Clay Minerals, (2017) **52**, 67–73

Adsorption studies of hydrogen and ethylene on cation-exchanged bentonite

BURCU ERDOĞAN ALVER*

Department of Physics, Faculty of Science, Anadolu University, Eskisehir 26470, Turkey

(*Received 17 August 2016; revised 7 December 2016; Editor: George Christidis*)

ABSTRACT: The adsorption of C_2H_4 and H_2 gases by bentonite from the Ünye region, Turkey both as raw (B) and as K^+-, Li^+-, Ag^+- and Mg^{2+}-exchanged forms, was investigated using automated volumetric equipment and pressures up to 100 kPa at 273 K and 77 K, respectively. X-ray powder diffraction (XRD) and specific surface area measurement (BET) methods were employed to characterize the bentonite samples. The C_2H_4 and H_2 gas adsorption capacities of the original and modified forms were in the ranges 1.817–0.201 mmol g^{-1} and 0.522–0.388 mmol g^{-1}, respectively. The influence of salt modifications on the gas adsorption properties of bentonite is discussed.

KEYWORDS: adsorption, bentonite, BET, ethylene, hydrogen, XRD.

Montmorillonite, a member of the smectite group, consists of an octahedral sheet sandwiched between two tetrahedral sheets (Grim & Güven, 1978). The clay rock, consisting predominantly of smectites, is bentonite. The isomorphic substitutions of Fe and Mg by Al in the octahedral sheet and of Al by Si in the tetrahedral sheet lead to a negative charge density (Brindley & Brown, 1980; Murray, 1999). This net positive charge deficiency is neutralized by loosely bound exchangeable cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) which are commonly hydrated and adsorbed in the interlayer space between the 2:1 layers and around the edges of the crystals (Murray, 1999, 2007).

Water available in the smectite is associated with the interlayer spaces, the layer surfaces and the pores (Güven, 1992). Variation in exchangeable cations affects properties such as the amount of interlayer water and hence swelling and gas adsorption. Hence, in order to ameliorate environmental damage caused by pollutant gases, the investigation of the clay minerals as adsorbents after ion-exchange with various metals is of great importance.

A large number of studies has been carried out on the characterization of the ion-exchanged bentonites (Adams, 1987; Komadel *et al*., 1990; Cases *et al*., 1997; Rutherford *et al*., 1997; Lee *et al*., 1999; Xu *et al*., 2000; Jozefaciuk & Bowanko, 2002; Yıldız & Çalımlı, 2002; Neaman *et al*., 2003; Huang *et al*., 2004; Volzone & Ortiga, 2004; Çağlar *et al*., 2009). Information is scarce, however, about the adsorption of ethylene (Choundry *et al*., 2002; Park *et al*., 2002; Cho *et al*., 2005; Saini *et al*., 2011; Erdoğan Alver & Sakızcı, 2012; Youngjan, 2012; Erdoğan Alver *et al*., 2016) and hydrogen (Gil *et al*., 2007, 2009; Didier, 2012; Bardelli *et al*., 2014; Edge, 2015; Mondelli *et al*., 2015) by clay and clay-based materials. Furthermore, very few publications are available in the literature that discuss the ethylene and hydrogen adsorption properties of K, Na-, Li-, Ag- and Mg-modified bentonites from Turkey. Hence, the aim of the present study was to assess the influence of cation exchange on the C_2H_4 and H_2 gas-adsorption properties of a bentonite sample from the Ünye region for possible food- and energy-storage applications.

*E-mail: burcuerdogan@anadolu.edu.tr
https://doi.org/10.1180/claymin.2017.052.1.04

