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A MODEL DEVELOPED FOR ACID DISSOLUTION THERMODYNAMICS OF A TURKISH BENTONITE

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A model was proposed to calculate some thermodynamic parameters for the acid dissolution process of a bentonite containing a calcium-rich smectite as clay mineral along with quartz, opal and feldspar as impurities. The bentonite sample was treated with H_2SO_4 by applying dry method in the temperature range 50–150°C for 24 h. The acid content in the dry bentonite-sulphuric acid mixture was 45 mass%. The total content (x) of Al_2O_3, Fe_2O_3 and MgO remained in the undissolved sample after treatment was taken as an equilibrium parameter. An apparent equilibrium constant, K_a, was calculated for each temperature by assuming $K_a=(x_m-x)/x$ where x_m is the total oxide content of the natural bentonite. Also, an apparent change in Gibbs free energy, ΔG_a^o, was calculated for each temperature by using the K_a value. The graphs of $\ln K_a$ *vs.* $1/T$ and ΔG_a^o *vs.* T were drawn and then the real change in both the enthalpy, ΔH^o and the entropy, ΔS^o, values were calculated from the slopes of the straight lines, respectively. Inversely, real ΔG^o and K values were calculated from the real ΔH^o and ΔS^o values through $\Delta G^\circ = -RT \ln K = \Delta H^\circ - T\Delta S^\circ$ equation. The best ΔH^o and ΔS^o fittings to this relation were found to be 65687 J mol^{-1} and 164 J $mol^{-1}K^{-1}$, respectively.

Keywords: *acid dissolution, bentonite, chemical analysis, thermodynamics*

Introduction

Bentonites which consist principally of smectites have been used either naturally or after modification in more than 40 applications [1–5]. Bentonites contain, besides smectites, other clay and non-clay minerals. Pure smectite is rarely found in the nature [6]. Bentonites may be purified and also subjected to acid, base, salt and thermal treatments to obtain various products with the desired properties [7–14]. The acid treated bentonites have been used as adsorbents, catalysts and catalyst supports [15–24]. To remove color pigments and impurities from edible oils, acid treated bentonites (bleaching earths) are used [25–30]. They are also used to prepare carbonless copy paper, pillared clays and organoclays [31–35]. HCl, HNO_3 and H_2SO_4 are commonly used in acid treatment either via the wet or the dry processes, which yield similar end products [36–40]. A gel prepared with optimum amount of bentonite, water and H_2SO_4 is heated at a definite temperature for a predetermined time for the dry process. A suspension of this gel which is prepared by adding sufficient amount of water is heated in the same manner by the wet process [41, 42]. The dry process has some technical advantages over the wet process.

Physicochemical characteristics such as specific surface area, pore volume, pore size distribution, surface acidity, and acid strength of the clay minerals can be improved by acid dissolution, by means of changing the mineralogical composition and rheology [43–49].

To understand the physicochemical aspects of bentonites, the kinetics of the acid dissolution process has been intensively investigated by many researchers previously [40, 50–53]. However, there seems lack of published work in the literature on the thermodynamics of acid dissolution phenomena. The aim of this study was to search for a thermodynamic model for the reaction of sulphuric acid with a Turkish bentonite based on the change of the chemical composition.

Experimental

The natural Hançılı (Keskin, Ankara, Turkey) bentonite with a cation exchange capacity of 0.79 mol kg^{-1} was used as starting material in this study. This bentonite could not be purified further by deflocculation in distilled water, without using any chemical agent. Some of the thermal properties of this bentonite sample, containing 85% smectite by volume, were previously investigated [14, 54].

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The natural bentonite was ground to 74 μm size, dried at 105°C for 24 h, and kept in a tightly closed plastic bottle. The optimum acid content of dry bentonite-sulphuric acid mixture was previously determined to be between 35–45 mass% [47]. In this study, the air dried bentonite samples were treated with H_2SO_4 using 45 mass% acid in the mixture in the temperature range 50–150°C.

Six samples, each of a mass of 30 g, natural bentonite were taken from the air dried material and kept in 40 mL distilled water for 24 h for swelling. The solution prepared by the corresponding amount of H_2SO_4 was added to each swelled bentonite to obtain a gel. The gels were heated to 50, 60, 75, 90, 125 and 150°C, respectively for 24 h to reach the thermodynamic equilibrium. The equilibrium was assumed to be established when the composition of the reaction system remained constant. According to the previous studies and our pretreatment experience, the time necessary to attain the equilibrium varies between 6–24 h depending on the mineralogical and chemical composition and the smectite content of the bentonite sample as well as the type and dosage of inorganic acid used, and the reaction temperature [12, 55].

