JOURNAL OF MATERIALS SCIENCE **35** (2000) 5291–5294

O_2, CH_4 and CO_2 gas retentions by acid smectites before and after thermal treatment

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Acid smectites in natural condition and after thermal treatment up to 900 °C were studied for their O_2, CH_4 and CO_2 gas retentions at 25 °C and 1 kg/cm^2. Two smectites, one dioctahedral and one trioctahedral, were treated with 5.0 N sulphuric acid solution for 15 and 60 min. The gas adsorptions by the smectites increased after acid treatments. The O_2 (0.014–0.030 mmol/g) and CH_4 (0.045–0.063 mmol/g) gas retention values were small whereas the values corresponding to CO_2 (0.206–0.357 mmol/g) retentions were high for acid smectites. The acid trioctahedral smectite showed higher gas adsorption values than acid dioctahedral smectite. The CO_2 gas adsorption values by acid smectites heated up to around 600 °C, decreased around 10% and 20% for acid trioctahedral and dioctahedral smectites, respectively. After that drastically decreased and at 900 °C both acid smectites showed very small adsorption values. The chemical composition, the structure and the texture of the smectites influenced the gas retention. © *2000 Kluwer Academic Publishers*

1. Introduction

Many textural and structural characteristics of the materials could be taken into account for adsorbent properties. Different papers give information about molecular sieves such as carbon and zeolites could be prepared as adsorbent for gas separation [1, 2]. In 1991, Yang and Baksh [3] proposed to pillared clays as a new class of sorbents for gas separation. Gas adsorption properties of modified clays materials by different methods (using inorganic and organic substances) have been studied by Yang and Cheng [4], Volzone and Ortiga [5, 6] and Volzone *et al.* [7–9]. Many of industrial uses of smectitic clays materials are related to adsorptive capacity (eg. deolorization, decolorization) which may be increased with acid treatment. The acid treatment for activation of smectites clays has been largely cited in the literature since 1950. In previous papers relationships between textural and structural properties of the acid smectitic materials were obtained [10–12]. Recently we have started the studies about the gas retention by acid smectites [5, 6] and we noticed that the adsorption capacity by acid clay is mainly function of operative condition acid treatments.

The smectite is a group of clay minerals. The smectites are 2 : 1 layer phyllosilicate constituted of an octahedral sheet containing Al or Mg ions between two tetrahedral silica sheets. There are two different series of smectites: dioctahedral and trioctahedral, according to whether the total number of ions in six-coordination per half-unit-cell layer lies close to 2.00 or 3.00, respectively.

In this paper we report the O_2, CH_4 and CO_2 gas retentions at 25 °C and 1 kg/cm^2 by two different smectite clays (dioctahedral and trioctahedral) before and after acid treatment. Also, the gas retention by acid smectites after thermal treatment up to 900 °C were analyzed.

2. Experimental

2.1. Smectite materials

One dioctahedral smectite, SAz-1 montmorillonite from Arizona, USA (Ch) and one trioctahedral smectite, Sap-Ca saponite from Ballarat, USA (S) were used. Both samples were characterized in previous papers [13, 14].

2.2. Acid treatment

The acid treatment was carried out using a 5.0 N sulphuric acid solution. The smectite in acid solution was heated at boiling temperature and left for two different time treatment: 15 min and 60 min.

The solid/acid ratio was 5% wt/wt. After treatment the solid was separated and washed with water several times. The solids were called ChX and SX where $X = 15$ or 60 corresponding to time treatment in minutes.

2.3. Thermal treatment

The thermal treatments of the acid smectites were made at 100, 450, 600, 800 and 900 °C in air atmosphere at a heating rate of 2 °C/min.

2.4. Characterization

Chemical analysis of the solid was determined by inductively coupled plasma emission spectrometry (ICP)

TABLE I Chemical composition of smectites before and after acid treatment. oct: cations in octahedral position: Al, Mg, Fe and Ti