EXPERIMENTAL

Materials

A natural bentonite (B) sample originating from the Ünye region of Turkey was supplied by Ünye Mining Company. The composition of the natural bentonite (wt.%) is as follows: 60.22 SiO_2; 20.83 Al_2O_3; 3.23 Fe_2O_3; 4.67 MgO; 2.36 CaO; 0.30 Na_2O; 1.82 K_2O; 6.22 LOI (loss on ignition) The sample was crushed, ground and sieved to pass through a <63 µm sieve. In order to determine the changes in adsorption properties, bentonite samples were treated with 100 mL of 1 M KNO_3, $LiNO_3$, $AgNO_3$ and $Mg(NO_3)_2$ solutions at 90° C for 4 h in a shaker. Inorganic chemicals were supplied by Merck (Darmstadt, Germany) and all solutions were prepared by using de-ionized water. After the treatment, samples were separated and washed several times with hot distilled water, dried at room temperature and then dried in an oven at 100°C for 20 h and stored in a desiccator. The resulting salt-modified samples were denoted as Ag-B, K-B, Li-B and Mg-B, according to their corresponding treatments with Ag- K-, Li-, and Mg-nitrate solutions, respectively.

Methods

Powder X-ray diffraction (XRD) measurements were performed with a Bruker D8 Advance X-ray diffractometer, using Cu-$K\alpha$ radiation ($\lambda = 1.54$ Å) at 40 kV and 40 mA, within the $5° < 2\theta < 40°$ range. The samples were scanned with a 0.02° 2θ step. The BET (Brunauer *et al*., 1938) surface areas were calculated from the first part of the N_2 adsorption isotherm ($0.05 < P/P_0 < 0.35$) obtained at liquid nitrogen temperature using N_2 in an Autosorb 1 instrument (Quantachrome Instruments, Boynton Beach, Florida, USA). The t-plot method was used to calculate the micropore surface area and micropore volume. High-purity (99.99%) nitrogen was used in adsorption measurements. All the samples were outgassed at 125°C for 12 h prior to N_2, C_2H_4 and H_2 adsorption. All experiments were run in duplicate in order to confirm the reproducibility of the results obtained.

RESULTS AND DISCUSSION

X-ray diffraction

The powder XRD patterns for raw (B) and ion-exchanged bentonite samples are shown in Fig. 1. Sample B consists mainly of smectite (Moore & Reynolds, 1997). In addition, the sample contained mica/illite and feldspar. According to the d_{001} spacing of smectite (14.45 Å) the original material was Ca-bentonite.

As a result of the ion-exchange treatment, considerable variation occurred in the XRD traces, especially in the positions of the 001 peaks due to the different amounts of water layers in the interlayer space of smectite. The d_{001} spacing values of K^+-, Li^+- and Mg^{2+}-exchanged forms of smectite were: $d_{001\text{Mg-B}}$ (14.04 Å) > $d_{001\text{Li-B}}$ (11.89 Å) > $d_{001\text{K-B}}$ (10.73 Å). The d_{001} spacing values increased as the cation valence and hydrated radius increased, in accordance with previous studies (Berend *et al*., 1995; Balek *et al*., 2008; Li *et al*., 2012). On the other hand, ion exchange with 1 M $AgNO_3$ solution led to the disappearance of the 001 peak in the XRD pattern of the Ag-B sample (Fig. 1). Pessanha *et al*. (2014) observed similar behaviour after treatment of montmorillonite with silver nitrate solution. In addition, the relative intensities of prismatic smectite reflections decreased after treatment with $AgNO_3$.

N_2 adsorption

The d_{001} spacing value indicating the distance between layers does not indicate the presence of free space to host gas molecules (Volzone & Ortiga, 2004). The specific surface area is a very effective method for providing quantitative assessment of the area available for the surface reactions. Nitrogen adsorption isotherms of raw bentonite (B) and of Ag-B, K-B, Li-B and Mg-B samples are shown in Fig. 2. All the isotherms were of type II (Brunauer *et al*., 1940; Gregg & Sing, 1982).

Table 1 presents some important parameters obtained from the analysis of the adsorption isotherms. The N_2 adsorption data show that the BET surface areas (72–98 $m^2\ g^{-1}$) of the ion exchanged bentonites are larger than those of the original Ca-bentonite (71 $m^2\ g^{-1}$), which might be due to the accommodation of the cations in interlayer space of the montmorillonite (Table 1). Except for the Ag-B, the specific surface areas increased with increasing ionic radius of the exchangeable cation. This result is in agreement with previous studies on bentonites saturated with different cations (Berend *et al*., 1995; Volzone & Ortiga, 2004; Li *et al*., 2012).

