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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 900ºC 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 m^2g^{-1}, 0.080 cm^3g^{-1} and 4.8×10^{-4} mol g^{-1}, respectively, stayed approximately constant as the temperature increased to 450ºC and then decreased almost in parallel with each other, reaching their minimum or zero at 900ºC. 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 ~600ºC. 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. Brönsted 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 μm is 85%. Part of the sample was dried at 105ºC 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 25ºC for 24 h and stored in polyethylene bags. From this stock, 10 g portions were heated at 13 temperatures ranging from 100 to 900ºC. 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 CuKα 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 1.0×10^{-4} M to 4.0×10^{-2} 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, λ = 227 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 250ºC. The 001 peak decreased from 1.29 to 0.99 nm after heating from 250 to 400ºC. The position and intensity of the 001 peak did not change after heating from 400 to 700ºC though it disappears after heating at 800ºC. The dominant XRD peaks after heating at 900ºC 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 900ºC 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 900ºC.

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 900ºC. According

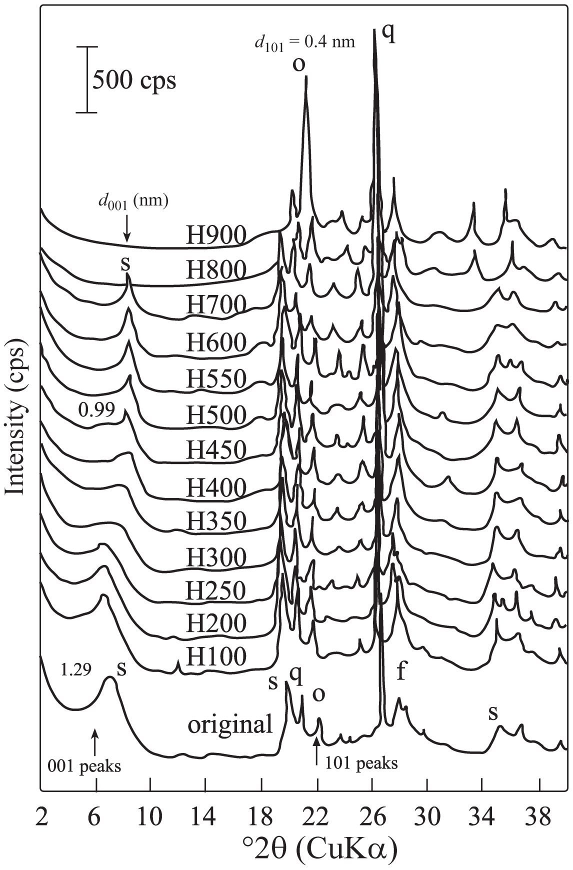

Figure 1. XRD patterns of the original bentonite and heated (H100, H200, ⋯*etc.*) samples (s: smectite, o: opal, q: quartz, f: feldspar, d: dolomite).

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 multimoleculer 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 multimoleculer 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; Sarıkaya *et al.*, 2002b).