Sample	SiO_2 %	Al_2O_3 %	MgO %	Fe_2O_3 %	TiO_2 %	Na_2O %	CaO %	K_2O %	LOI %	Si/Al molar	Si/Mg molar	Si/oct molar
Ch	50.99	14.79	5.08	1.31	0.19	0.06	2.44	0.15	23.86	3.04	7.81	1.99
Ch15	56.01	12.89	4.21	1.06	0.18	0.08	0.17	0.06	25.31	3.83	10.34	2,55
Ch60	58.08	8.52	2.39	0.64	0.13	0.07	0.14	0.01	29.98	6.00	18.90	4.17
S	47.87	4.17	24.35	0.86	0.32	2.59	2.54	0.52	16.74	10.11	1.53	1.26
S15	69.63	1.51	4.41	0.24	0.40	0.01	2.1	0.48	21.21	40.61	12.28	8.30
S60	73.46	1.45	2.35	0.13	0.28	0.04	1.8	0.42	20.06	44.65	24.31	13.83

by fusion dissolution technique. Equilibrium adsorption was measured using standard volumetric apparatus. Samples were outgassed at 100 °C for 12 h prior to measurement. Adsorption was measured after 30 min at 25 °C and 1 kg/cm^2. The gases tested for their adsorption behaviour were O_2, CH_4 and CO_2.

Adsorption-desorption isotherms were obtained at liquid nitrogen temperature with N_2 in a Micromeritics Accusorb equipment. Surface area (BET) was calculated from the first part of the isotherm ($P/Po < 0.3$). The micropore and external surface values of samples were obtained according to the method of Gregg and Sing [15].

X-ray diffraction (XRD) of the sample was obtained with a Philips 3020 Goniometer with PW 3710 Controller using Cu K_α radiation and Ni filter at 40 kV and 20 mA.

3. Results and discussion

3.1. Structural characteristics of acid smectites

XRD patterns for the Ch and S smectites before and after acid treatments are given in Fig. 1. The Ch dioctahedral smectite showed the characteristic peaks of montmorillonite with a little impurity of quartz (3.34 Å). After 15 and 60 min acid treatments the 00*l* reflexions of original sample situated at 15.40, 5.13, 3.02, 2.50 Å were shifted to higher values with important reduction of the intensities with broader peaks. This increase could be attributed to some Al and/or Mg species in interlayer position coming from the structure [10]. Other reflexions peaks: 100, 110, 200, 210 and 060 situated at 4.47, 2.58, 2.24, 1.70 and 1.50 Å, respectively, also were reduced and amorphous solid appeared. An important structural change was observed for trioctahedral smectite (S) after acid treatments (S15, S60) and more amorphyzed materials were obtained. An increase in the broad characteristic band of free silica placed between 15–32°(2θ) was observed in the diagram of S15 and S60 smectites. All characteristics peaks of saponite smectite were reduced. The insoluble impurity with reflexions at the same position of amphibole magnesium was found to become more intense as the attack progressed.

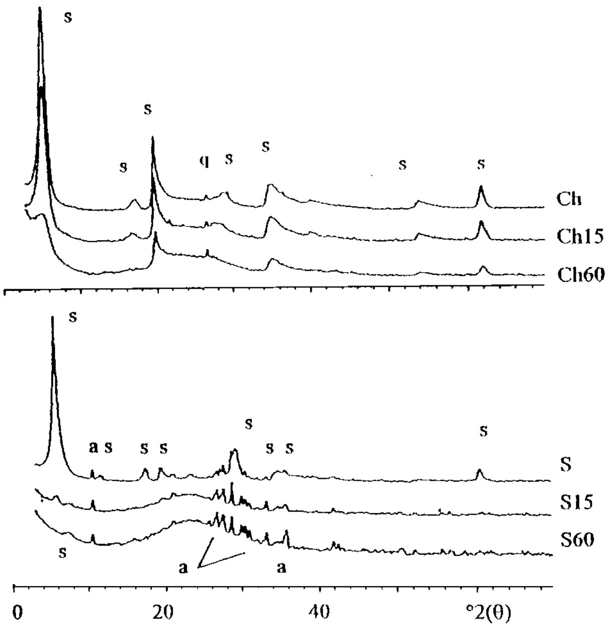

Figure 1 X-ray diffraction of Ch and S smectites before and after acid treatment: s: smectite; q: quartz; a: amphibole magnesium.

The Table I shows the chemical composition of the smectites. The Si/(Al + Fe + Ti + Mg) molar ratio changed from 1.99 to 4.17 after acid treatment for the Ch smectite and from 1.26 to 13.83 for S smectite. The Si/Al molar ratio changed from 3.04 to 6.00 and 10.11 to 44.65 for Ch and S smectites, respectively. The acid treatment removed important amount of octahedral cation in the follow order: Mg > Fe > Al > Ti. The smectite structure decomposition increased, for example, in the same order as the octahedral Mg content. This is agreement with finding in previous paper [10, 11] and by Nóvak and Cícel [16] who studied Mg, Fe dissolution rate of smectites in HCl. On the other hand, the dissolution of the octahedral sheets by acid treatment was found by infrared analysis in previous paper [10]. Then, the high degree of saponite S decomposition (Fig. 1) was due to higher Mg content than the montmorillonite Ch (Table I).