Adsorption of C_2H_4

Adsorption of high-purity C_2H_4 gas on the B, Ag-B, K-B, Li-B and Mg-B samples was done at 273 K and

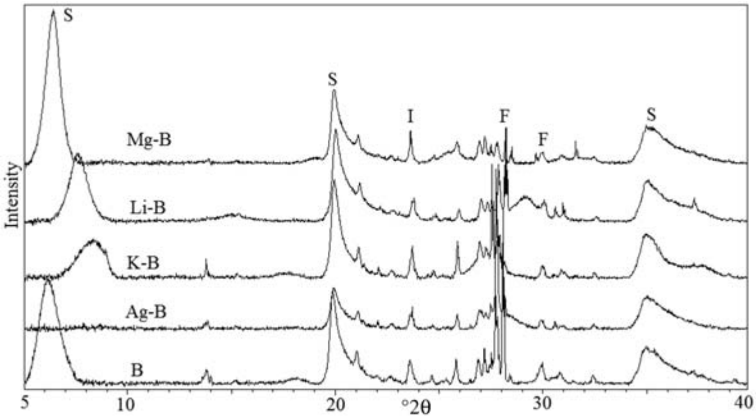

FIG. 1. XRD patterns of B, Ag-B, K-B, Li-B and Mg-B samples (S: smectite; F: feldspar; I: illite).

pressures up to 100 kPa and the absolute amounts of C_2H_4 adsorbed per gram of bentonite are listed in Table 2. Experimental C_2H_4-adsorption isotherms are presented in Fig. 3. The maximum ethylene adsorption capacity was obtained for bentonite modified by Ag^+ ions. The adsorption of C_2H_4 by the different ion-exchanged montmorillonites decreased in the following order: Ag-B > K-B > B > Li-B > Mg-B.

The physicochemical characteristics of the adsorbate gas and the adsorbents such as clay minerals and zeolites play an important role in the gas-adsorption capacity (Baksh & Yang 1992). Changes in the interlayer space, the size of exchangeable cation, the amount of internal and external surface area, the porosity and the pore volume result in significant variations in gas retention (Volzone & Ortiga, 2004; Volzone, 2007). In the present study, other than for Ag-B, the amount of C_2H_4 retention was found to increase as a function of the specific surface area. Ag^+ exchange in smectite influenced its gas-adsorption behaviour significantly and the Ag-B sample exhibited preferential adsorption towards ethylene. Nevertheless, the specific surface area of the Ag-B sample was moderate ($72\ m^2\ g^{-1}$). The adsorption selectivity was ascribed to specific interaction between the π electrons of C_2H_4 and silver ions (Choundry *et al.*, 2002; Yang, 2003; Cho *et al.*, 2005). Due to the presence of π electrons, the high polarizability and the quadrupole moment, ethylene interacts with the surface of Ag-B more strongly than the remaining ion-exchanged forms.

Adsorption of C_2H_4 by Ag-B determined in the present study ($1.817\ mmol\ g^{-1}$ at 273 K) was slightly

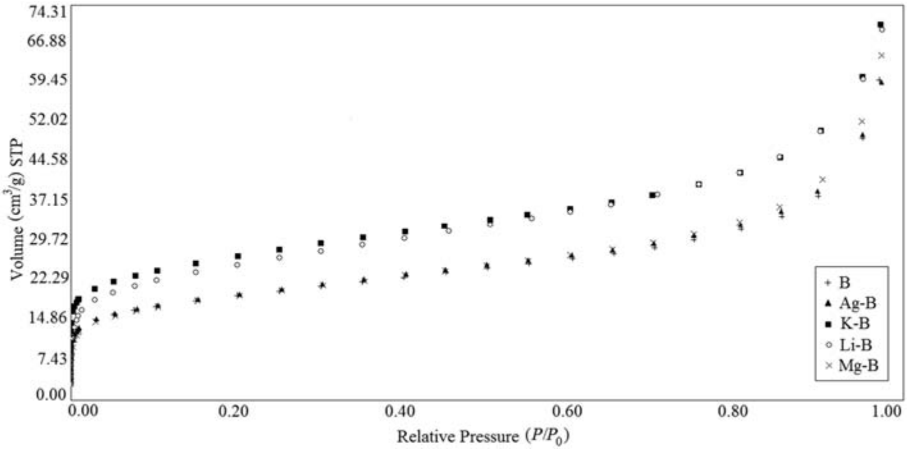

FIG. 2. N_2 adsorption isotherms of B, Ag-B, K-B, Li-B and Mg-B samples.