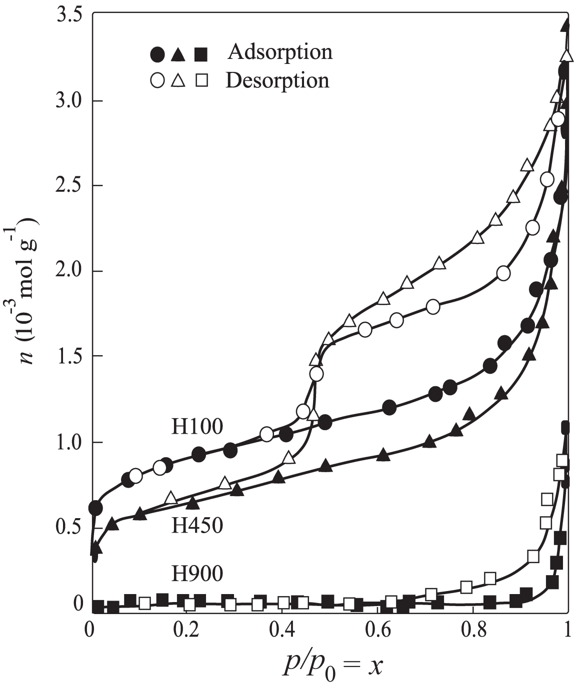

Figure 2. Adsorption and desorption isotherms of N_2 at liquid N_2 temperature for some heated bentonite samples (H100, H450, H900). (n (mol g^{-1}): adsorption capacity defined as the molar amount of nitrogen adsorbed on 1 g of adsorbent at any x, p: the adsorption and desorption equilibrium pressure, 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^{2}g^{-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; Sarıkaya *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^{3}g^{-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 100−550ºC and dehydroxylation over the interval 550−700ºC (Sarıkaya *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 25ºC 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.

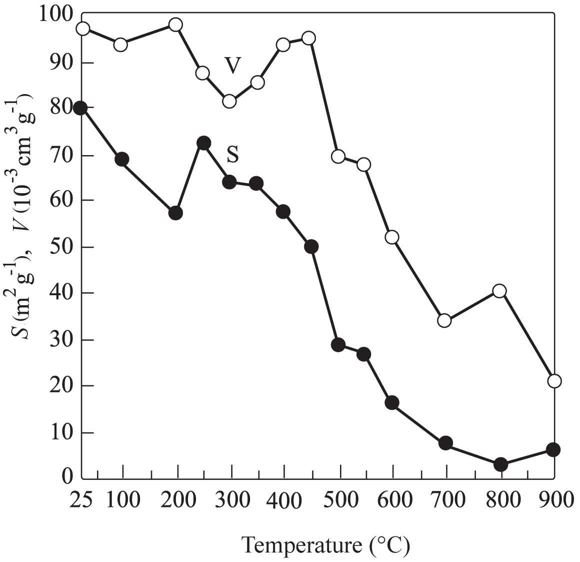

Figure 3. Variation of the specific surface area (S) and the specific micro-mesopore volume (V) with heating temperature.

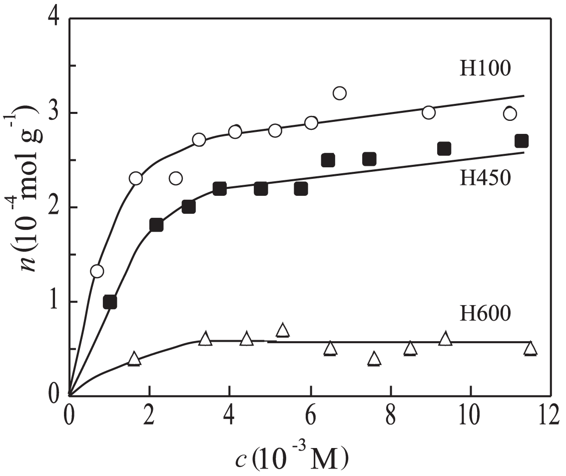

Figure 4. Adsorption isotherms of *n*-butylamine from the solution in cyclohexane on the heated samples (H100, H450, H600) (*c* (M): the molarity of *n*-butylamine solution, *n* (mol g^{-1}): the adsorption capacity defined as the molar amount of *n*-butylamine adsorbed on 1 g of adsorbent at any *c*).

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:

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

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).