3.2. Textural characteristics

The shape of N_2 adsorption-desorption isotherm of the starting smectites (Ch, S) corresponded to the H3 type [17] according Gregg and Sing [15]. The hysteresis loop can be formed by pores shaped by parallel plates at some distance from each other (slit-shaped pore). After acid treatment the smectites preserved the shape (not shown here) but an important increase of total volume was observed due to partial dissolution of the octahedral layer.

After 15 min acid treatment the developed high total and BET surface up to 276 and 322 m^2/g for Ch15 and S15, respectively. Both smectites reached around 450 m^2/g after 60 min acid treatment. The increase of the surface area resulted mainly from increase in the micropore surface (Table II). The increase in surface

TABLE II Total, micropore and external surface, BET surface and total volume obtained from N_2 adsorption isotherm

Sample	total surface (m^2/g)	micropore surface (m^2/g)	external surface (m^2/g)	BET surface (m^2/g)	total volume (cm^3/g)
Ch	78	71	7	81	0.175
Ch15	276	222	54	264	0.288
Ch60	467	419	48	474	0.441
S	8	6	2	4	0.031
S15	322	288	34	281	0.257
S60	437	390	47	390	0.347

area by acid treatment is due to an increase in porosity caused meanly by leaching octahedral layer cations of the clay (Table I), [10, 11].

3.3. Gas adsorption

Table III shows adsorptions of gases of the starting smectites and after acid treatments. Both smectites showed better gas adsorption after 60 min acid treatment than the ones treated after 15 min. The level of O_2 and CH_4 gas adsorptions was relatively low for the starting materials and increased after acid treatments. The CO_2 adsorption also increased after acid treatment, although the starting smectite S showed high adsorption. The acid smectites showed an increase in O_2, CH_4 and CO_2 adsorption of 3–5, 2–5.5 and 1.5–3 times, respectively. The diferent retention values amoung O_2, CH_4 and CO_2 by acid smectites could be attributes to the influence of the physicochemical properties of the adsorbates (critical size, polarizability, etc.) as was observed by Baksh and Yang [18] using pillared clays as adsorbent.

The relative increase of modified Ch (Ch15, Ch60) were higher than modified S (S15, S60), but the S smectites (S, S15, S60) showed adsorptions over Ch smectites (Ch, Ch15, Ch60). The gas retentions of the dioctahedral smectite after acid treatment (Ch15, Ch60) were similar to those found for acid bentonites reported in previous work [5].

A higher destruction of the structure of smectite originated the increase in gas adsorption. The saponite, S, was more easily destroyed than montmorillonite, Ch, due to magnesium composition (above mentioned). CO_2 gas adsorptions by acid trioctahedral smectites (S15: 0.329 mmol/g, S60: 0.357 mmol/g) were higher than Al-, Zr-, Cr- and Ti-pillared clays (0.210, 0.185, 0.100 and 0.141 mmol/g) and modified Al-PILCs (0.300 mmol/g) but were smaller than smectites treated with organic compounds (0,480 mmol/g) under the same experimental adsorption conditions as they were reported in previous work [7, 9].

TABLE III Gas adsorptions by starting smectites and after acid treatment at 25 °C and 1 kg/cm^2

	Gas adsorption, mmol/g of sample		
Sample	O_2	CH_4	CO_2
Ch	0.004	0.009	0.065
Ch15	0.014	0.049	0.206
Ch60	0.020	0.045	0.217
S	0.009	0.030	0.214
S15	0.028	0.063	0.329
S60	0.030	0.062	0.357

Certain correlation between total surface of smectite material and gas adsorption for all gases (Tables II and III) was found, similar that was found in the same adsorption conditions using amorphous kaolin [8].

The retention gas ratio value of 3 is considered to be good for gas separation for commercial viability [18], nevertheless, also the value of gas loading is very important. The materials studied here could be proposed as potential material for CO_2/CH_4 separation.

3.4. Gas adsorption by thermally treated acid smectites

Fig. 2a and b present the O_2, CH_4 and CO_2 gas adsorptions by acid Ch and acid S smectites, respectively, after thermal treatment up to 900 °C.

