

THE EFFECT OF HEATING ON THE SURFACE AREA, POROSITY AND SURFACE ACIDITY OF A BENTONITE

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Abstract—The Hançılı bentonite from Turkey shows significant changes in surface area, micro- and mesoporosity, surface acidity and acid strength with heating from 100 to 900°C for 2 h. The specific surface area (S) and specific micro-mesopore volume (V) of the original and heated samples were evaluated from N_2 adsorption and desorption data, respectively, by standard methods. The adsorption of n -butylamine from the solution in cyclohexane on the samples was used to determine the total surface acidity (n_m) and the adsorption equilibrium constant (K) was taken as a measure of the acid strength. S , V and n_m having initial values of $98 \text{ m}^2\text{g}^{-1}$, $0.080 \text{ cm}^3\text{g}^{-1}$ and $4.8 \times 10^{-4} \text{ mol g}^{-1}$, respectively, stayed approximately constant as the temperature increased to 450°C and then decreased almost in parallel with each other, reaching their minimum or zero at 900°C. The total surface acidity, in general, declines with increasing temperature. The most acidic sites, however, increase with heating, and especially at dehydration and dehydroxylation. Acid strength reaches its maximum during the dehydroxylation phase at ~600°C. It was concluded that the total surface acidity does not necessarily parallel the strength of the most acid sites.

Key Words—Acid Strength, Bentonite, Heating, Surface Acidity, Surface Area.

INTRODUCTION

Bentonites, together with their principal constituent, smectite, have a wide range of uses as industrial minerals (Barrer, 1989; Grim, 1968; Grim and Güven, 1978; Pinnavaia, 1983; Srasra *et al.*, 1989; Gamiz *et al.*, 1992; Murray, 1991, 2000; Varma, 2002). In some of these uses, the bentonite may experience high temperatures (Wang *et al.*, 1990; Abu-Zreig *et al.*, 2001; Chandrasekhar and Ramaswamy, 2002; Tan *et al.*, 2004). Such thermal treatment can affect properties such as strength, swelling and adsorption, and these are reflected in changes in cation exchange capacity, pore structure, surface acidity and catalytic activity (Bradley and Grim, 1951; Brindley, 1978; Mozas *et al.*, 1980; Reicle, 1985; Ceylan *et al.*, 1993; Joshi *et al.*, 1994; Chorom and Rengasamy, 1996; Neaman *et al.*, 2003). Surface acidity is implicit in acid catalysis wherein petroleum cracking, polymerization, and Diels-Alder and Friedel-Crafts reactions are only a few examples (Adams *et al.*, 1983; Jacobs, 1984; Laszlo, 1987; Occelli *et al.*, 1987; Tanabe *et al.*, 1989; Ravichandran and Sivasankar, 1997; Varma, 2002).

The empty spaces in a solid, the widths of which are <2 nm, between 2 nm and 50 nm, and >50 nm, are known as micropores, mesopores and macropores, respectively (Gregg and Sing, 1982). The radius of a pore, assumed to be cylindrical, can be taken as half of the pore width. The volume of pores in 1 g of solid is

defined as the specific pore volume, V . The area of the inner and outer walls of the pores located within and between particles in 1 g of solid is taken as specific surface area, S . Numerous methods have been used to measure V and S (Rouquerol *et al.*, 1999).

Clay minerals, particularly smectites, behave as solid acid. Brønsted and Lewis acid sites on their surfaces are proton donors and electron pair acceptors, respectively. Of particular interest is change in surface acidity, n , with heating, and how it relates to changes in other properties. The acid strength of a surface can be characterized by the equilibrium constant, K , and its neutralization reaction with a base. Methods to determine acid strength include titration using Hammett indicators, infrared spectroscopy of adsorbed molecules, and vapor-phase adsorption of ammonia at elevated temperatures (Walling, 1950; Benesi, 1956, 1957; Parry, 1963; Basila *et al.*, 1964; Mortland and Raman, 1968; Frenkel, 1974; Breen *et al.*, 1987; Brown and Rhodes, 1997a; Blumenfeld and Fripiat, 1997; Kou *et al.*, 2000; Flessner *et al.*, 2001; Ruiz *et al.*, 2002).

