

Synthesis and Characterization of Mesoporous Silica from Anorthite-Clay Mineral: Role of Mechanical Activation

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Mesoporous silica was prepared from anorthite-clay via mechanical activation (i.e., grinding) and selective acid leaching method. The pore characteristics of the mesoporous silica with different grinding time and acid treatment time were systematically characterized and compared with those prepared via heat treatment followed by acid treatment. Particle size, X-ray diffraction (XRD), BET surface area, thermal gravity (TG), and solubility analyses were carried out to characterize the samples. The XRD results showed that grinding and heat treatment dramatically altered the crystal structure of the samples, resulting in the change in weight loss curves of the corresponding samples from TG analysis. The results for pore size distribution of the prepared samples revealed that acid-treatment led to significant changes in the pore structure of the samples while grinding and heat-treatment without acid-treatment showed negligible influence on the pore structure. More specifically, acid-treatment increased the specific surface area of the ground and heat-treated samples regardless of acid-treatment. Furthermore, solubility tests for anorthite-clay samples showed that there is a positive relationship between the solubility of anorthite-clay and the specific surface area of mesoporous silica, indicating that the increase in the specific surface area of mesoporous silica was attributed to the increase in the solubility of anorthite-clay. [doi:10.2320/matertrans.M2014297]

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1. Introduction

The industrial utilization of clay minerals covers a wide range of applications including the production of ceramics, paper, paints, plastics, rubber, ink, cracking catalysts, adsorbents, etc.^{1–5)} The physical, chemical, structural, and surface properties of clay determine its applicability. These properties can be significantly modified by mechanochemical activation through grinding. Earlier studies showed that grinding considerably increases the surface area, the ion-exchange capacity, and the solubility in hydrochloric acid.^{6–13)} It has been found that the grinding of clay brings about a progressive lowering of the temperature at which the structural water is evolved.^{6,14)} Takahashi¹³⁾ found that prolonged dry grinding resulted in a disordered phase which yielded an amorphous material due to the complete destruction of the layer structure. This disintegration of clay crystals should be seen as a real amorphization of the structure characterized by the cleavage of bonds between clusters of atoms and the irreversible displacement of atomic groups which do not revert on release of the external load.^{8,15–17)} The product of such amorphization is a water-containing xerogel with random structure, in which the original hydroxyl groups of clay are converted into coordinated water bonded to the clay.^{12,17–21)} The solubility of the clay minerals in acids is of fundamental importance because it reveals certain attributes of the clay minerals.^{22–25)} Solubility characteristics are important in determining the utility of various clays as sources of aluminum and silicon.^{23,24,26,27)} The solubility of clay in acids varies with

the nature and concentration of the acid, the acid-to-clay ratio, the temperature, and the duration of treatment.^{7,23,26–28)} Most of these investigations have indicated that the clay is more soluble in sulfuric than in hydrochloric acid. Under similar condition of acid treatment, after amorphization by heating or grinding, all or substantially all the alumina of the clay is soluble.^{23,26–28)} Temuujin *et al.*²⁷⁾ prepared porous silica via mechanochemical and thermal amorphization of clay (kaolinite) followed by sulfuric acid leaching, and they found that the mechanically amorphized acid-treated clay showed a uniform pore size distribution in the mesopore region.²⁷⁾ Although the formation of mesoporous silica using heated and ground clay has been studied, to the best of our knowledge, no study has been conducted to investigate the effects of grinding on the pore characteristics of mesoporous silica prepared using anorthite-clay, suggesting relevant research is required since the grinding and leaching process is highly dependent on the nature of starting materials by which the pore properties of mesoporous materials are expected to vary. Hence, the aim of this study was to prepare mesoporous silica using mechanically amorphized anorthite-clay by selective acid leaching and to examine the pore characteristics of the materials according to grinding time. To better understand the phenomena, the pore characteristics of mesoporous silica prepared via mechanical amorphization and those via heat treatment, which is widely used for the synthesis of mesoporous silica, were compared.

