Adsorption (2011) 17:739–745
DOI 10.1007/s10450-011-9352-4

Influence of the exchangeable cations on SO_2 adsorption capacities of clinoptilolite-rich natural zeolite

Meryem Sakizci · Burcu Erdoğan Alver · Ertuğrul Yörükoğullari

Received: 22 October 2010 / Accepted: 28 February 2011 / Published online: 16 March 2011

Abstract The sulfur dioxide adsorption on clinoptilolite-rich tuff from Bigadiç region of Western of Turkey and its modified forms (Na^+, K^+, Ca^{2+} and Mg^{2+}) have been studied at 273 K and 293 K up to 100 kPa. The structural properties of clinoptilolites were studied by X-ray diffraction (XRD) and Fourier transform infrared (FT-IR). The quantitative XRD analysis demonstrated that the Natural-B sample is mainly constituted by clinoptilolite (80–85%) with minor contents of quartz (7–8%), feldspar (5–6%) and mica-illit (4–5%). It was found out that the adsorption capacity and the affinity of SO_2 with clinoptilolite samples depended mainly on the type of exchanged cations and decreased as Na-B > K-B > Mg-B > Natural-B > Ca-B for both temperature. These results show that clinoptilolite-rich zeolites are considered potentially good adsorbents for SO_2 removal.

Keywords Adsorption · Clinoptilolite · Sulphur dioxide · XRD · FT-IR

1 Introduction

One of the most dangerous pollutants resulting from fuel combustion is known to be sulfur dioxide (SO_2). SO_2 emissions cause negative effect on human health including breathing difficulties and respiratory illnesses (Balmes et al. 1987). SO_2 is a source of acid rains and can be harmful to the environment including damages to plants, animals and building materials (Srivastava 2003). Therefore, control of SO_2 emissions is of great importance to avoid environmental damage. The designed technologies for controlling sulfur dioxide emissions from combustion of fossil fuels can be categorized into either dry or wet processes. Because of their simplicity and relatively low cost, the dry processes are generally advantageous over the wet methods. Among the dry processes, physical adsorption processes normally operated at ambient temperature proposed an alternative and promising way for emission control of SO_2 from combustion of fossil fuels because of minimum energy requirements for the regeneration of the adsorbent, relatively simple design as compared with a chemical reactor and minimum waste disposal problems (Kopaç 1999; Srivastava 2003). For the reducing SO_2 emissions, two types of solid adsorbents are commonly used. CaO and MgO obtained from different sources such as hydroxide, carbonate and acetates are non-regenerative solid adsorbents, whereas solid adsorbents such as zeolites, silica gel and charcoal are regenerative. $Ca(OH)_2$ is one of the oldest sorbents (Gupta et al. 2004). However, the efficiency of SO_2 removal was considerably less than other systems (Lee et al. 2006).

Zeolites are alumina silicate molecular sieves and are well known for their excellent sorption properties (Breck 1974). They have extensively been used in adsorption processes (Triebe et al. 1996; Hernandez-Huesca et al. 1999; Dong et al. 2007; Erdoğan et al. 2008; Sun et al. 2009). Clinoptilolite is a HEU-type zeolite and characterized by a two-dimensional pore system with three different channels having pore openings of 7.2 × 4.4 Å, 4.7 × 4.1 Å and 5.5 × 4.0 Å, respectively. Channels of 10-member rings (channel A) and 8-member rings (channel B) are parallel to each other and the c axis of the unit cell, while a third channel C of eight member rings lies along a axis, intersection both A and B channels (Breck 1974; Tsitsishvili et al. 1992; Baerlocher et al. 2001). Gas molecules penetrate the clinoptilolite crystalline structure by a series of in-

M. Sakizci (✉) · B. Erdoğan Alver · E. Yörükoğullari
Department of Physics, Science Faculty, Anadolu University, 26470, Eskisehir, Turkey
e-mail: msakizci@anadolu.edu.tr

tersecting channels, each layer of channels separated by a dense gas-impermeable layer of tetrahedral network (Merkle and Slaughter 1968). The adsorption characteristics of zeolites are strongly dependent upon their cation composition. Clinoptilolite has multiple cations (e.g. Na^+, K^+, Ca^{2+}, Mg^{2+}) and four sites. M(1) site is located in channel A, where Na > Ca, M(2) site is located in channel B, where Ca > Na. M(1) and M(2) sites located at the channel intersections are not coordinated in either the 8- or 10-membered rings. M(3) site is located almost at the center of the channel C, where there is only K^+ and M(4) is located in channel A, where there is only Mg^{2+} (Koyama and Takeuchi 1977).