There are many studies on the adsorptive and catalytic properties of bentonites, smectites and their products (Adams, 1987; Ge *et al.*, 1994; Kumar *et al.*, 1995; Brown and Rhodes, 1997a; Önal *et al.*, 2002, 2003). However, there are few published works on the effects of the heating temperature on those properties (Reicle, 1985; Brown and Rhodes, 1997b; Sarıkaya *et al.*, 2000; Alemdaroğlu *et al.*, 2003; Neaman *et al.*, 2003). Therefore, the aim of this study was to investigate of the effect of the heating temperature on the surface area, porosity, surface acidity and acid strength of a bentonite.

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MATERIALS AND METHODS

Selected material and preparation

The bentonite in this study is from the upper section of the Hançılı bed (Keskin, Ankara, Turkey). The volume percentage of particles which are $<2 \mu\text{m}$ is 85%. Part of the sample was dried at 105°C for 4 h. The bulk chemical analysis of the dried bentonite (wt.%) is: SiO_2 , 61.25; Al_2O_3 , 16.85; Fe_2O_3 , 5.77; TiO_2 , 0.90; MgO , 2.78; CaO , 1.53; Na_2O , 2.54; K_2O , 1.12 and loss on ignition (LOI), 7.05. The cation exchange capacity, by the methylene blue method frequently used in industrial measurements, is 0.80 mol g^{-1} . A further part of the sample was dried at 25°C for 24 h and stored in polyethylene bags. From this stock, 10 g portions were heated at 13 temperatures ranging from 100 to 900°C . These were labeled H100, H200, etc.

Instrumentation

The X-ray diffraction (XRD) patterns of the original and heated bentonite were obtained from random mounts using a Rikagu D-Max 2200 powder diffractometer with $\text{CuK}\alpha$ radiation and a Ni filter.

The adsorption and desorption isotherms of N_2 , at liquid N_2 temperature, on the heated samples were determined by a volumetric adsorption instrument of pyrex glass connected to high vacuum (Sarıkaya and Aybar, 1978; Sarıkaya *et al.*, 2001).

The adsorptions of *n*-butylamine from the solution in cyclohexane on the heated samples were followed by a UV-VIS spectrophotometer (Varian, Cary 50). The cyclohexane and *n*-butylamine used are of analytical grade and were supplied by Merck Chemical Company. In each experiment, a series of 10 mL test tubes was loaded with 0.1 g each of a heated sample. Then, 10 mL each of freshly prepared *n*-butylamine solutions in cyclohexane with a concentration range of $1.0 \times 10^{-4} \text{ M}$ to $4.0 \times 10^{-2} \text{ M}$ were pipetted into each of the tubes. To reach adsorption equilibrium, the tubes were shaken mechanically at 298 K for 75 h. The solutions then were measured at the wavelength of maximum absorption, $\lambda = 227 \text{ nm}$, and concentrations determined by Lambert-Beer Law.

RESULTS AND DISCUSSION

Mineralogy of the bentonite

The XRD patterns of the original and heated samples are given in Figure 1. The bentonite contains a Na-rich smectite (NaS) with a d_{001} value of 1.29 nm and quartz (q), opal (o), feldspar (f) and dolomite (d). These minerals were identified by their characteristic XRD peaks (Moore and Reynolds, 1997). According to the XRD peak intensities, the amount of non-clay minerals seems too small, a result supported by the chemical analysis. For example, the free silica (quartz and opal) content was estimated at $<5\%$ by evaluating the chemical analysis.

As seen in Figure 1, the 001 peak of smectite decreases in intensity while maintaining its position after heating from 25 to 250°C . The 001 peak decreased from 1.29 to 0.99 nm after heating from 250 to 400°C . The position and intensity of the 001 peak did not change after heating from 400 to 700°C though it disappears after heating at 800°C . The dominant XRD peaks after heating at 900°C belong to quartz and opal. The peak for crystalline quartz remained virtually the same after each thermal treatment indicating that the crystallinity of quartz is unaffected by heating. The peak for opal intensifies greatly between 800 and 900°C with the opal becoming more crystalline (Elzea *et al.*, 1994; Kahraman *et al.*, 2005). The increasing intensity of the opal peak may also be due to the creation of new opal-like material from the decomposition of the smectite at 900°C .