Each acid treated sample was suspended in distilled water, and centrifuged. The precipitates thus obtained were washed with distilled water until free from SO_4^{2-} ions. The removal of SO_4^{2-} ions was checked by the formation of $BaSO_4$ by adding $BaCl_2$ solution to the filtrate. These samples were kept in tightly sealed plastic bottles following the drying process at 105°C for 4 h.

The X-ray diffraction (XRD) patterns of the randomly chosen natural and acid treated bentonite powders were recorded using a Rikagu D-Max 2200 Powder Diffractometer with CuK_α radiation and Ni filter.

Before chemical analysis, each sample was dried at 105°C for 4 h, and then fired at 1000°C for 2 h. The mass loss was taken as the loss on ignition (LOI). For each chemical analysis, approximately 0.25 g of the fired samples were mixed with 3 g LiB_4O_7 and fused at 1000°C for 1 h in a platinum crucible. The fusions were then cooled to room temperature, and dissolved in 100 mL of 10% HCl at 90°C. The solution was diluted to 250 mL in a volumetric flask. The elemental composition of the sample was determined by a Hitachi Z-8200 Atomic Absorption Spectrometer. The results were presented by the mass percentage of the metal oxides.

Results and discussion

XRD analysis

The XRD patterns of the natural and acid treated bentonite samples are given in Fig. 1. This yellowish-green bentonite contains calcium-rich smectite (S) as a major clay mineral and quartz (Q), opal (O) and feldspar (F) as external clay components.

The intensity of the 001 diffraction maximum does not change considerably for acid treatment temperatures up to 90°C (Fig. 1). The intensity of the (001) peak de-

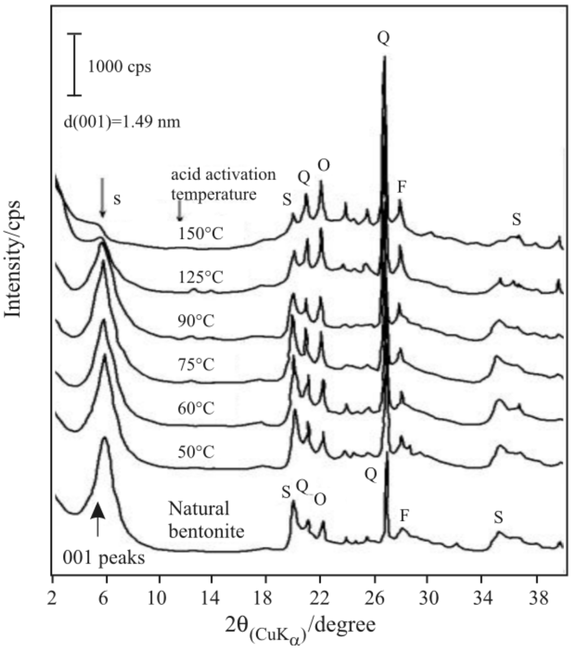

Fig. 1 XRD patterns of the natural and acid treated bentonites (S – smectite, Q – quartz, O – opal, F – feldspar)

Table 1 The bulk chemical analyses of natural bentonite (NB) and acid treated samples at different temperatures as mass of metal oxides (H_2SO_4 ratio is 45 mass%)

Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	LOI
NB	60.85	0.85	16.50	5.74	2.71	2.37	1.53	0.83	8.40
50°C	62.05	0.81	17.45	5.21	2.09	0.58	0.54	0.78	10.25
60°C	62.35	0.84	16.90	5.42	2.12	0.66	0.55	0.79	10.15
75°C	63.75	0.83	16.65	4.82	2.00	0.56	0.49	0.73	9.95
90°C	65.10	0.83	16.55	4.48	1.89	0.41	0.48	0.75	9.30
125°C	76.50	0.92	9.95	1.84	0.83	0.29	0.56	0.77	8.10
150°C	84.40	0.96	5.50	0.57	0.35	0.16	0.16	0.71	6.45

creases significantly at 125°C and then almost disappears at 150°C because of the deformation and collapse of 2:1 layers. The position of the (001) peak is not affected by acid treatment, suggesting that the thickness of the interlayer space remains constant during dissolution. The external clay components (Q, O and F) appear to be unaffected by acid treatment significantly, suggesting that these impurities are more resistant to acid attacks than smectite [29].