2. Materials and Methods

2.1 Synthesis of mesoporous silica

The anorthite-clay was used in this experiment. The

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chemical composition of the Sanchung anorthite-clay in mass% is: SiO₂, 45.6; Al₂O₃, 34.5; Fe₂O₃, 0.53; MgO, 0.25; CaO, 9.9; Na₂O, 3.36; FeO, 0.22; K₂O, 0.19; TiO₂, 0.1; Ignition loss, 4.62. It was wet ground for 8 h using attrition mill (KMDC-1B, Korea Material Development Co., South Korea). Milling was carried out with a 300 g air-dried sample and 1000 g water in an 3000 cm³ capacity alumina jar filled with 5 mm alumina balls (ball packing ratio = 0.5). The applied rotation speed was 600 rpm. Ground clay sample was dried for 96 h at 105°C and then reground by agate. After grinding, 30 g of sample was selectively leached with 300 mL of 20 mass% H₂SO₄ solution for 2–6 h at 90°C, followed by the addition of distilled water. The leached material was filtered through a glass filter, washed three times with distilled water and dried at 105°C overnight. For comparison, the original anorthite-clay sample ($d_{50} = 40 \mu\text{m}$) was heat-treated at 600°C for 4 h. The calcined material was also leached as it was described above. In order to obtain the silicate solution, 60 g of the acid leached residues (the calcined and the ground) were stirred vigorously in 0.5 M NaOH solution (2000 mL) at 60°C for 24 h.

For mesoporous silica synthesis, 4 g of Pluronic P123 (EO₂₀PO₇₀EO₂₀, Mw = 5800) was dissolved in 120 g of 2 M HCl solution and then stirred at 35°C. Then, 46 g of the prepared silicate solution was added into HCl solution and then stirred for 20 h. The mixture was aged at 90°C for 24 h. The precipitated product was filtered, washed, dried and calcined at 600°C for 2 h.²⁹⁾

2.2 Characterization

The particle size distribution was measured by Accusizer 780 (At Frontier Co., South Korea). The XRD of products was performed using a powder X-ray diffractometer (D-MAX III, Rigaku, Japan) operating at 100 kV and 40 mA using the K α 1 emission of copper at $\lambda = 0.154 \text{ nm}$. Thermogravimetric (TG) analyse of the samples were performed with a TA Instruments SDT2960. The sample powders were heated in flowing air from ambient temperature to 400°C at a rate of 5°C min⁻¹. Surface and shape of the mesoporous samples were observed with a field-emission scanning electron microscope (JSM-6330F, JEOL). The nitrogen adsorption-desorption isotherms were obtained using a physisorption analyzer (ASAP 2020, Micromeritics) at liquid nitrogen temperature (−196°C). The samples were evacuated in a high vacuum for 3 h at 300°C before each measurement. The specific surface area was assessed from nitrogen adsorption data in the partial relative pressure range of 0.05–0.25 using the Brunauer-Emmett-Teller (BET) method,³⁰⁾ and the mesopore size distributions (2.0–50 nm) were analyzed using the BJH method.³¹⁾ In addition, the ground and calcined samples according to acid-treatment time were digested in an HNO₃-HF-HClO₄ solution, and then the metal concentration was analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES, iCAP 7000DUO, Thermo Scientific).³²⁾ The Si concentration of the silicate solution was also measured by ICP-OES.

3. Results and Discussion

3.1 Effect of grinding on the physical and chemical property of anorthite-clay

The domestic anorthite-clay was wet ground for 8 h by

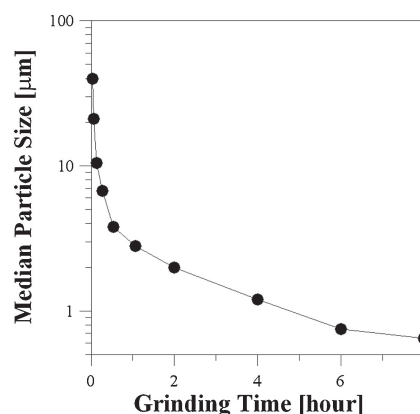


Fig. 1 Change of median size of anorthite-clay according to grinding time.

attrition mill. Generally, particle size of clay material is under 2 μm . It is necessary for the clay material to grind under 2 μm in order to confirm the grinding effect of clay mineral. Figure 1 shows the median particle size of ground clay sample. The median particle size of clay mineral was under 2 μm after 2 h grinding. The grinding rate decreased as further grinding. It can be obtained 0.67 μm sized clay particles by grinding for 8 h.