Although zeolites are very good adsorbents for many gasses, a limited number of studies were reported on the adsorption of SO_2 by natural (Roux et al. 1973; Valyon et al. 1976; Ma and Lee 1978; Ma et al. 1978; Hayhurst 1980; Kallo et al. 1982; Axente et al. 1983; Asenov et al. 1984; Sirkecioğlu et al. 1995; Mihaila et al. 1997; Caputo et al. 2001; Demirtaş 2006; Ivanova and Koumanova 2009) and synthetic zeolites (Sharonova et al. 1991; Deng and Lin 1995; Srinivasan and Grutzeck 1999; Marcu and Săndulescu 2004). The aim of this study is to evaluate the structural behavior and SO_2 adsorption of Bigadiç clinoptilolite-rich zeolite and those of modified forms.

2 Experimental

2.1 Materials and methods

Clinoptilolite-rich mineral from the Western Turkey (Bigadiç) was used for the experimental study. Clinoptilolite samples were crushed and sieved to obtain <63 μm fractions. The investigation of the natural and cation exchanged Bigadiç clinoptilolites by using XRF, DTA, TGA, DSC and N_2 adsorption techniques have already been discussed elsewhere (Erdoğan Alver et al. 2010).

The clinoptilolite-rich samples were washed with deionized water (100 ml deionized water for 5 g of clinoptilolite) at 60 °C for 2 h in order to remove the soluble impurities. These samples were activated by washing with 100 ml of 0.2 M HCI solution followed by a washing in de-ionized water. Then the nitrate solutions were prepared with KNO_3, $NaNO_3$, $Mg(NO_3)_2$ and $Ca(NO_3)_2$ for ion-exchange batch experiments. All cationic solutions were intensely shaken using 1 M solutions at 80 °C for 4 hours. The treated samples were washed repeatedly with de-ionized water and dried out in air and then at 110 °C for 16 h before the measurements. Inorganic chemicals such as HCI, KNO_3, $NaNO_3$, $Mg(NO_3)_2$ and $Ca(NO_3)_2$ were supplied by Merck (Darmstadt, Germany) and all solutions were prepared by using de-ionized water.

2.2 Instrumentation

Clinoptilolite-rich minerals from Bigadiç and those of modified forms were characterized with XRD and FT-IR techniques. The XRD diffractograms were obtained with a Rigaku, RINT-2200 model instrument, using CuKα radiation ($\lambda = 1.54$ Å), 40 kV and 30 mA power supply, divergence and antiscatter slits at 1°, detector slit 0.3 mm, 0.02°θ step size a counting time of 0.6 s/step. XRD patterns were collected from 5° to 40°. Monoclinic crystal system was used for the determination of unit-cell parameters (a, b, c, V and β). The values of the unit cell parameters were calculated from the characteristic diffraction reflections of clinoptilolite. Infrared spectra of the clinoptilolite samples were recorded in the region of (4000–400) cm^{-1} via Perkin-Elmer FT-IR 2000 spectrometer at a resolution of 4 cm^{-1} using KBr pellet technique. The adsorption isotherms of sulphur dioxide (SO_2) on natural and modified clinoptilolite-rich minerals were determined using automated volumetric equipment (Autosorb 1-Quantachrome Instruments, USA) at 273 K and 293 K. The samples were degassed at 300 °C for 7h before SO_2 adsorption measurements. All of the experimental runs were repeated in order to confirm desired reproducibility of the obtained results.