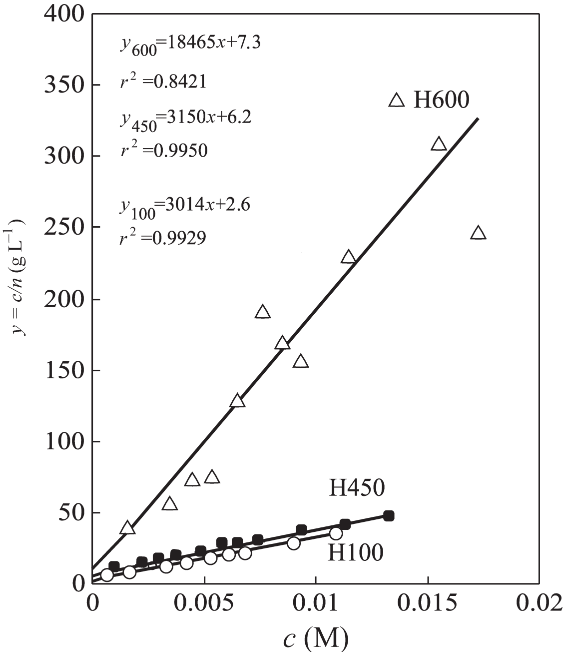

Figure 5. Langmuir straight lines for some heated samples (H100, H450, H600).

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

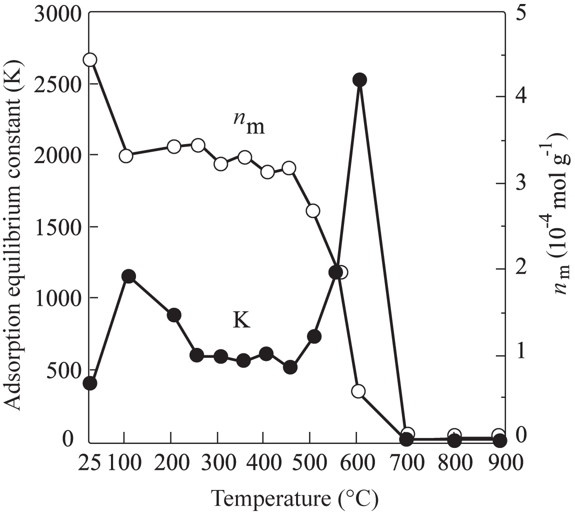

Figure 6. Variation of the surface acidity (n_m) and adsorption equilibrium constant (K) assumed as acid strength by heating temperature.

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

$$[M(\mathrm{OH}_2)_x]^{n+} \rightarrow [M(\mathrm{OH})(\mathrm{OH}_2)_{x-1}]^{(n-1)+} + \mathrm{H}^+_{(\mathrm{aq})}$$

According to this reaction, the Brönsted 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:

$$\mathrm{H{-}O{-}}R\mathrm{{-}O{-}H} \longrightarrow \mathrm{H_2O} + \mathrm{{-}O{-}}R$$

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 550−700ºC. After dehydroxylation is complete at 700ºC, 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 Brönsted and Lewis acid strengths reach their maxima by the dehydration and dehydroxylation of a smectite, respectively. Therefore, smectites heated at temperatures of 150ºC and 600ºC can be used as Brönsted acid catalysts and Lewis acid catalysts, respectively.

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REFERENCES

Abu-Zreig, M.M., Al-Akhras, N.M. and Attom, M.F. (2001) Influence of heat treatment on the behaviour of clayey soils. *Applied Clay Science*, **20**, 129−135.

Adams, J.M. (1987) Synthetic organic chemistry using pillared cation-exchanged and acid-treated montmorillonite catalysts: a review. *Applied Clay Science*, **2**, 309−342.

Adams, J.M., Clapp, T.V. and Clement, D.E. (1983) Catalysis by montmorillonites. *Clay Minerals*, **18**, 411−421.

Alemdaroğlu, T., Akkuş, G., Önal, M. and Sarıkaya, Y. (2003) Investigation of the surface acidity of a bentonite modified by acid activation and thermal treatment. *Turkish Journal of Chemistry*, **27**, 675−681.

Barrer, R.M. (1989) Shape-selective sorbents based on clay minerals: a review. *Clays and Clay Minerals*, **37**, 385−395.

Basila, M.R., Kantner, T.R. and Rhee, K.H. (1964) The nature of the acidic sites on a silica-alumina. Characterization by infrared spectroscopic studies of trimethylamine and pyridine chemisorption. *The Journal of Physical Chemistry*, **68**, 3197−3207.

Benesi, H.A (1956) Acidity of catalyst surfaces. I. Acid strength from colors of adsorbed indicators. *Journal of the American Chemical Society*, **78**, 5490−5494.

