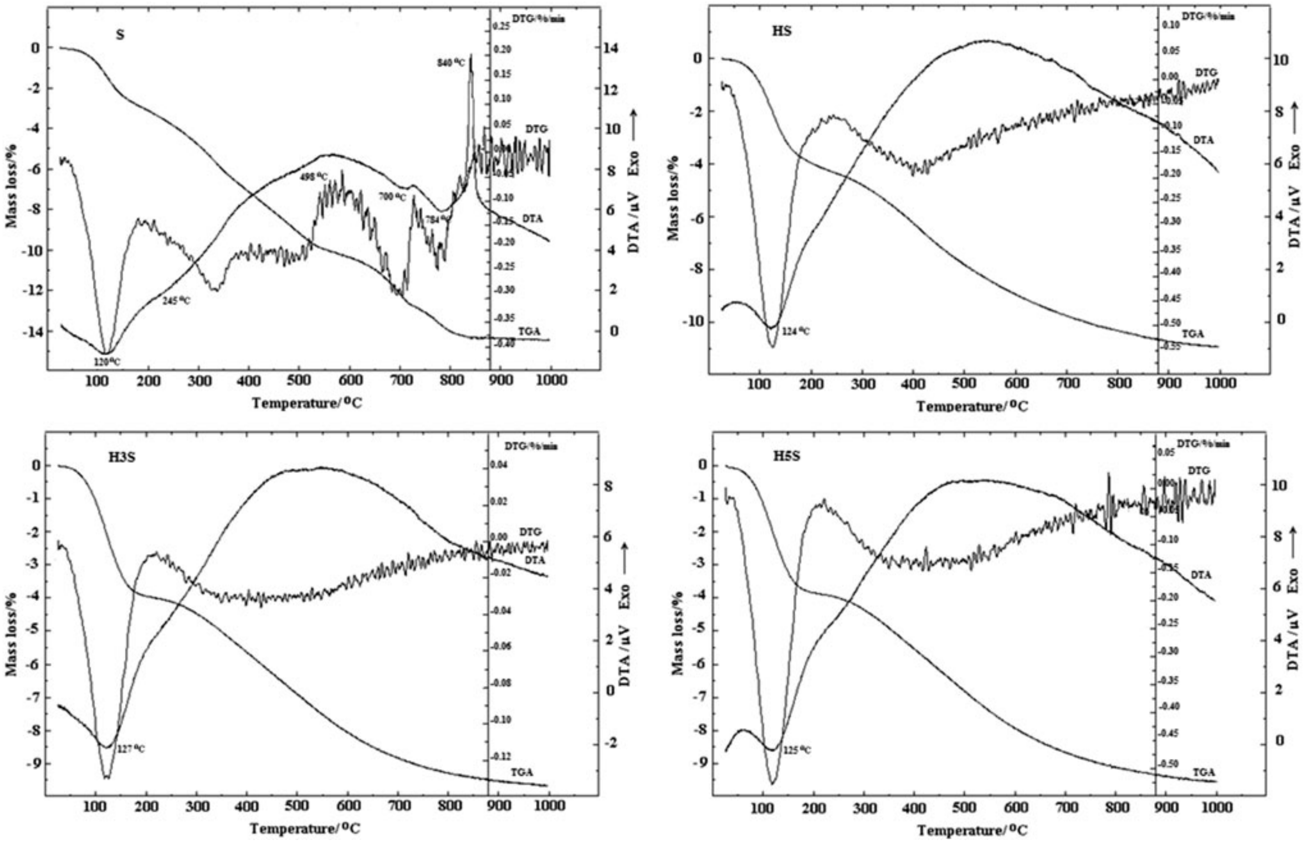

Fig. 3 TG–DTG and DTA curves for the natural and acid-activated sepiolite samples

Table 3 TG and DTA analysis data of natural and salt modified sepiolite samples

Sample	Step 1 (°C)	Mass loss (%)	Step 2 (°C)	Mass loss (%)	Step 3 (°C)	Step 4 (°C)	Mass loss (%)	Step 5 (°C)	Mass loss (%)	Step 6 (°C)	Step 7 (°C)	Total mass loss (%)
S	120	3.09	245	4.00	–	498	2.82	700	2.81	784	840	14.43
KS	120	3.03	246	3.91	–	525	2.70	703	2.59	784	838	13.95
NaS	116	2.84	246	4.00	–	527	2.90	693	2.56	776	835	14.03
CaS	120	3.60	248	4.08	334	515	2.77	717	2.95	782	838	15.06
MgS	120	3.18	239	4.33	327	481	2.86	697	2.49	783	841	14.68