3 Results and discussion

3.1 X-ray analysis

The X-Ray diffraction (XRD) patterns of clinoptilolite samples are shown in Fig. 1. Natural and cation exchanged samples exhibit good crystallinity and give sharp peaks. The characteristic peaks of clinoptilolite were observed at $2\theta = 9.80°$, 22.36°, 26° and 31.94° (Petrov 1995; Mozgawa 2000; Korkuna et al. 2006). The presence of other peaks arises from some impurities in the clinoptilolite sample. The quantitative XRD analysis demonstrated that the Natural-B sample is mainly constituted by clinoptilolite (80–85%) with minor contents of quartz (7–8%), feldspar (5–6%) and mica-illit (4–5%). The method given by Esenli and Sirkecioğlu (2005) was used to determine the ratio of clinoptilolite. No appreciable change has been observed either in the position of the most intense peaks of the clinoptilolite nor in its crystallinity with different salt solutions. In addition, the unit-cell parameters of the natural and modified samples are presented in Table 1. The calculated unit-cell parameters of natural and modified forms of the samples do not show significant changes.

3.2 Adsorption

In this work, a volumetric-type apparatus was used to measure the SO_2 adsorption capacities of clinoptilolites. In each

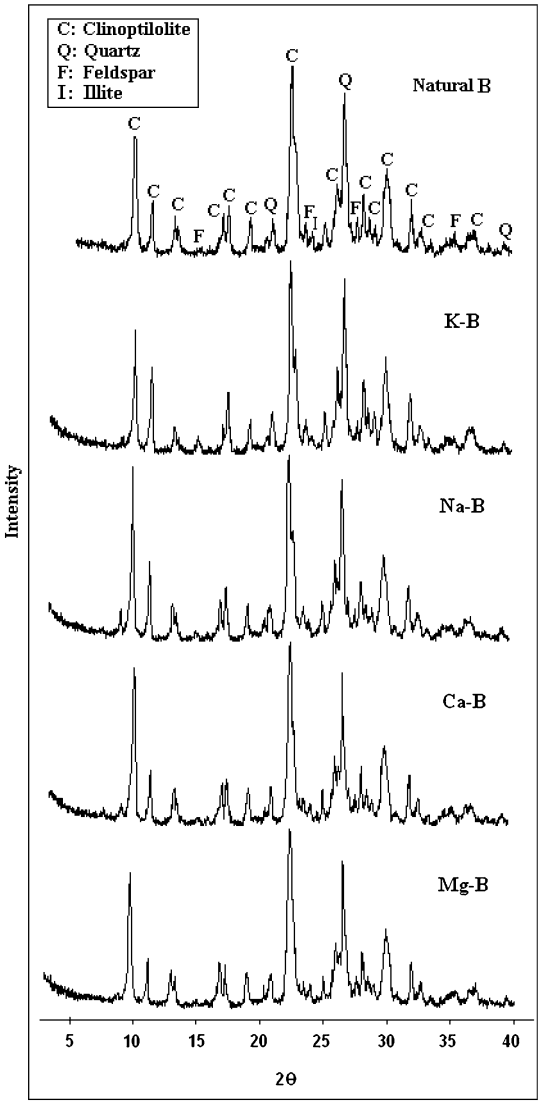

Fig. 1 X-ray diffraction patterns of the clinoptilolite samples

Table 1 Unit-cell parameters and volumes of natural and that of modified forms of Bigadiç clinoptilolites

Samples	*a* (Å)	*b* (Å)	*c* (Å)	*β* (°)	*V* (Å^3)
Natural-B	17.7114	17.9362	7.4113	116.22	2112
K-B	17.7514	17.9928	7.4341	116.37	2127
Na-B	17.6630	17.9726	7.4214	116.20	2113
Ca-B	17.7371	17.9726	7.4227	116.45	2118
Mg-B	17.8291	18.0092	7.4295	116.84	2128

experimental run, the amount of adsorbent samples was about 0.070 g. Helium was the carrier gas. Zeolites can be improved by cation-exchange to desired gas adsorption. The two-dimensional channel structure of clinoptilolite was altered by cation exchange to investigate the effect of cation type on the adsorption of SO_2. Adsorption isotherms for sulfur dioxide on natural and all cation-exchanged forms of clinoptilolite samples were obtained at 273 K and 293 K up to 100 kPa (Figs. 2 and 3).