In order to investigate the structural alterations resulted from mechanochemical, acid and heat treatment, XRD analysis was carried out. Figure 2 shows the XRD profiles of the untreated and acid treated anorthite-clay. The diffractograms indicate that the grinding for 8 h and the calcination at 600°C cause significant structural degradation. Comparing the main peak of anorthite-clay for original anorthite-clay, those for the ground sample and for the calcined sample decrease about 89% and 68%, respectively. The halloysite peak for original sample by 11° 2 θ disappeared after the calcination and the grinding. After the sulfuric acid treatment, all sample have the broad reflection of amorphous silica (2 θ = 20–30°). The mechanical amorphization of the anorthite-clay causes a reduction of the relative peak of anorthite-clay phases. The anorthite-clay peak of calcined sample reduces and the alumina peak grows up, as the sulfuric acid treatment time increases. The anorthite-clay peak of ground sample was disappeared and the very strong aluminum peak appeared in all acid treated samples. Stronger alumina peaks of ground sample than calcined sample indicate that anorthite-clay and halloysite phases of ground one are more destroyed.^{28,33)} The changes in the peak parameters demonstrate that a sufficiently disordered part of the anorthite-clay and halloysite phase reacts with sulfuric acid.

Table 1 shows the element concentration of ground and calcined anorthite samples according to acid-treatment time. Overall, element concentration was observed to more decrease for ground samples than calcined ones after acid-treatment. Especially, the content of Al and Ca elements that existed as high content in the samples before acid-treatment was largely reduced after acid-treatment. Based on the results, it was found that the pre-treatment process via a mechanical grinding could remove the impurity from the anorthite more efficiently.

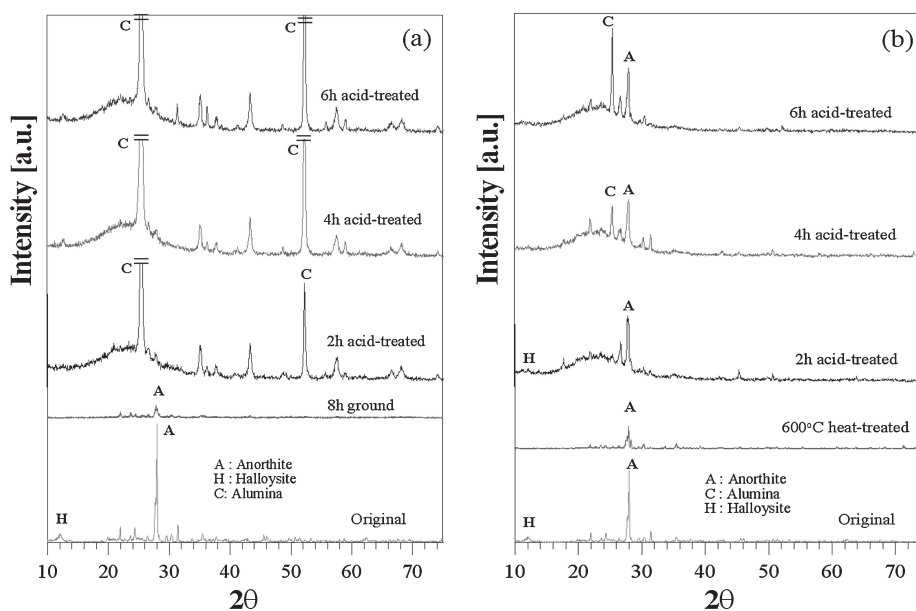


Fig. 2 X-ray diffraction patterns of the original, mechanically activated (ground) (a), and heat-treated (b) anorthite-clays before and after acid leaching.

Table 1 Element concentration of the ground and calcined samples according to acid-treatment time.