Adsorption and desorption isotherms

The N_2 adsorption and desorption isotherms at the liquid N_2 temperature for all heated samples were examined, and representative ones, for H100, H450 and H900 are shown in Figure 2. The isotherms show that adsorption capacity decreases with increasing temperature and approaches zero at 900°C . According

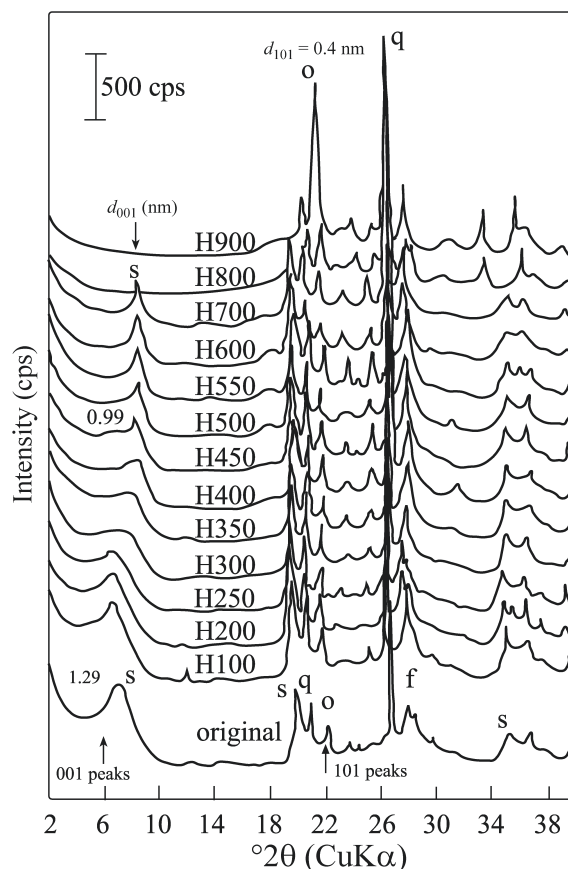


Figure 1. XRD patterns of the original bentonite and heated (H100, H200, ...etc.) samples (s: smectite, o: opal, q: quartz, f: feldspar, d: dolomite).

to Brunauer, the classification of these isotherms is similar to Type II (Brunauer *et al.*, 1940; Rouquerol *et al.*, 1999). The shapes of the adsorption and desorption isotherms indicate that the bentonite is mainly a mesoporous solid but also contains some micropores. Micropores filled by monomolecular adsorption at the relative equilibrium pressure interval of $0 < x < 0.05$. After multimolecular adsorption up to $x = 0.35$ was complete, capillary condensation began, and all mesopores filled up to $x = 0.96$. Bulk liquid nitrogen forms at $x = 1$ (Linsen, 1970). The liquid nitrogen outside and within the mesopores evaporates spontaneously as soon as the relative equilibrium pressure by desorption is low enough, at the intervals $1 < x < 0.96$ and $0.96 < x < 0.35$, respectively. The coincidence of the adsorption and desorption isotherms over the interval $0.35 < x < 0$ shows that the multimolecular and monomolecular adsorption are reversible. Capillary condensation begins from the narrowest mesopores and capillary evaporation begins from the largest mesopores. This difference causes the hysteresis between adsorption and desorption isotherms. The sharp decrease in the desorption isotherm at $x \approx 0.5$ shows that the bentonite has a group of mesopores which are of almost the same width. The radii of these mesopores was calculated as being ~ 2 nm by using the corrected Kelvin equation (Gregg and Sing, 1982; Sarikaya *et al.*, 2002b).