Chemical analysis

The bulk chemical analyses of the natural bentonite and acid treated samples are given in Table 1. The variations of the relative oxides' content M/M_o in the bentonite, where M_o and M are the mass% of metal oxides in the natural and treated bentonite samples, respectively, are given in Fig. 2.

As shown in Fig. 2, the cations are released into the solution in the order Ca^{2+}>Na^+>Mg^{2+}>$Fe^{2+,3+}$>K^+>Ti^{4+}>Al^{3+}> and Si^{4+} up to 90°C. Up to this point, the exchangeable cations, Ca^{2+} and Na^+, are mostly replaced by H^+ ions and H-smectite is formed. Besides these phenomena, the smectite structure is affected by the temperatures as low as 60°C, due to the partial dissolution of Mg^{2+}, Fe^{3+} or Fe^{2+} cations (Fig. 2). The removal rate of Mg^{2+}, Fe^{3+}, and Al^{3+} rapidly increases in the temperature range 90–150°C. Even up to the temperature of 150°C, Na^+ and Ca^{2+} cannot be removed from bentonite completely during acid dissolution. Probably, the Na^+ and Ca^{2+} residues are likely to remain in feldspar.

The undissolved K^+ and Si^{4+} cations may originate from smectite and feldspar. K^+ located in the crystal structure of feldspar, but it is also an exchangeable cation of smectite. The increase in the relative amounts of K^+, Si^{4+}, and Ti^{4+} may be explained by the release of other cations during dissolution. Titanium is present mainly as free TiO_2 anatase or breaute in bentonite and it is not normally affected by acid treatment. The variation of the total amount of undissolved octahedral cations represented by oxides Al_2O_3, Fe_2O_3 and MgO which are labeled as R_xO_y mass% is given in Fig. 3. This R_xO_y mass% that is retained by bentonite was used as a thermodynamic variable in this study. The rate of dissolution of Mg^{2+}, Fe^{3+} and Al^{3+} cations increases in parallel with the reaction temperature in the range 90–150°C. Even at 90°C these cations are not removed completely, indicating that the crystal structure of smectite was partly preserved (Fig. 1).

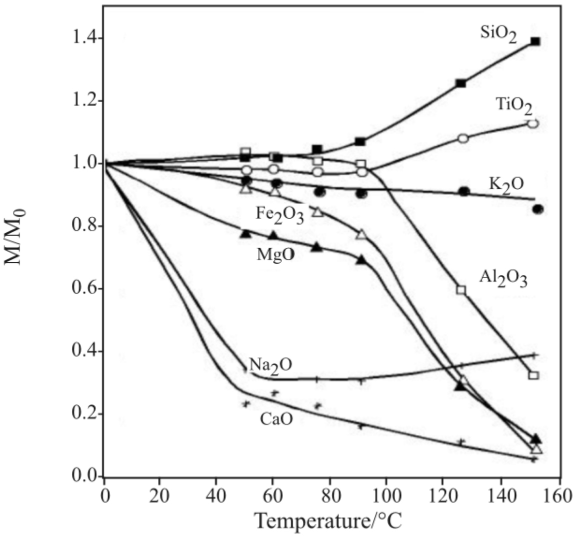

Fig. 2 Variations of M/M_o values of individual oxides in the acid treated bentonites with temperature

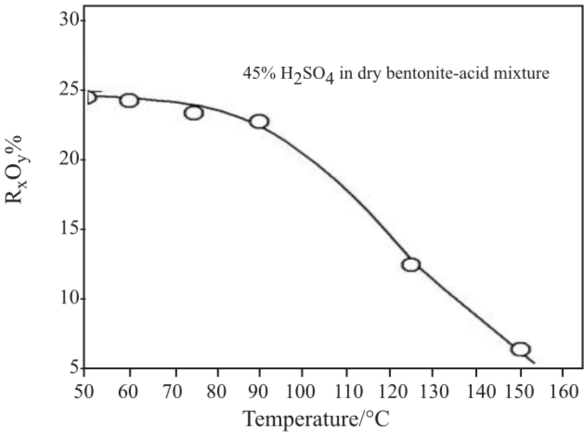

Fig. 3 Variations of R_xO_y of the acid treated smectites with the process temperature

The proposed model

Since exact data for the basic thermodynamic quantities such as molar heat capacities, standard formation enthalpies, and standard absolute entropies are not available for bentonites as for many natural materials, thermodynamic calculations can not be directly performed from physicochemical changes. Such difficulties become more prominent when external clay components exist in bentonite structures. To overcome these obstacles, an indirect thermodynamic model for acid dissolution of bentonites is proposed, on the basis of the following assumptions.