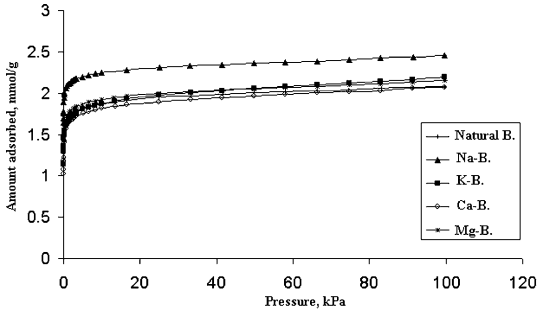

Fig. 2 Adsorption of sulphur dioxide on natural Na, K, Mg and Ca cationic forms of Bigadiç clinoptilolite at 293 K up to 100 kPa

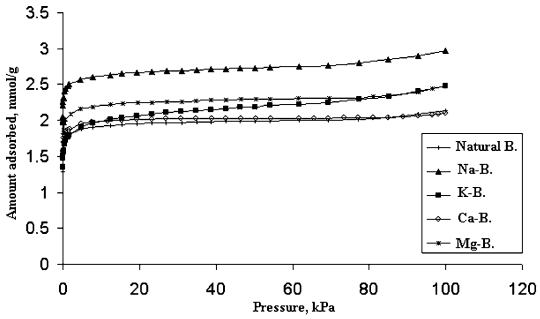

Fig. 3 Adsorption of sulphur dioxide on natural, Na, K, Mg and Ca cationic forms of Bigadiç clinoptilolite at 273 K up to 100 kPa

Table 2 The SO_2 adsorption capacities of natural and modified clinoptilolite samples at 273 K, 293 K and 100 kPa

Sample	Amount adsorbed (mmol/g zeolite)	
	273 (K)	293 (K)
Natural-B	2.139	2.083
Na-B	2.967	2.458
K-G	2.482	2.191
Ca-G	2.099	2.070
Mg-G	2.478	2.158

It is seen that the SO_2 adsorption isotherms for all samples showed Type I. The adsorption temperatures of SO_2 were below critical temperature. The adsorption capacities are expressed as mmol SO_2 adsorbed per gram of zeolite (Table 2). The adsorption capacity and the affinity of SO_2 with clinoptilolite samples depended mainly on the type of exchanged cations and decreased as Na-B > K-B > Mg-B > Natural-B > Ca-B. In addition, the increasing temperature caused the adsorbed amount to decrease. It was found that the adsorption capacity of SO_2 depended on the cation electronegativity and ionic potential. This is in agreement with previous papers (Sirkecioğlu et al. 1995;

Ivanova and Koumanova 2009). A similar order for SO_2 adsorption was determined for cationic forms of Turkey clinoptilolite: $H^+ > Na^+ > K^+ > Ca^{2+}$ (Sirkecioğlu et al. 1995). Ivanova and Koumanova (2009) found that the adsorption capacity of the Na-form of natural clinoptilolite from Bulgaria was the highest. Capacity of clinoptilolites for SO_2 ranged from 2.083 mmol/g to 2.967 mmol/g in this study (Table 2). Considering the adsorption capacity, Na form exhibited the greatest affinity for SO_2 removal among the cation exchanged-clinoptilolite samples (Table 2). As shown in Figs. 2 and 3 the isotherms of SO_2 were strongly favorable for the Na-B. Ionic exchange with sodium nitrate produced an important increase of the SO_2 adsorption capacity. SO_2 adsorption amounts of Ca-B, Mg-B, K-B and Na-B samples at 293 K and 100 kPa were 2.070, 2.158, 2.191 and 2.458 mmol/g, respectively (Table 2). At 273 K and 100 kPa, the SO_2 adsorption capacity of Na-B sample is found to be 2.967 mmol/g. From 293 K to 273 K at 100 kPa, SO_2 adsorption amount is increased from 2.191 mmol/g to 2.482 mmol/g for KB. Ca-form for both temperatures has been observed to have the lowest adsorption capacities for SO_2 gas, resulting from the channel blockage caused by the cation locations in the sample (Sirkecioğlu et al. 1995). It has a value of 2.099 mmol/g at 273 K and 100 kPa (Table 2).