Acid-treatment (h)	Ground sample (mg/kg)				Calcined sample (mg/kg)			
	Al	Ca	Fe	Mg	Al	Ca	Fe	Mg
0	32040	8541	745	188	33155	8674	766	195
2	9.56	2.87	0.08	0.04	11.87	4.08	0.31	0.08
4	9.03	0.65	0.05	0.04	10.80	0.66	0.23	0.08
6	7.46	0.61	0.03	0.02	9.82	0.63	0.17	0.07

3.2 Effect of grinding on the pore characteristics of mesoporous silica

Figure 3 is the pore size distributions of samples calculated from N_2 adsorption-desorption isotherms. Concerning the fact that many natural clays consist of mixtures of at least two minerals with different crystallinity, it can be concluded that the sulfuric acid reacts first with high defect part of the raw material. The calcined sample is little different to the original material (see Fig. 3(a)). The micropore of ground sample is a little increase, while mesopore (3 nm–5 nm) is disappeared as compared to the original sample.

Acid treatment can cause a more drastic increase in both the micropore and the mesopore of calcined sample (Fig. 3(b)). The halloysite and anorthite-clay may be converted to the porous silica by the extraction of alumina in crystalline of aluminosilicate. Continuous acid treatment over 2 h, however, causes the decrease of micropore. It is considered that the micropore structure of gel-like silica collapse by attack of acid for a long time over 2 h. After the acid treatment, a little mesopore (3–5 nm) of ground samples is shown in Fig. 3(c). This is for the collapse of crystal structure of sample by the long time grinding before the acid treatment. The three samples with different acid time have the similar (almost same) specific surface area and the pore size distribution. It is indicating that 2 h is enough to extract all acid soluble components (Al, Fe, Mg, Ca, etc.).^{33–35)}

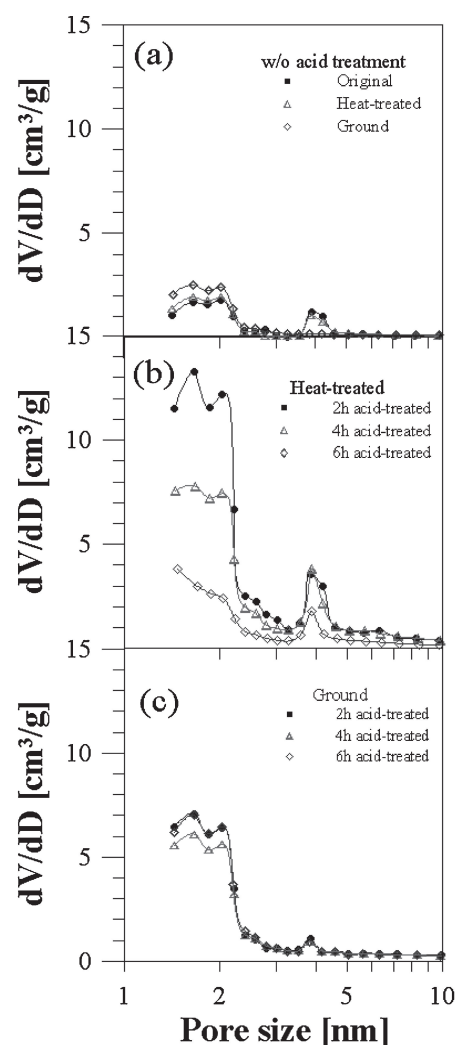


Fig. 3 Pore size distributions of the mesoporous silica prepared without (a) and with (b) and (c) acid-treatment: the mesoporous silica prepared with original, ground, and heat-treated anorthite-clays (a), the mesoporous silica prepared with heat-treated anorthite-clay (b), and the mesoporous silica prepared with ground anorthite-clay (c).

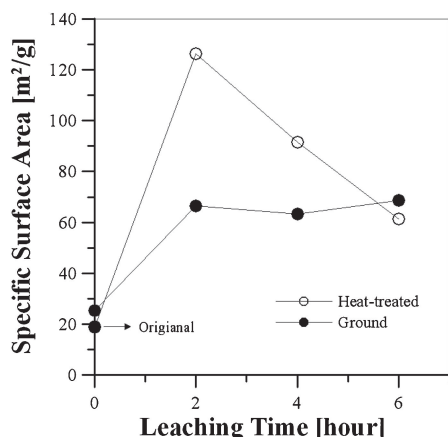


Fig. 4 Specific surface area of original, ground, and heat-treated anorthite-clays as a function of acid leaching time.