- The time elapsed during acid dissolution should be sufficient to establish a thermodynamic equilibrium. As the oxide content of the bentonite remains constant after 24 h, either the chemical reaction ceases entirely so that the system is stationary, or the forward and reverse reactions take place simultaneously at exactly the same rate. Relying on our own experience and a number of previous studies, we conclude that the chemical equilibrium of the acid dissolution process is reached at constant temperature and pressure within the time interval of 6–24 h [12, 38, 45, 55, 56].

- The chemical composition of the heated sample remains constant at room temperature and this position can be used to calculate the equilibrium data.
- When the dissolution reaction of smectite is at equilibrium, the apparent constant (K_a) defined below can be assumed to represent the equilibrium position:

$$\text{Residual } R_xO_y\ (x) \leftrightarrow \text{Dissolved } R_xO_y\ (x_m - x) \tag{1}$$

$$K_a = (x_m - x)/x \tag{2}$$

In this expression, x_m is the R_xO_y% in the untreated bentonite, x is the residual R_xO_y% and (x_m–x) is the dissolved R_xO_y% at equilibrium. We also assume that the effect of R_xO_y content arising from the impurities is negligible.

- The basic thermodynamic equations used for calculating apparent thermodynamic quantities are given below:

$$\Delta G^o = \Delta H^o - T\Delta S^o = -RT\ln K \tag{3}$$

where ΔG^o is the change in Gibbs free energy, ΔH^o and ΔS^o are the enthalpy and entropy changes, respectively, K is the equilibrium constant, T is the absolute temperature, and R is the universal gas constant.

- Temperature dependence of the apparent and real thermodynamic functions may be different from each other, but their temperature derivative or slopes of the related straight lines should be the same. An exact match of these lines is not generally expected but if that happens, it may be a sign of the validity of the equilibrium constant selected.

Calculations of thermodynamic quantities

The apparent equilibrium constant (K_a) and corresponding apparent change in Gibbs free energy (ΔG_a^o) for each temperature were calculated using Eqs (2) and (3), respectively. The variations of the equilibrium constant and Gibbs free energy with the temperature provide useful ways of determining the enthalpy and entropy differences, respectively. According to Eq. (3), the slopes of the graphs of $\ln K_a$ *vs.* $1/T$ and ΔG_a^o *vs.* T in Figs 4 and 5 give the real enthalpy (ΔH^o) and real entropy (ΔS^o) changes for acid dissolution. These quantities were calculated as ΔH^o=65687 kJ mol^{-1} and ΔS^o=164 J K^{-1} mol^{-1}. Therefore, the acid dissolution reaction of the bentonite is of endothermic nature and gives rise to an entropy increase.

The real equilibrium constant (K) and real Gibbs free energy change (ΔG^o) were calculated for each temperature from Eq. (3) using the calculated ΔH^o and ΔS^o values. The plots of $\ln K$ *vs.* $1/T$ and ΔG^o *vs.* T are also given in Figs 4 and 5, respectively. The overlapping of the apparent and real straight lines proves the validity of the definition of the apparent equilibrium constant. The temperature dependence of the real Gibbs free energy and the real equilibrium constant of the acid dissolution process between 50 and 150°C may be expressed by the function (SI units):

$$\Delta G^o = -RT\ln K = 65687 - 164T \tag{4}$$

If T is low enough, ΔG^o will be positive and the dissolution process will not occur spontaneously. In contrast, when T is high enough, ΔG^o will be negative, which means a spontaneous dissolution process. This result fits the experimental data.

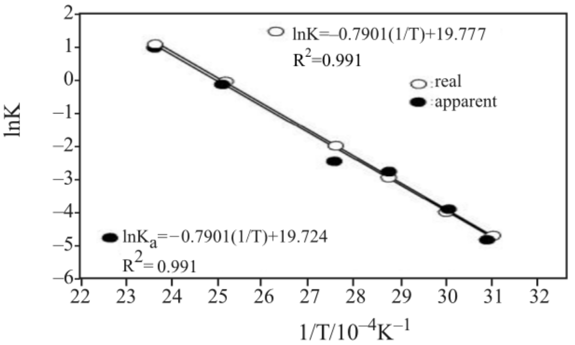

Fig. 4 The apparent and real van't Hoff plots for the dissolution process of acid treated smectites