TABLE 1. N_2 adsorption data of the B, Ag-B, K-B, Li-B and Mg-B samples at 77 K.

Sample	BET surface area ($m^2\ g^{-1}$)	Micropore surface area ($m^2\ g^{-1}$)	Micropore volume ($cm^3\ g^{-1}$)
B	71	29.6	0.012
Ag-B	72	27.2	0.011
K-B	98	41.3	0.017
Li-B	92	32.6	0.013
Mg-B	72	26.9	0.011

TABLE 2. C_2H_4 and H_2 adsorption data of the B, Ag-B, K-B, Li-B and Mg-B samples.

Sample	C_2H_4 adsorption (mmol/g) at 273 K and up to 100 kPa	H_2 adsorption (mmol/g) at 77 K and up to 100 kPa
B	0.292	0.396
Ag-B	1.817	0.436
K-B	0.335	0.522
Li-B	0.240	0.388
Mg-B	0.201	0.503

greater than the same bentonite from the same region treated with Ag-, Cu- and Fe-nitrate solutions (1.738–0.167 mmol g^{-1} at 273 K) at 90°C for 3 h (Erdoğan Alver & Günal, 2016) or modified with various HCl solutions (0.249–0.719 mmol g^{-1}) at 273 K (Erdoğan Alver *et al*., 2016). Similarly it was greater than that of the natural and acid-modified bentonites from the Çankırı and Mihalıçık regions (0.101–0.144 mmol g^{-1}) at 273 K (Erdoğan Alver & Sakızcı, 2012), of an Ag^+-impregnated clay-based adsorbent, olesorb-1 (1.17 mmol/g), at 30°C (Choundry *et al*., 2002) and of a $AgNO_3$/clay (1.26 mmol g^{-1}) at 25°C (Cho *et al*., 2005), probably due to structural and textural properties. The greatest gas-retention level of C_2H_4 was achieved by the Ag-B sample, which could therefore be used to delay the deterioration of food (*e.g.* fruit and vegetables), by removing the ethylene gas generated during storage.

Adsorption of H_2

Adsorption isotherms of H_2 for raw and cation-exchanged forms were measured at 77 K up to 100 kPa

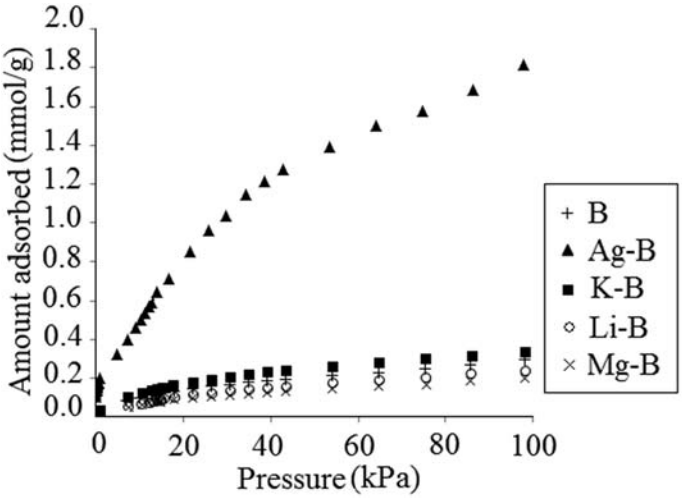

FIG. 3. Adsorption isotherms of C_2H_4 on B, Ag-B, K-B, Li-B and Mg-B samples.