Benesi, H.A (1957) Acidity of catalyst surfaces. II. Amine titration using Hammett indicators. *The Journal of Physical Chemistry*, **61**, 970−973.

Blumenfeld, A.L. and Fripiat, J.J. (1997) ^{27}Al-^{1}H Redor NMR and ^{27}Al Spin-Echo Editing: A new way to characterize Brönsted and Lewis acidity in zeolites. *Journal of Physical Chemistry* B, **101**, 6670−6675.

Bradley, W.F. and Grim, R.E. (1951) High temperature thermal effects of clay and related materials. *American Mineralogist*, **36**, 182−201.

Breen, C., Deane, A.T. and Flynn, J.J. (1987) The acidity of trivalent cation-exchanged montmorillonite. Temperature-programmed desorption and infrared studies of pyridine and *n*-butylamine. *Clay Minerals*, **22**, 169−178.

Brindley, G.W. (1978) Thermal reactions of clay and clay minerals. *Ceramica*, **24**, 217−224.

Brown, D.R. and Rhodes, C.N. (1997a) Brönsted and Lewis acid catalysis with ion-exchanged clays. *Catalysis Letters*, **45**, 35−40.

Brown, D.R. and Rhodes, C.N. (1997b) A new technique for measuring surface acidity by ammonia adsorption. *Thermochimica Acta*, **294**, 33−37.

Brunauer, S., Emmett, P.H. and Teller, E. (1938) Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society*, **60**, 308−319.

Brunauer, S., Deming, L.S., Deming, D.M. and Teller, E. (1940) On a theory of the van der Waals adsorption on gases. *Journal of the American Chemical Society*, **62**, 1723−1732.

Ceylan, H., Yıldız, A. and Sarıkaya, Y. (1993) Investigation of adsorption of fatty acids on two different clays using IR, DTA and TGA techniques. *Turkish Journal of Chemistry*, **17**, 267−272.

Chandrasekhar, S. and Ramaswamy, S. (2002) Influence of mineral impurities on the properties of kaolin and its thermally treated products. *Applied Clay Science*, **21**, 133−142.

Chorom, M. and Rengasamy, P. (1996) Effect of heating on swelling and dispersion of different cationic forms of a smectite. *Clays and Clay Minerals*, **44**, 783−790.

Drits, V.A., Besson, G. and Muller, F. (1995) An improved model for structural transformations of heat-treated aluminous dioctahedral 2:1 layer silicates. *Clays and Clay Minerals*, **43**, 718−731.

Emmerich, K. and Kahr, G. (2001) The cis- and trans-vacant variety of a montmorillonite − an attempt to create a model smectite. *Applied Clay Science*, **20**, 119−127.

Emmerich, K., Madsen, F.T. and Kahr, G. (1999) Dehydroxylation behavior of heat-treated and steam-treated homoionic cis-vacant montmorillonites. *Clays and Clay Minerals*, **47**, 591−604.

Elzea, J.M., Odom, J.E. and Miles, W.J. (1994) Distinguishing well-ordered opal-CT and opal-C from high temperature α-cristobalite by X-ray diffraction. *Analytica Chimica Acta*, **286**, 107–116.

Everett, D.H., Parfitt, G.D., Sing, K.S.W. and Wilson, R. (1974) The SCI/IUPAC/NPL project on surface area standards. *Journal of Applied Chemistry and Biotechnology*, **24**, 199–219.

Flessner, U., Jones, D.J., Rozière, J., Zajac, J., Storaro, L., Lenardo, M., Pavan, M., Jimènez-Lòpez, A., Rodrìguez-Castellòn, E., Trombetta, M. and Busca, G. (2001) A study of the surface acidity of acid-treated montmorillonite clay catalysts. *Journal of Molecular Catalysis A: Chemical*, **168**, 247–256.

Frenkel, M. (1974) Surface acidity of montmorillonites. *Clays and Clay Minerals*, **22**, 435–441.