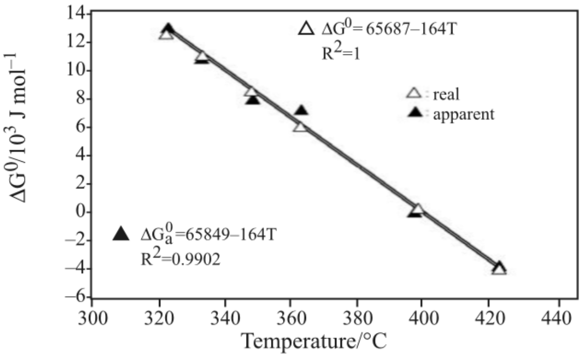

Fig. 5 The plots of the apparent and real free enthalpy changes *vs.* temperature for the dissolution process of acid treated smectites

Conclusions

Acid dissolution process of a bentonite could be examined thermodynamically as well as kinetically. Although there seem several kinetic studies on this process, no thermodynamic treatment of such solid phase reactions has been reported so far. For this reason, a thermodynamic model has been presented in present study to investigate the acid dissolution process of a Turkish bentonite based upon the total content of metal oxides (R_xO_y) of the undissolved Al^{3+}, Fe^{3+} and Mg^{2+} cations as an equilibrium parameter. The dissolved R_xO_y concentration in filtrate could also be taken as an equilibrium parameter instead of the undissolved R_xO_y content in residual material. However, the determination of the dissolved cation concentration was found to be troublesome since the amount of the unreacted H_2SO_4 was too difficult to remove by evaporation. The R_xO_y content arising from the impurities in bentonite affects the result. This effect is partly eliminated by taking a ratio through the description of the apparent equilibrium constant. The changes in the real thermodynamic quantities such as Gibbs free energy, enthalpy and entropy during acid dissolution were determined through well known thermodynamic formulas.