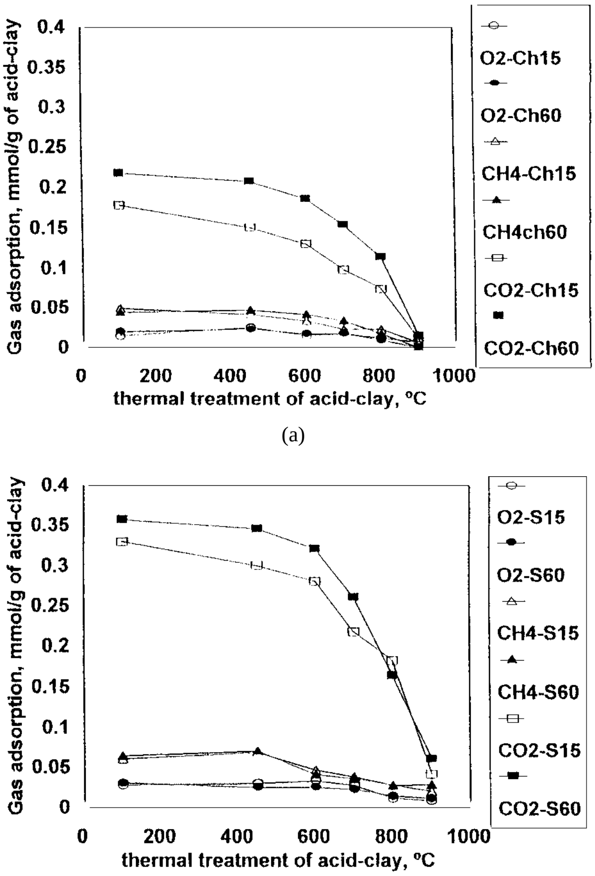

Figure 2 Gas adsorptions at 25 °C and 1 kg/cm^2 by acid smectites after thermal treatment up to 900 °C. a) Ch dioctahedral smectite; b) S trioctahedral smectite.

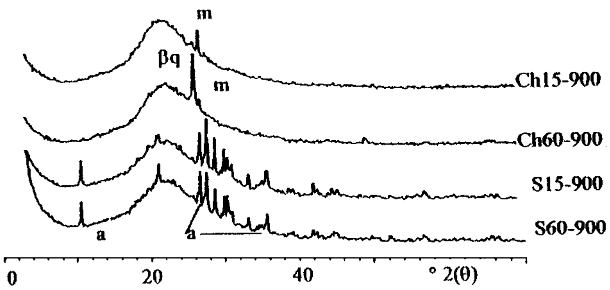

Figure 3 X-ray diffraction of acid Ch and acid S treated at 900 °C. a: amphibole magnesium; βq: beta quartz; m: mullite.

The acid trioctahedral smectite heated at the different temperatures showed, for all gases, better gas adsorption values than acid dioctahedral smectite treated at the same temperatures. The acid smectites heated up to 600 °C decreased, around 20% for acid Ch and 10% for acid S, adsorption CO_2 value regarding the ones obtained without thermal treatment. Then, they rapidly decreased. The drop adsorption of the acid samples after the treatment to 900 degrees can be attributed by important structural changes as shown XRD diagram of heated acid smectites (Fig. 3). The treatment of smectite clays at high temperature originate new phases [19] according to element constitutions of the structure. The heating of raw Ch smectite up to 1000 °C originates quartz, crystobalite, anorthite, whereas the high Mg contents in S smectite allowed the presence of clino-enstatite [14]. The acid treatment of smectites removed structural cations (Al^{3+}, Mg^{2+}, Fe^{3+}, Ti^{4+}) and interlayer cations (Na^+, Ca^{2+}, K^+) of the original sample, then, different phases at 900 °C were found. The XRD peaks of acid smectites heated at 900 °C corresponded to β-quartz and mullite for Ch and amphibole magnesium for S samples, with high amorphous silica content in both types of heated acid smectitic materials. The high intensity of β-quartz peak at 3.43 Å of Ch60 sample could be attibuted to relative content high silica in the sample (Table I).

4. Conclusions

The gas adsorption by smectites increases after acid treatment, and could be atributed to structural and textural properties.

The different retentions of O_2, CH_4 and CO_2 gases by acid smectites could give information that this material will be a potential for gas separation. The CO_2 gas adsorption values by acid smectites heated up to around 600 °C, decreased around 10% and 20% for acid trioctahedral and dioctahedral smectites, respectively.

The acid trioctahedral smectite showed higher capacity of retention than acid dioctahedral smectite before and after thermally treated up to 900 °C. The chemical composition, the structure and the texture of the acid smectites influenced the gas retention.

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Received 15 November 1999
and accepted 30 March 2000