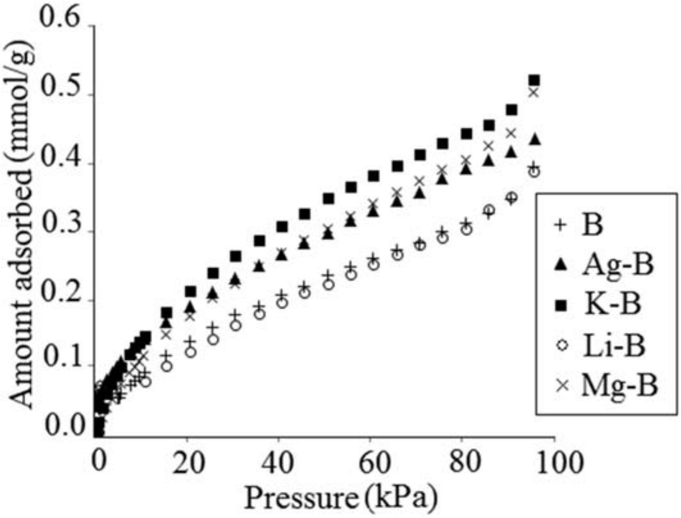

FIG. 4. Adsorption isotherms of H_2 on B, Ag-B, K-B, Li-B and Mg-B samples.

(Fig. 4). High-purity hydrogen gas was used. The hydrogen isotherms were of type I. Other than for Li-B, the treatment of bentonite with alkaline solutions led to an increase in adsorption capacity for H_2 gas. Uptake values of H_2 by different cation-exchanged forms of montmorillonite were in the following sequence: K-B > Mg-B > Ag-B > B > Li-B. The ion-exchanged bentonites showed different tendencies with respect to H_2. The different retention values of C_2H_4 and H_2 gases by the alkaline-treated bentonites could be attributed to differences in temperature and physicochemical properties of the adsorbates (Venaruzzo *et al.*, 2002).

Due to the different experimental conditions used, it is difficult to compare the results of experiments with H_2 adsorption data reported in the literature. Hydrogen adsorption by the K-B sample (0.522 mmol g^{-1} at 77 K) was comparable to that of montmorillonite (from Gador) calcined at 473 K for 4 h (~0.5 mmol g^{-1}) (Gil *et al.*, 2007) and slightly less than that of intercalated montmorillonite (from Tsukinuno) calcined for 4 h at 473 K (Gil *et al.*, 2009), Na-montmorillonite for H_2 adsorption at high pressures (up to 90 bar) and 363 K (Mondelli *et al.*, 2015) and a Callovo-Oxfordian clay rock studied by Bardelli *et al.* (2014). Experimental results indicated that ion exchange of B with aqueous solutions of KNO_3, $LiNO_3$, $AgNO_3$ and $Mg(NO_3)_2$ had a marked influence on H_2 gas adsorption. The degree of retention of H_2 was small in the original bentonite. In contrast, the Ag^+-, Li^+- and Mg^{2+}-exchanged forms and the K-B sample may be proposed as a potential material for energy-storage applications. The results here revealed that retention of C_2H_4 and H_2 could be improved by cation-exchange treatments with K^+, Ag^+ and Mg^{2+} due to the changes in the interlayer space.

CONCLUSIONS

The XRD patterns of all samples are not identical and different *d* spacings are observed due to the different interlayer cations and different numbers of water layers in the interlayer space. The original bentonite B had a smaller specific surface area than that of its alkaline-treated counterparts. As a whole, ion exchange of natural bentonite with aqueous solutions of KNO_3, $LiNO_3$, $AgNO_3$ and $Mg(NO_3)_2$ and subsequent washing with deionized water improved significantly both the specific surface areas and retentions of C_2H_4 and H_2 gases. The K^+-exchanged form of bentonite was found to be suitable for adsorption of H_2 and the Ag-form for C_2H_4 adsorption, which could therefore be used for applications in food storage and energy storage.

ACKNOWLEDGEMENTS

The author thanks Dr Matthias Thommes and Prof. Dr. Fahri Esenli for their helpful comments and suggestions during review.

REFERENCES

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

Baksh M.S.A. & Yang R.T. (1992) Unique adsorption properties and potential energy profiles of microporous pillared clays. *American Institute of Chemical Engineers Journal*, **38**, 1357–1368.

Balek V., Beneŝ M., Ŝubrt J., Pérez-Rodríguez J.L., Sánchez-Jiménez P.E., Pérez-Maqueda L.A. & Pascual-Cosp J. (2008) Thermal characterization of montmorillonite clays saturated with various cations. *Journal of Thermal Analysis and Calorimetry*, **92**, 191–197.