Table 4 TG data of acid-activated sepiolite samples

Sample	30–200 °C	200–900 °C	Total mass loss (%)
HS	3.97	6.77	10.91
H3S	3.95	5.58	9.66
H5S	3.84	5.56	9.54

Figure 3 showed that there was a pronounced difference in thermal behavior between the samples of natural sepiolite and those treated with acid solutions. The DTA patterns showed that the low-temperature endothermic peak, corresponding in acid-treated samples to hydroscopic and zeolitic water was more intense than in natural sepiolite sample (Fig. 3). Also, the other endothermic peaks disappeared in the acid-treated samples compared to the natural and salt modified samples. As can be seen Table 4, the total weight loss decreases, as expected, with the acid treatment given to the sepiolite samples. The acid treatment caused the partial dissolution of magnesium (Campelo et al. 1989). During this partial dissolution, some parts of the bound water and hydroxyl water associated with magnesium ions could be taken away from the structure. As expected, the observed weight loss values by the removal of bound water and hydroxyl water from the acid-treated samples followed each other. Therefore, no flatness in TG curve and no separate peaks in DTG curve were observed for the removal of each

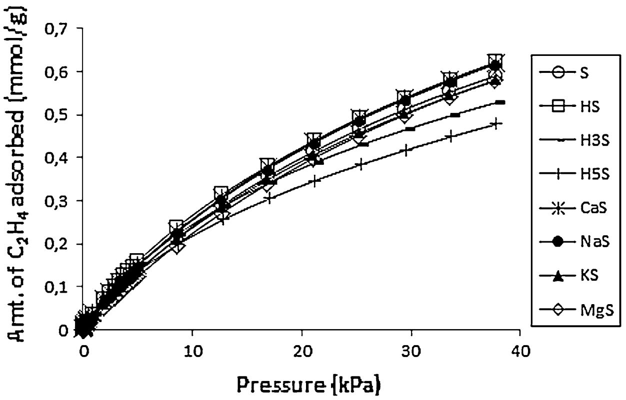

Fig. 4 Adsorption of C_2H_4 on the natural and salt modified and acid-activated sepiolite samples

water molecule. Finally, the endo–exothermic peak characteristic of sepiolite around 840 °C was completely disappeared in the acid-treated samples. The presence of amorphous silica in the acid treated samples is also supported by smaller weight losses with respect to natural sepiolite samples recorded by TGA in the 245–400 °C range corresponding to the reduced amounts of crystallization water. Between 200 and 900 °C, about 5.56 % weight loss for H5S sample was observed. This value was approximately half of the value observed in the same temperature range for natural sample. The acid treatment caused the removal of about half of the bound water and hydroxyl water from the structure (Fig. 3) (Corma et al. 1984; Campelo et al. 1989 Balcı 1996; Belzunce et al. 1998). The mass loss of the H5S is 9.54 % while that of the S sample is 14.43 %. The total mass losses of HS and H3S were determined as 10.91 and 9.66 %, respectively.

3.5 Adsorption of C_2H_4

Adsorption of C_2H_4 gas by natural (S), salt modified (NaS, KS, CaS and MgS) and acid-treated (SH, S3H and S5H) clay minerals were carried out using volumetric apparatus at 20 °C up to 37 kPa. The adsorption isotherm at 20 °C was above the critical temperature of C_2H_4 ($T_c = 9.35$ °C). Adsorption isotherms for C_2H_4 on natural and all cation-exchanged forms of sepiolite were shown in Fig. 4. High purity of C_2H_4 gas was used as the adsorbate. The absolute amounts of adsorbed C_2H_4 per gram of all sepiolite samples were given in Table 2. It can be observed that sepiolite shows high adsorption capacity to C_2H_4, which can be attributed to the significant polarity of sepiolite surface and the quadropole moment of C_2H_4.