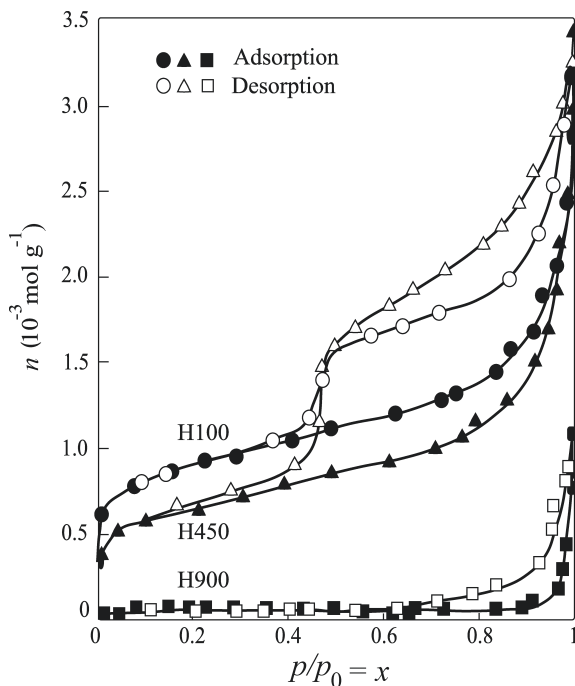


Figure 2. Adsorption and desorption isotherms of N_2 at liquid N_2 temperature for some heated bentonite samples (H100, H450, H900). (n (mol g^{-1}): adsorption capacity defined as the molar amount of nitrogen adsorbed on 1 g of adsorbent at any x , p : the adsorption and desorption equilibrium pressure, p_0 : the vapour pressure of bulk liquid nitrogen at experimental temperature, $p/p_0 = x$: the relative equilibrium pressure).

Surface area and micro-mesopore volume

The specific surface areas, S (m^2g^{-1}), were obtained from the standard Brunauer, Emmett and Teller (BET) procedure by using the adsorption data from the interval $0.05 < x < 0.35$ (Brunauer *et al.*, 1938; McClellan and Hornsberger, 1967; Everett *et al.*, 1974; Sarikaya *et al.*, 2002a). The adsorption capacities as liquid nitrogen volumes which were estimated from desorption isotherms at $x = 0.96$ are taken as the specific micro-mesopore volumes, V (cm^3g^{-1}) of the samples. As the temperature increases, the S and V values show a 'zig-zag' change at the beginning, then the values decrease rapidly (Figure 3). The zig-zag change in S and V originates mostly from the deformation of the smectite during dehydration over the interval of $100\text{--}550^\circ\text{C}$ and dehydroxylation over the interval $550\text{--}700^\circ\text{C}$ (Sarikaya *et al.*, 2000). Because of the very low adsorptive capacities and evidence of smaller amounts in the bentonite, the effects of non-clay minerals on S and V are negligible. The decomposition of the 2:1 layers of the smectite and collapsing of micro- and mesopores by intra- and interparticle sintering causes the rapid decrease in S and V values as the temperature increases, as a result of dehydroxylation.

Surface acidity and acid strength

The adsorption isotherms for the bentonite of *n*-butylamine from solution in cyclohexane for the H100, H450 and H600 sample at 25°C are given in Figure 4 as examples. The same isotherms of the other samples have also been determined but are not shown here. The isotherms show that the adsorption capacity decreases with increasing heating temperature. The shapes of the isotherms, which are similar to Type I, according to the Brunauer (1940) classification, indicate that the adsorptions are monomolecular.

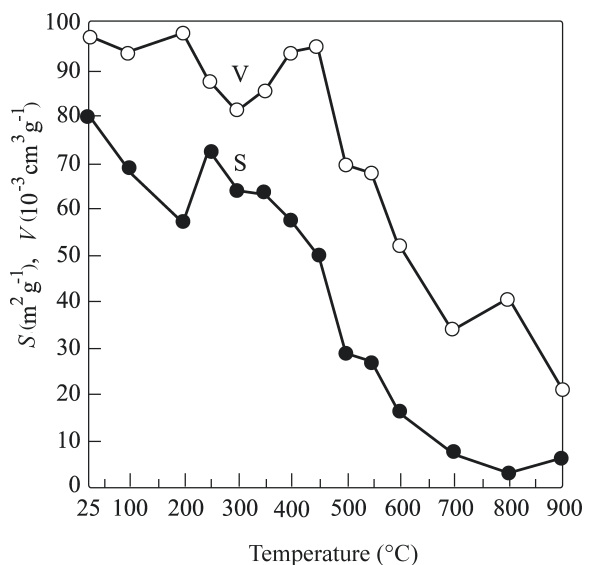


Figure 3. Variation of the specific surface area (S) and the specific micro-mesopore volume (V) with heating temperature.