Bardelli F., Mondelli C., Didier M., Vitillo J.G., Cavicchia D.R., Robinet J.C., Leone L. & Charlet L. (2014) Hydrogen uptake and diffusion in Callovo-Oxfordian clay rock for nuclear waste disposal technology. *Applied Geochemistry*, **49**, 168–177.

Berend I., Cases J.M., François M., Uriot J.P., Michot L., Masion A. & Thomas F. (1995) Mechanism of adsorption and desorption of water vapor by homoionic montmorillonites: 2. The Li^+, Na^+, K^+, Rb^+ and Cs^+-exchanged forms. *Clays and Clay Minerals*, **43**, 324–336.

Brindley G.W. & Brown G. (1980) *Crystal Structures of Clay Minerals and Their X-ray Identification.* Monograph No. 5, Mineralogical Society, London.

Brunauer S., Emmett P.H. & Teller E. (1938) Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society*, **60**, 309–319.

Brunauer S., Deming L.S., Deming W.E. & Teller E. (1940) On a theory of the van der Waals adsorption of gases. *Journal of the American Chemical Society*, **62**, 1723–1732.

Çağlar B., Afsin B., Tabak A. & Eren E. (2009) Characterization of the cation-exchanged bentonites by XRPD, ATR, DTA/TG analyses and BET measurement. *Chemical Engineering Journal*, **149**, 242–248.

Cases J.M., Berend I., Francois M., Uriot J.P., Michot L.J. & Thomas F. (1997) Mechanism of adsorption and desorption of water vapor by homoionic montmorillonite: 3. The Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} exchanged forms. *Clays and Clay Minerals*, **45**, 18–22.

Cho S.H., Park J.H., Han S.S. & Kim J.N. (2005) Comparison of $AgNO_3$/clay and $AgNO_3$/ALSG sorbent for ethylene separation. *Adsorption*, **11**, 145–149.

Choundry N.V., Kumar P., Bhat T.S.G., Cho S.H., Han S.S. & Kim J.N. (2002) Adsorption of light hydrocarbon gases on alkene-selective adsorbent. *Industrial & Engineering Chemistry Research*, **41**, 2728–2734.

Didier M., Leone L., Greneche J.M., Giffaut E. & Charlet L. (2012) Adsorption of hydrogen gas and redox processes in clays. *Environmental Science & Technology*, **46**, 3574–3579.

Edge J. (2015) *Hydrogen adsorption and dynamics in clay minerals*. PhD thesis, University College London, UK.

Erdoğan Alver B. & Günal A. (2016) Thermal, structural and ethylene adsorption properties of Ag-, Cu- and Fe-modified bentonite from Turkey. *Journal of Thermal Analysis and Calorimetry*, **126**, 1533–1540.

Erdoğan Alver B. & Sakizci M. (2012) Ethylene adsorption on acid-treated clay minerals. *Adsorption Science & Technology*, **30**, 265–273.

Erdoğan Alver B., Alver Ö., Günal A. & Dikmen G. (2016) Effects of hydrochloric acid treatment on structure characteristics and C_2H_4 adsorption capacities of Ünye bentonite from Turkey: a combined FT-IR, XRD, XRF, TG/ DTA and MAS NMR study. *Adsorption*, **22**, 287–296.

Gil A., Trujillano R., Vicente M.A. & Korili S.A. (2007) Adsorption of nitrogen, hydrogen and carbon dioxide on alumina-pillared clays. *Studies in Surface Science and Catalysis*, **160**, 327–334.

Gil A., Trujillano R., Vicente M.A. & Korili S.A. (2009) Hydrogen adsorption by microporous materials based on alumina-pillared clays. *International Journal of Hydrogen Energy*, **34**, 8611–8615.

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

Grim R.E. & Güven N. (1978) *Bentonites, Geology, Mineralogy, Properties and Uses.* Developments in Sedimentology, Elsevier, Amsterdam.