In this study, the C_2H_4 adsorption capacity of all forms of sepiolite samples ranged from 0.478 to 0.622 mmol/g at 20 °C and 37 kPa (Table 2). The adsorption capacity and affinity of C_2H_4 with clay samples decreased with increasing acid concentrations. HS (0.622 mmol/g) sample adsorbed much greater amount of C_2H_4 than H3S (0.528 mmol/g) and H5S (0.478 mmol/g) samples, indicating that the acid concentration is the important factor for the adsorption capacity. The amount of adsorbed C_2H_4 on HS was also more than those on natural and salt modified samples. The surface acid activated with 1 M HCl solution could raise the C_2H_4 adsorption from 0.590 mmol/g (S) to 0.622 mmol/g (HS). The amount of C_2H_4 adsorbed on CaS (0.620 mmol/g) was higher than that adsorbed on NaS (0.617 mmol/g) and KS (0.579 mmol/g), probably due to the interactions of the double bonds (π-bonds) of C_2H_4 molecules with calcium ion on the surfaces of these samples. C_2H_4 has a strong quadropole moment. In the case of the adsorption on salt modified samples, sample KS exhibited the lowest adsorption capacity for C_2H_4 gas because of blockages of adsorption sites which arise from high populations of large K^+ ions on the surface. The adsorption capacities are related to numbers of adsorption sites and surface interactions between clays and C_2H_4's π-bonds. For the sepiolite exchanged with large cations, the contribution of cation-π is large but at the same time the large ions can block the adsorption sites on surface of sepiolite sample and reduce C_2H_4 adsorption capacity. The capacity of the natural sepiolite lie somewhere in between, which can be explained be its mixed cationic composition.

The adsorption capacities of the samples decreased in the order HS > CaS > NaS > S > MgS > KS > H3S > H5S for C_2H_4 adsorptions. The results showed that the maximum adsorption capacity was obtained for HS treated by 1 M HCl solution. However, the sepiolite samples treated with 3 and 5 M HCl solutions observed to have the lowest adsorption capacities for C_2H_4 gas. Clearly, cation-exchange processes and the resulting induced structural changes greatly affected the gas adsorption capacity of sepiolite samples. The adsorption properties of a clay adsorbent are strongly influenced by various factors such as the particle size distribution, microporosity, capillary structure, surface area, negative charge and active sorption sites (especially silanol groups). In addition, the nature of the gas molecule to be adsorbed importantly affects the adsorption function of the clay mineral. For example, the polarization, size and shape of the adsorbate molecules may affect such adsorption function. Sepiolite is easily destroyed because of its magnesic composition and the layer size of its structural microchannels. Even though a considerably increase in surface area upon acid treatment, the lesser affinity of sepiolite surface to C_2H_4 adsorption may be attributed to collapse of octahedral layer which is the principal force holding the magnesium ions in the lattice. As a result of reduction in the number of silanol groups (Si–OH) along the axis of fibers can lead to changes in the size and number of pores. Thus, the sepiolite structure along the c axis collapses.

4 Conclusions

Natural (S) and salt treated (NaS, KS, CaS and MgS) and acid-treated (HS, H3S and H5S) clay samples were characterized using XRD, TG–DTG, DTA and nitrogen adsorption methods. The salt treated samples displayed the characteristic sepiolite reflections indicating the sepiolite structure is almost unaltered after the treatment. However, the acid-treatment using 1, 3 and 5 M concentrations had significant effect on crystallinity of sepiolite samples. These samples showed a decrease in the intensity of the characteristic XRD peaks after acid treatment. In addition, partial dealumination and partial removal of exchangeable cations and ion oxides occurred. Acid-treated sepiolites had higher SiO_2 contents and smaller contents of Al_2O_3, MgO, CaO and Fe_2O_3 than natural sample.

The salt modified sepiolite samples exhibited a similar thermal behavior to natural sepiolite. However, the acid-treated sepiolites showed different thermal behavior due to their rearranged crystal structure and chemical composition. The partial disappearance of Mg^{2+} ions is confirmed by the disappearance of the exotherm component in the endo–exothermic peak around 840 °C in DTA curves. In addition, in the TG curves of acid-treated sepiolite samples, the total mass losses were lower than those of the natural sepiolite samples. The acid-activation of the clay mineral led to increase in the specific surface area. It is also found that the treatment with 3 M and 5 M HCl noticeably decreases the surface area with respect to the sample with 1 M HCl.

The C_2H_4 adsorption properties of natural and cation-exchanged sepiolite samples at 20 °C up to 37 kPa were experimentally investigated by comparing C_2H_4 adsorption ability of the natural sepiolite sample to those of the samples after treatments with salt and acid solutions. It was found that the value of C_2H_4 adsorption on natural sepiolite (S) 0.590 mmol/g and the best C_2H_4 adsorption on HS was 0.622 mmol/g. H5S sample exhibited the lowest capacity for the adsorption of C_2H_4 and the C_2H_4 adsorption amount of H5S was 0.478 mmol/g. The results show that adsorption for sepiolite samples decreased with acid concentrations and sepiolite form treated with 1 M HCl solution is more beneficial for the removal of C_2H_4.

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