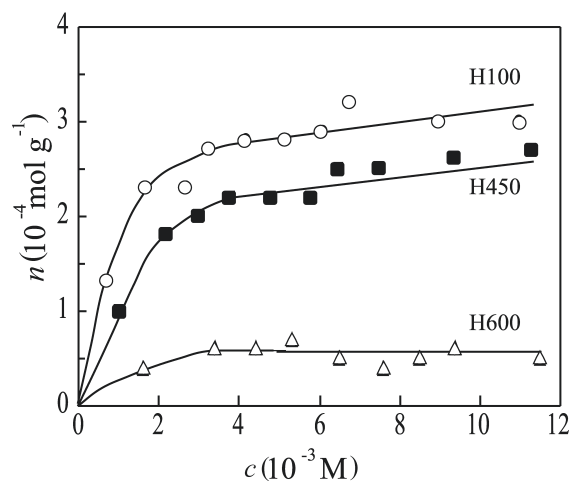


Figure 4. Adsorption isotherms of *n*-butylamine from the solution in cyclohexane on the heated samples (H100, H450, H600) (c (M): the molarity of *n*-butylamine solution, n (mol g^{-1}): the adsorption capacity defined as the molar amount of *n*-butylamine adsorbed on 1 g of adsorbent at any c).

The Langmuir isotherm equation is derived to examine the monomolecular chemical adsorption and can also be used for monomolecular physical adsorption. To obtain a straight line by the application to experimental data, the Langmuir equation can be written as follows:

$$c/n = 1/Kn_m + c/n_m \quad (1)$$

where c is the equilibrium concentration, n is adsorption capacity at any value of c , n_m is the monomolecular adsorption capacity and K is a constant. By using *n*-butylamine adsorption data, c/n is plotted against c and a Langmuir plot is obtained for each sample (Figure 5). Two equations were obtained from the slope and intercept of this Langmuir plot. From the solution of these two simultaneous equations, n_m and K were found for each sample. The monomolecular adsorption capacity, n_m , is taken as the specific surface acidity which shows the molar Brönsted and Lewis acid sites on 1 g of bentonite (Brown and Rhodes, 1997a). According to the basis of the derivation of the Langmuir isotherm $K = k_a/k_d$ is defined as the adsorption equilibrium constant, where k_a and k_d are rate constants for adsorption and desorption, respectively (Laidler and Meiser, 1982). Chemical adsorption of *n*-butylamine on the acidic bentonite surface is a neutralization reaction. However, the adsorption equilibrium constant can be taken as the equilibrium constant of the neutralization reaction. Furthermore, the magnitude of the adsorption equilibrium constant must be a measure of the acid strength. Therefore, it was assumed that the K value can be taken as the relative acid strength which is defined as the ability of the surface to convert an adsorbed neutral base to its conjugate acid (Hammett and Deyrup, 1932; Walling, 1950; Frenkel, 1974; Loeppert *et al.*, 1986).