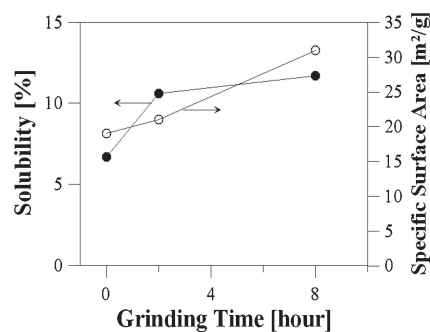


Fig. 6 Silicate solubility behavior and specific surface area of anorthite-clay as a function of grinding time. The weight ratio between a solution of ground anorthite-clays and NaOH solution was 6 : 4.

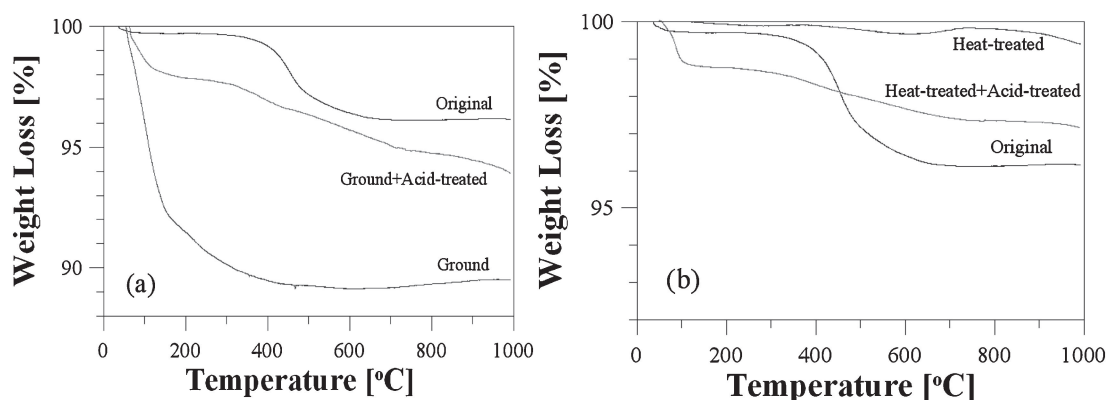


Fig. 5 Thermal gravity analysis results for ground versus ground+acid-leached samples (a) as well as heat-treated versus heat-treated+acid-treated samples (b). For comparison, the result for original sample is also presented.

Figure 4 is showing the changes of specific surface area of both calcined and ground samples. Ground sample with $0.7\ \mu\text{m}$ particle size reacts rapidly with sulfuric acid, so that longer leaching time over 2 h is not necessary, while calcined sample is slowly reacted with sulfuric acid due to its big particle size ($40\ \mu\text{m}$).³⁶⁾

The TG curves of anorthite-clay samples are shown in Fig. 5. The TG curve of original anorthite-clay shows the weight loss at around 500°C related to the dehydroxylation of halloysite. TG curve of metahalloysite (calcined halloysite) showed the less weight loss. TG curve of ground sample shows a broad profile indicating complex water loss. First, adsorbed water is removed, while the gel-like water which is coordinated to the halloysite surface is liberated at higher temperatures. The TG curves for both acid-treated ground and acid-treated calcined samples are similar, though weight losses are different. The TG curves of the acid treated samples show two stepped curves, with a steep weight loss beneath 200°C , followed by a second, gradual loss which continues even in higher temperatures. The first mass loss is attributed to the liberation of adsorbed water in the micropore, while the second stage (above 200°C) indicates the removal of the hydroxyls (coordinated water) of the silanol groups.³⁷⁾