Gamiz, E., Linares, J. and Delgado, R. (1992) Assessment of two Spanish bentonites for pharmaceutical uses. *Applied Clay Science*, **6**, 359–368.

Ge, Z., Li, D. and Pinnavaia, T.J. (1994) Preparation of alumina-pillared montmorillonites with high thermal stability, regular microporosity and Lewis/Brönsted acidity. *Microporous Materials*, **3**, 165–175.

Gregg, S.J. and Sing., K.S.W. (1982) *Adsorption, Surface Area and Porosity*, 2nd edition. Academic Press, London.

Grim, R.E. (1968) *Clay Mineralogy*, 2nd edition. McGraw-Hill, New York.

Grim, R.E. and Güven, N. (1978) *Bentonites – Geology, Mineralogy, Properties and Uses.* Developments in Sedimentology, **24**, Elsevier, New York.

Hammett, L.P. and Deyrup, A.J. (1932) A series of simple basic indicators I. The acidity functions of mixtures of sulphuric and perchloric acid with water. *Journal of the American Chemical Society*, **54**, 2721–2739.

Jacobs, P.A. (1984) The measurement of surface acidity. Pp. 1–28 in: *Characterization of Heterogeneous Catalysts* (F. Delannay, editor). Dekker, New York.

Joshi, R.C., Achari, G., Horfield, D. and Nagaraj, T.S. (1994) Effect of heat treatment on strength of clays. *Journal of Geotechnical Engineering-ASCE*, **120**, 1080–1088.

Kahraman, S., Önal, M., Sarıkaya, Y. and Bozdoğan, İ. (2005) Characterization of silica polymorphs in kaolins by X-ray diffraction before and after phosphoric acid digestion and thermal treatment. *Analytica Chimica Acta*, **552**, 201–206.

Kou, M.R.S., Mendioroz, S. and Munoz, V. (2000) Evaluation of the acidity of pillared montmorillonites by pyridine adsorption. *Clays and Clay Minerals*, **48**, 528–536.

Kumar, P., Jasra, R.V. and Bhat, T.S.G. (1995) Evolution of porosity and surface acidity in montmorillonite clay on acid activation. *Industrial and Engineering Chemistry Research*, **34**, 1440–1448.

Laidler, K.J. and Meiser, J.H. (1982) *Physical Chemistry*. Benjamin/Cumnings London, 772 pp.

Laszlo, P. (1987) Chemical reactions on clay. *Science*, **235**, 1473–1477.

Linsen, B.G. (1970) *Physical and Chemical Aspects of Adsorbents and Catalysts*. Academic Press, London.

Loeppert, R.H., Zelazny, L.W. and Volk, B.G. (1986) Acidic properties of montmorillonite in selected solvents. *Clays and Clay Minerals*, **34**, 87–92.

McClellan, A.L. and Hornsberger, H.F. (1967) Cross-sectional areas of molecules adsorbed on solid surfaces. *Journal of Colloid and Interface Science*, **23**, 577–599.

Moore, D.M. and Reynolds, R.C. Jr. (1997) *X-ray Diffraction and the Identification and Analysis of Clay Minerals*, 2nd edition. Oxford University Press, New York.

Mortland, M.M. and Raman, K.V. (1968) Surface acidity of smectite in relation to hydration, exchangeable cation, and structure. *Clays and Clay Minerals*, **16**, 393–398.

Mozas, T., Bruque, S. and Rodriquez, A. (1980) Effect of thermal treatment on lanthanide montmorillonites: Dehydration. *Clay Minerals*, **15**, 421–428.

Murray, H.H. (1991) Overview – clay mineral applications. *Applied Clay Science*, **5**, 379–395.

Murray, H.H. (2000) Traditional and new applications for kaolin, smectite and palygorskite. A general overview. *Applied Clay Science*, **17**, 207–221.

Neaman, A., Pelletier, M. and Villiéras, F. (2003) The effect of exchanged cation, compression, heating and hydration on textural properties of bulk bentonite and its corresponding purified montmorillonite. *Applied Clay Science*, **22**, 153–168.