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References

1 R. E. Grim, Clay Mineralogy, 2nd Ed. McGraw Hill, New York 1968.
2 R. E. Grim and N. Güven, Bentonites-Geology, Mineralogy, Properties and Uses (Developments in Sedimentology, 24). Elsevier, New York 1978.
3 H. H. Murray, Appl. Clay Sci., 5 (1991) 379.
4 H. H. Murray, Clay Miner., 34 (1999) 39.
5 H. H. Murray, Appl. Clay Sci., 17 (2000) 207.
6 D. M. Moore and R. C. Reynolds, Jr., X-ray Diffraction Identification and Analysis of Clay Minerals, Oxford University Press, Oxford 1997.
7 R. L. Bleifuss, Clay Miner., 10 (1973) 41.
8 G. Lagaly, M. M. Vonmoos, G. Kahr and R. Fahr, Keram., Z. 33 (1981) 278.
9 P. Komadel, D. Schmidt, J. Madejovâ and B. Cicel, Appl. Clay Sci., 5 (1990) 113.
10 Y. Sarıkaya, M. Önal, B. Baran and T. Alemdaroğlu, Clays Clay Miner., 48 (2000) 557.
11 G. Jozefacıuk and G. Bowanko, Clays Clay Miner., 50 (2002) 771.
12 P. Komadel, Clay Miner., 38 (2003) 127.
13 Ö. Tan, L. Yılmaz and S. Zaimoğlu, Mater. Lett., 58 (2004) 1176.
14 H. Noyan, M. Önal and Y. Sarıkaya, Clays Clay Miner., 54 (2006) 375.
15 T. J. Pinnavaia, Science, 220 (1983) 365.
16 J. M. Adams, Appl. Clay Sci., 2 (1987) 309.
17 D. R. Brown and C.N. Rhodes, Catal. Lett., 45 (1997) 35.
18 S. R. Chitnis and M.M. Sharma, React. Funct. Polym., 32 (1997) 93.
19 F. Kooli and W. Jones, Clay Miner., 32 (1997) 633.
20 A. Tabak and B. Afsin, Adsorpt. Sci. Technol., 19 (2001) 673.
21 R. S. Varma, Tetrahedron, 58 (2002) 1235.
22 A. G. Espantaleon, J. A. Nieto, M. Fernandez and A. Marsal, Appl. Clay Sci., 24 (2003) 105.
23 M. G. F. Rodrigues, Ceramica, 49 (2003) 146.
24 W. T. Tsai, C. Y. Chang, C. H. Ing and C. F. Chang, J. Colloid Interface Sci., 275 (2004) 72.
25 M. K. H. Siddiqui, Bleaching Earths, Pergamon, Oxford 1968.
26 E. Srasra, F. Bergaya, H. Van Damme and N. K. Ariguib, Appl. Clay Sci., 4 (1989) 411.
27 P. Falaras, I. Kovanis, F. Lezou and G. Seiragakis, Clay Miner., 34 (1999) 221.
28 P. Falaras, F. Lezou, G. Seiragakis and D. Petrakis, Clays Clay Miner., 48 (2000) 549.
29 W. P. Gates, J. S. Anderson, M. D. Raven and G. J. Churchman, Appl. Clay Sci., 20 (2002) 189.
30 G. E. Christidis and S. Kosiari, Clays Clay Miner., 51 (2003) 327.
31 D. Plee, L. Gatineau and J. J. Fripiat, Clays Clay Miner., 35 (1987) 81.
32 M. Takashima, S. Sono and S. Ohara, J. Imaging Sci. Technol., 37 (1992) 163.
33 C. Breen, R. Watson, J. Madejova, P. Komadel and Z. Klapyta, Langmuir, 13 (1997) 6473.
34 A. Tabak, B. Afsin, B. Caglar and E. Koksal, J. Colloid Interface Sci., 313 (2007) 5.
35 A. Tabak, B. Afsin, S. F. Aygun and E. Koksal, J. Therm. Anal. Cal., 87 (2007) 377.
36 G. A. Mills, J. Holmes and E. B. Cornelius, J. Phys. Colloid Chem., 54 (1950) 1170.
37 R. D. Heyding, R. Ironside, A. R. Norris and R. Y. Pryslazniuk, Can. J. Chem., 38 (1960) 1003.
38 P. Komadel, J. Bujdak, J. Madejova, V. Sucha and F. Elsass, Clay Miner., 31 (1996a) 333.
39 P. Komadel, M. Janek, J. Madejova, A. Weekes and G. Breen, J. Chem. Soc. Faraday Trans., 93 (1997) 4207.
40 K. Van Rompaey, E. Van Ranst, F. De Coninck and N. Vindevogel, Appl. Clay Sci., 21 (2002) 241.
41 Z. Vunkovic, A. Milutinovic-Nikolic, J. Krstic, A. Abu-Rabi, T. Novakovic and D. Jovanovic, Mater. Sci. Forum, 494 (2005) 339.
42 Z. Vunkovic, A. Milutinovic, L. Rozic, A. Rosic, Z. Nedic and D. Jovanovic, Clays Clay Miner., 54 (2006) 697.
43 N. Jovanovic and J. Janackovic, Appl. Clay Sci., 6 (1991) 59.
44 J. Ravichandran and B. Sivasankar, Clays Clay Miner., 45 (1997) 854.
45 J. Madejova, J. Bujdak, M. Janek and P. Komadel, Spectrochim. Acta Part A, 54 (1998) 1397.
46 U. Flessner, D.J. Jones, J. Roziere, J. Zajac, L. Storaro, M. Lenarda, M. Pavan, A. Jimenez-Lopez, E. Rodriguez-Castellon, M. Trombetta and G. Busca, J. Mol. Catal. A: Chem., 168 (2001) 247.
47 M. Önal, Y. Sarıkaya, T. Alemdaroğlu and İ. Bozdoğan, Turk. J. Chem., 26 (2002) 409.
48 M.P. Hart and D.R. Brown, J. Mol. Catal. A: Chem., 212 (2004) 315-321.

49 J. Temuujin, Ts. Jadambaa, G. Burmaa, Sh. Erdenechimeg, J. Amarsanaa and K. J. D. MacKenzie, Ceram. Inter., 30 (2004) 251.
50 B. B. Osthaus, Clays Clay Miner., 2 (1954) 404.
51 B. B. Osthaus, Clays Clay Miner., 4 (1956) 301.
52 W. T. Granquist and G. Gardner-Sumner, Clays Clay Miner., 6 (1959) 292.
53 I. Tkac, P. Komadel and D. Müller, Clay Miner., 29 (1994) 11.
54 H. Noyan, M. Önal and Y. Sarıkaya, J. Therm. Anal. Cal., 91 (2008) 299.
55 W. P. Gates, J. Madejovâ, M. Janek and P. Komadel, Acta Universitas Carolinae Geologica, 38 (1996) 183.
56 P. Komadel, J. Madejovâ, M. Janek, W. P. Gates, R. J. Kirkpatrick and J. W. Stucki, Clays Clay Miner., 44 (1996b) 228.

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