Figure 6 shows the silicate solubility in NaOH solution of ground samples. A solution of ground anorthite-clay samples and 1.6M NaOH in the ratio of 6 : 4 (weight) is stirred

vigorously at 90°C for 24 h. The silicate solubility of ground samples is about twice of that of raw sample, due to the increase of specific surface area of ground sample. The specific surface area of sample increase about 1.8 times after the grinding. The smaller particle size is by grinding, the more silica is soluble. Figure 7 shows that silicate solubility (extraction rate) of ground sample ($d_{50} = \sim 0.7\ \mu\text{m}$) is a little higher than that of calcined sample ($d_{50} = \sim 40\ \mu\text{m}$). This is due to the particle size effect caused by Thompson-Gibbs effect.^{38,39)} The amorphous silica was found to form after the acid leaching as can be seen in XRD results (Fig. 2). The amorphous silica is easy to dissolve in NaOH solution. Thus, it is considered that the silicate solubility of samples in NaOH solution increased about 4 or 5 times after the sulfuric acid leaching of them for 6 h.

4. Conclusions

This study was conducted to prepare mesoporous silica using mechanically amorphized anorthite-clay by selective acid leaching and to examine the pore characteristics of the materials according to mechanical activation (i.e., grinding) time. Additionally, the pore characteristics of mesoporous silica prepared via mechanical amorphization were compared those via heat treatment. The findings from this study are as follows:

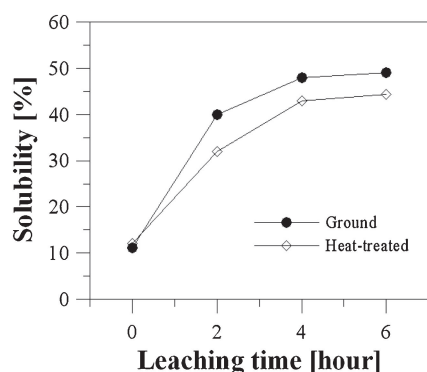


Fig. 7 Silicate solubility of ground and heat-treated anorthite-clays as a function of acid leaching time. The weight ratio between a solution of anorthite-clays and NaOH solution was 6 : 4.

- (1) Through XRD analysis, it was found that grinding and heat treatment substantially altered the crystal structure of the samples, which resulted in huge differences in the trend of weight loss of the corresponding samples from TG analysis.
- (2) The results for nitrogen adsorption tests of the mesoporous silica prepared via grinding and heat-treatment revealed that acid-treatment led to significant changes (i.e., increased micropore volume) in the pore structure of the samples while the samples without acid-treatment showed negligible influence on the pore structure regardless of pre-treatment methods (i.e., grinding and heat-treatment).
- (3) Based on the solubility test results obtained for the ground anorthite-clay, a positive relationship was observed between the solubility of anorthite-clay in NaOH solution and the specific surface area of mesoporous silica, indicating that the increase in the specific surface area of mesoporous silica was attributed to the increase in the solubility of anorthite-clay due to grinding.