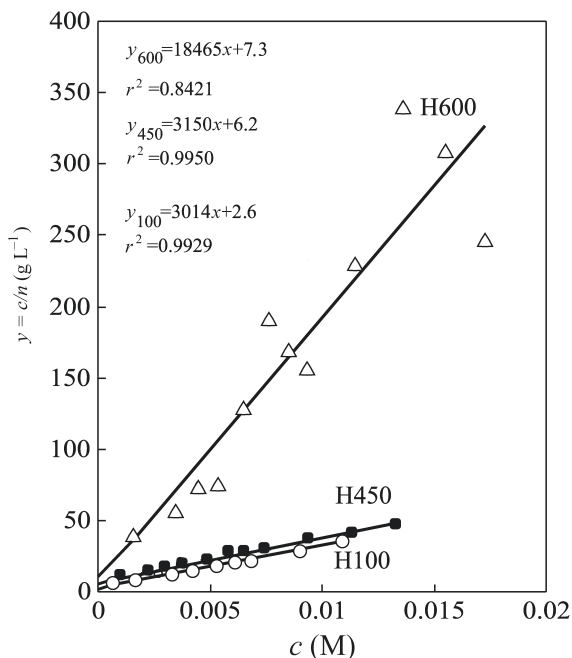


Figure 5. Langmuir straight lines for some heated samples (H100, H450, H600).

The variation of n_m and K values with heating temperature are given in Figure 6. It can be seen by comparing Figures 3 and 6 that the n_m values change virtually in parallel with S and V values. Despite the decrease in n_m values, the K values show two maxima near the dehydration and dehydroxylation temperatures. A greater increase in K is noted for dehydroxylation than for dehydration.

The increase in K by dehydration originated from the increase in the proton donation by the disassociation of

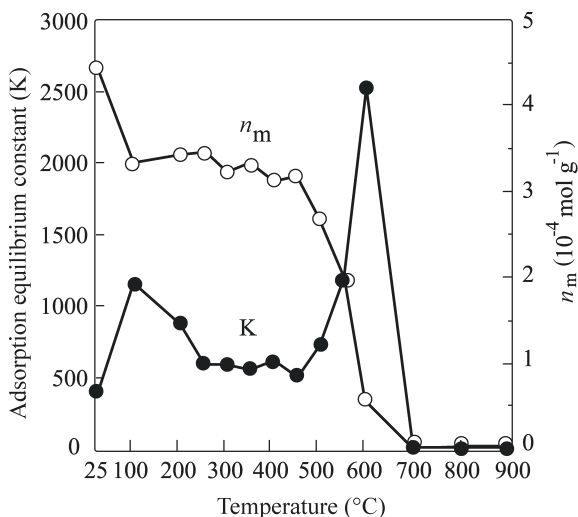
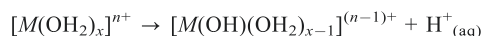


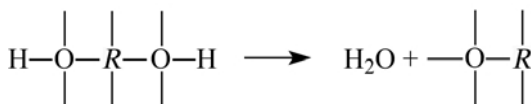
Figure 6. Variation of the surface acidity (n_m) and adsorption equilibrium constant (K) assumed as acid strength by heating temperature.

water molecules coordinated by exchangeable cations (M) as given in the reaction below:



According to this reaction, the Brønsted acid strength of smectite can be influenced by the number of water molecules and the nature of exchangeable cations between layers (Adams *et al.*, 1983; Breen *et al.*, 1987; Brown and Rhodes, 1997a, Varma, 2002).

The increase in K is due to the octed vacancies which originated from the dehydroxylation reaction, as seen below:



where R shows the octahedral cations of Al^{3+} or Fe^{3+} , Fe^{2+} and Mg^{2+} (Drits *et al.*, 1995; Emmerich *et al.*, 1999; Emmerich and Kahr, 2001). These residual octahedral cations in structures with octed vacancies cause a significant increase in acid strength due to dehydroxylation over the temperature interval 550–700°C. After dehydroxylation is complete at 700°C, the surface acid sites and the acid strength disappear.

CONCLUSIONS

The surface area, the micro-mesopore volume, the number of the acid sites, and the acid strength of a smectite change significantly under increased heating temperature. (The decrease in the surface area is smaller until the beginning of dehydroxylation and greater thereafter). We propose that the adsorption equilibrium constant evaluated from the Langmuir adsorption isotherm for a weak base as well as *n*-butylamine can be taken as the measure of the acid strength of a solid surface. The Brønsted and Lewis acid strengths reach their maxima by the dehydration and dehydroxylation of a smectite, respectively. Therefore, smectites heated at temperatures of 150°C and 600°C can be used as Brønsted acid catalysts and Lewis acid catalysts, respectively.

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