Güven N. (1992) Molecular aspects of clay–water interactions. Pp. 1–80 in: *Clay–Water Interface and its Rheological Implications* (N. Güven & R.M. Pollastro, editors). CMS Workshop Lectures, **5**, The Clay Minerals Society, Boulder, Colorado, USA.

Huang F.C., Lee J.F., Lee C.K. & Chao H.P. (2004) Effects of cation exchange on the pore and surface structure and adsorption characteristics of montmorillonite. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **239**, 41–47.

Jozefaciuk G. & Bowanko G. (2002) Effect of acid and alkali treatment on surface areas and adsorption energies of selected minerals. *Clays and Clay Minerals*, **50**, 771–783.

Komadel P., Schmidt D., Madejová J. & Čičel B. (1990) Alteration of smectites by treatments with hydrochloric acid and sodium carbonate solutions. *Applied Clay Science*, **5**, 113–122.

Lee J.F., Lee C.K. & Juang L.C. (1999) Size effects of exchange cation on the pore structure and surface fractality of montmorillonite. *Journal of Colloid and Interface Science*, **217**, 172–176.

Li Y., Wang X. & Wang J. (2012) Cation exchange, interlayer spacing, and thermal analysis of Na/Ca-montmorillonite modified with alkaline and alkaline earth metal ions. *Journal of Thermal Analysis and Calorimetry*, **110**, 1199–1206.

Mondelli C., Bardelli F., Vitillo J.G., Didier M., Brendlé J., Cavicchia D.R., Robinet J.C. & Charlet L. (2015) Hydrogen adsorption and diffusion in synthetic Na-montmorillonites at high pressures and temperature. *International Journal of Hydrogen Energy*, **40**, 2698–2709.

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

Murray H.H. (1999) Applied clay mineralogy today and tomorrow. *Clay Minerals*, **34**, 39–49.

Murray H.H. (2007) *Applied Clay Mineralogy: Occurrences, Processing, and Application of Kaolins, Bentonites, Palygorskite-sepiolite, and Common Clays.* Elsevier, Amsterdam.

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

Park J.H., Lee H.K., Han S.S., Kim J.N. & Cho S.H. (2002) Adsorption equilibrium of ethane/ethylene on $AgNO_3$/clay adsorbent. *Korean Chemical Engineering Research*, **40**, 467–473.

Pessanha N.F.N., Kawase K.Y.F. & Coelho G.L.V. (2014) Preparation and characterization of silver/organo-clay nanocomposites. *Chemical and Materials Engineering*, **2**, 173–178.

Rutherford D.W., Chiou C.Y. & Eberl D.D. (1997) Effects of exchanged cation on the microporosity of montmorillonite. *Clays and Clay Minerals*, **45**, 534–543.

Saini V.K., Pinto M. & Pires J. (2011) High pressure adsorption studies of ethane and ethylene on clay-based adsorbent materials. *Separation Science Technology*, **46**, 137–146.

Venaruzzo J.L., Volzone C., Rueda M.L. & Ortiga J. (2002) Modified bentonitic clay minerals as adsorbents of CO, CO_2 and SO_2 gases. *Microporous and Mesoporous Materials*, **56**, 73–80.

Volzone C. (2007) Retention of pollutant gases: Comparison between clay minerals and their modified products. *Applied Clay Science*, **36**, 191–196.

Volzone C. & Ortiga J. (2004) Influence of the exchangeable cations of montmorillonite on gas adsorptions. *Process Safety and Environmental Protection*, **82**, 170–174.

Yang R.T. (2003) *Adsorbents: Fundamentals and Applications.* Wiley-Interscience, New Jersey.

Yıldız N. & Çalımlı A. (2002) Alteration of three Turkish bentonites by treatment with Na_2CO_3 and H_2SO_4. *Turkish Journal of Chemistry*, **26**, 393–402.

Youngjan S. (2012) *Ethylene adsorption on modified bentonite*. Master Thesis, Department of Chemistry, Suranaree University of Technology, Thailand.

Xu W., Johnston C.T., Parker P. & Agnew S.F. (2000) Infrared study of water sorption on Na-, Li-, Ca-, and Mg-exchanged (SWy-1 and SAz-1) montmorillonite. *Clays and Clay Minerals*, **48**, 120–131.