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REFERENCES

- 1) R. O. Ajemba and O. D. Onukwuli: *Physicochem. Probl. Miner. Process.* **50** (2014) 349–358.
- 2) Y. Jiang, H. Ruan, S. Lai, C. Lee, C. Yu, Z. Wu, X. Chen and S. He: *Earth Sci.* **2** (2013) 40–46.
- 3) Y. Liu, Y. Kang, B. Mu and A. Wang: *Chem. Eng. J.* **237** (2014) 403–410.
- 4) H. H. Murray: *Appl. Clay Sci.* **5** (1991) 379–395.
- 5) C. Viseras, C. Aguzzi, P. Cerezo and A. Lopez-Galindo: *Appl. Clay Sci.* **36** (2007) 37–50.
- 6) J. Gamelas, E. Ferraz and F. Rocha: *Colloid. Surface. A* **455** (2014) 49–57.
- 7) S. Gregg, T. Parker and M. J. Stephens: *J. Appl. Chem.* **4** (1954) 666–674.
- 8) J. Hlavay, K. Jonas, S. Elek and J. Inczedy: *Clay. Clay Miner.* **25** (1977) 451–456.
- 9) W. P. Kelley and H. Jenny: *Soil Sci.* **41** (1936) 367–382.
- 10) W. D. Laws and J. Page: *Soil Sci.* **62** (1946) 310–336.
- 11) K. R. Marra, G. S. Soreghan, M. E. Elwood Madden, L. J. Keiser and B. L. Hall: *Geomorphology* **206** (2014) 483–491.
- 12) J. G. Miller and T. D. Oulton: *Clay. Clay Miner.* **18** (1970) 313–323.
- 13) H. Takahashi: *B. Chem. Soc. Jpn.* **32** (1959) 235–245.
- 14) A. K. Chakraborty: *Phase Transformation of Kaolinite Clay*, (Springer, 2014).
- 15) S. Mohammadnejad, J. L. Provis and J. S. van Deventer: *Miner. Eng.* **52** (2013) 31–37.
- 16) M. Valaskova, K. Barabasova, M. Hundakova, M. Ritz and E. Plevova: *Appl. Clay Sci.* **54** (2011) 70–76.
- 17) R. L. Frost, E. Horvath, E. Mako and J. Kristof: *J. Colloid Interf. Sci.* **270** (2004) 337–346.
- 18) E. Horvath, R. L. Frost, E. Mako, J. Kristof and T. Cseh: *Thermochim. Acta* **404** (2003) 227–234.
- 19) E. Kristof, A. Z. Juhasz and I. Vassanyi: *Clay. Clay Miner.* **41** (1993) 608–612.
- 20) J. Kristof, R. L. Frost, J. T. Klopogge, E. Horvath and E. Mako: *J. Therm. Anal. Calorim.* **69** (2002) 77–83.
- 21) E. Mako, R. L. Frost, J. Kristof and E. Horvath: *J. Colloid Interf. Sci.* **244** (2001) 359–364.
- 22) M. Ebinger and D. Schulze: *Clay. Clay Miner.* **37** (1989) 151–156.
- 23) R. E. Grim: *Clay Mineralogy*, 2nd ed., (McGraw-Hill, Inc., New York, 1968).
- 24) M. G. Stapleton, D. L. Sparks and S. K. Dentel: *Environ. Sci. Technol.* **28** (1994) 2330–2335.
- 25) S. J. Traina, G. Sposito, D. Hesterberg and U. Kafkafi: *Soil Sci. Soc. Am. J.* **50** (1986) 45–52.
- 26) K. Okada, A. Shimai, T. Takei, S. Hayashi, A. Yasumori and K. J. D. MacKenzie: *Micropor. Mesopor. Mat.* **21** (1998) 289–296.
- 27) J. Temuujin, G. Burmaa, J. Amgalan, K. Okada, T. Jadambaa and K. J. D. MacKenzie: *J. Porous Mat.* **8** (2001) 233–238.
- 28) E. F. Aglietti, J. M. P. Lopez and E. Pereira: *Int. J. Miner. Process.* **16** (1986) 125–133.
- 29) J. Park, J. Park and H. Shin: *Mater. Lett.* **61** (2007) 156–159.
- 30) Y. Han, H. Kim, J. Park, S. Lee and J. Kim: *Int. J. Hydrogen Energy* **37** (2012) 14240–14247.
- 31) Y. Han, J. Choi, M. Tong and H. Kim: *Mater. Charact.* **90** (2014) 31–39.
- 32) Y. Han, G. Hwang, D. Kim, S. Park and H. Kim: *J. Hazard. Mater.* **283** (2015) 44–52.
- 33) H. Misran, R. Singh, S. Begum and M. A. Yarmo: *J. Mater. Process. Technol.* **186** (2007) 8–13.
- 34) M. Gomez-Cazalilla, J. Merida-Robles, A. Gurbani, E. Rodriguez-Castellon and A. Jimenez-Lopez: *J. Solid State Chem.* **180** (2007) 1130–1140.
- 35) P. Kumar, N. Mal, Y. Oumi, K. Yamana and T. Sano: *J. Mater. Chem.* **11** (2001) 3285–3290.
- 36) M. I. Mahadi and S. Palaniandy: *Int. J. Miner. Process.* **94** (2010) 172–179.
- 37) L. Peng, W. Qisui, L. Xi and Z. Chaocan: *Colloid. Surf. A* **334** (2009) 112–115.
- 38) Q. Cheng, Z. Cui, J. Li, S. Qin, F. Yan and J. Li: *J. Power Sources* **266** (2014) 401–413.
- 39) S. A. Kim and L. A. Archer: *Macromolecules* **47** (2014) 687–694.