Occelli, M.L., Landau, S.D. and Pinnavaia, T.J. (1987) Physicochemical properties of a delaminated clay cracking catalyst. *Journal of Catalysis*, **104**, 331–338.

Önal, M., Sarıkaya, Y., Alemdaroğlu, T. and Bozdoğan, İ. (2002) The effect of acid activation on some of the physicochemical properties of a bentonite. *Turkish Journal of Chemistry*, **26**, 409–416.

Önal, M., Sarıkaya, Y., Alemdaroğlu, T. and Bozdoğan, İ. (2003) Isolation and characterization of a smectite as a micro-mesoporous material from a bentonite. *Turkish Journal of Chemistry*, **27**, 683–693.

Parry, E.P (1963) An infrared study of pyridine adsorbed on acidic solids. Characterization of surface acidity. *Journal of Catalysis*, **2**, 371–379.

Pinnavaia, T.J. (1983) Intercalated clay catalysis. *Science*, **220**, 365–371.

Ravichandran, J. and Sivasankar, B. (1997) Properties and catalytic activity of acid-modified montmorillonite and vermiculite. *Clays and Clay Minerals*, **45**, 854–858.

Reicle, W.T. (1985) Catalytic reactions by thermally activated, synthetic, anionic clay minerals. *Journal of Catalysis*, **94**, 547–557.

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. *Materials Research*, **5**, 173–178.

Rouquerol, F., Rouquerol, J. and Sing, K. (1999) *Adsorption by Powder and Porous Solids*. Academic Press, London.

Sarıkaya, Y. and Aybar, S. (1978) The adsorption of NH_3, N_2O and CO_2 gases on the 5A molecular sieve. *Communication of the Faculty of Science, University of Ankara*, **B24**, 33–39.

Sarıkaya, Y., Önal, M., Baran, B. and Alemdaroğlu, T. (2000) The effect of thermal treatment on some of the physicochemical properties of a bentonite. *Clays and Clay Minerals*, **48**, 557–562.

Sarıkaya, Y., Sevinç, İ. and Akınç, M. (2001) The effect of calcination temperature on some of the adsorptive properties of fine alumina powders produced by emulsion evaporation. *Powder Technology*, **116**, 109–114.

Sarıkaya, Y., Ada, K., Alemdaroğlu, T. and Bozdoğan, İ. (2002a) The effect of Al^{3+} concentration on the properties of alumina powders obtained by reaction between aluminium sulphate and urea in boiling aqueous solution. *Journal of the European Ceramic Society*, **22**, 1905–1910.

Sarıkaya, Y., Alemdaroğlu, T. and Önal, M. (2002b) Determination of the shape, size and porosity of fine α-Al_2O_3 powders prepared by emulsion evaporation. *Journal of the European Ceramic Society*, **22**, 305–309.

Srasra, E., Bergaya, F., van Damme, H. and Ariquib, N.K. (1989) Surface properties of an activated bentonite-decolorisation of rape-seed oils. *Applied Clay Science*, **4**, 411–421.

Tan, Ö., Yilmaz, L. and Zaimoğlu, S. (2004) Variation of some engineering properties of clays with heat treatment. *Materials Letters*, **58**, 1176–1179.

Tanabe, K., Misono, M., Ono, Y. and Hattori, H. (1989) *New Solid Acids and Bases, Their Catalytic Properties*. Elsevier, Amsterdam.

Varma, R.S. (2002) Clay and clay-supported reagents in organic synthesis. *Tetrahedron*, **58**, 1235–1255.

Walling, C. (1950) The acid strength of surfaces. *Journal of the American Chemical Society*, **72**, 1164–1168.

Wang, M.C., Benway, J.M. and Arayssi, A.M. (1990) The effect of heating on engineering properties of clays. Pp. 1139–1158 in: *Physicochemical Aspects of Soil and Related Materials* (K.B. Hoodinott, R.O. Lamb, and A.J. Lutenegger, editors). ASTM STP 1095, Philadelphia.

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