The adsorption properties of the zeolites depend on the size and shape of the adsorbate molecules as well as on the size and locations of the cations. Therefore, the type, number, charge density and distribution of the charge-balancing cations in the A, B and C channels of clinoptilolite are particularly influential in adsorption (Munson 1973; Breck 1977; Ackley et al. 1992). Considering the each unit cell of clinoptilolite, M(1)–M(3) sites and M(1)–M(4) sites are forbidden pairs of atomic locations. Therefore, these locations cannot be simultaneously occupied (Koyama and Takeuchi 1977). Na and Ca occupies both M(1) and M(2) sites. If Ca^{2+} is situated at the intersections of channels, it creates the blockage of all three channels. Mg^{2+} can completely block channel C but has slight effect upon intersecting channels. Therefore, SO_2 molecule cannot penetrate at an appreciable rate and diffuses more slowly. Most zeolites are polar adsorbents due to the presence of the exchangeable cations (Koyama and Takeuchi 1977; Ruthven 1988). In addition, the polarity of adsorbed molecules plays a crucial role in adsorption properties of the zeolites. SO_2 molecule has a high permanent dipole moment (1.63 Debye) (Weast et al. 1985) and higher adsorption capacities and a larger increase in the amount adsorbed at higher pressures were observed resulting in stronger ion-dipole and dipole-dipole interactions for this molecule (Sirkecioğlu et al. 1995).

Clinoptilolite's unique pore structure preferentially adsorbs SO_2 molecule (3.6 Å) that are smaller than pore dimension (about 4 Å) of clinoptilolite. Higher SO_2 adsorption for Na-B is due to larger interaction between SO_2 with a large dipole moment with electric field energy created by Na^+ cation in the zeolite structure. Electronegativity value of potassium is lower than that of sodium. In addition, potassium has greater atomic diameter compared to sodium. Hence, interaction energy between K-B and SO_2 should be lower than that with the Na-B. K^+ occupies M(3) site and the outer edge of A channel, causing a lowering of the adsorption capacity.

Clearly, modifications and the resulting induced structural changes greatly affected the gas adsorption capacity of natural zeolites. Experimental results showed that clinoptilolite-rich zeolite could be considered potentially good candidate due to its low cost, abundance and reusability for SO_2 removal.

3.3 FT-IR analysis

Infrared spectroscopy has been widely used for studying the structural properties of zeolites. FT-IR spectra of natural and Na-, K-, Mg- and Ca-exchanged clinoptilolite samples were presented in Figs. 4 and 5. All of the samples showed the same structural properties and following bands were observed. The strongest band around 1055 cm^{-1} due to the external tetrahedra linkage asymmetric stretching (Daulo et al. 2002; Castaldi et al. 2005; Ruiz-Serrano et al. 2010). The second strongest band at 465 cm^{-1} arises from internal tetrahedra bending (Rodriguez-Fuentes et al. 1998; Perraki and Orfanoudaki 2004; Ruiz-Serrano et al. 2010). The bands ca. 1208 cm^{-1}, 795 cm^{-1} and 720 cm^{-1} are attributed to internal tetrahedra asymmetric stretching, external tetrahedra symmetric stretching and internal tetrahedra symmetric stretching, respectively (Rodriguez-Fuentes et al. 1998; Ruiz-Serrano et al. 2010). In addition, the bands ca. 670 cm^{-1} and 609 cm^{-1} in the spectra are related to the symmetric tetrahedra stretching and double ring vibrations, respectively (Rodriguez-Fuentes et al. 1998; Ruiz-Serrano et al. 2010). There are three typical bands due to the presence of zeolite water. An isolated band peaked at 1645 cm^{-1} is due to bending vibrations of sorbed water. In addition, a broad band at 3450 cm^{-1} is associated with hydrogen bonded OH and the band at 3630 cm^{-1} is attributed to the isolated OH (Perraki and Orfanoudaki 2004; Korkuna et al. 2006; Elaiopoulos et al. 2008). The change of the cations does not result in the distinct shift of these band positions (Castaldi et al. 2005). As shown in Figs. 4 and 5, FT-IR spectra of natural and cation exchanged forms of clinoptilolite samples after adsorption of sulphur dioxide at 273 K and 293 K were also presented. In all FT-IR spectra, sulphur dioxide was adsorbed on natural and modified clinoptilolites as one species characterized by an S–O stretching band at ca. 1340 cm^{-1}.

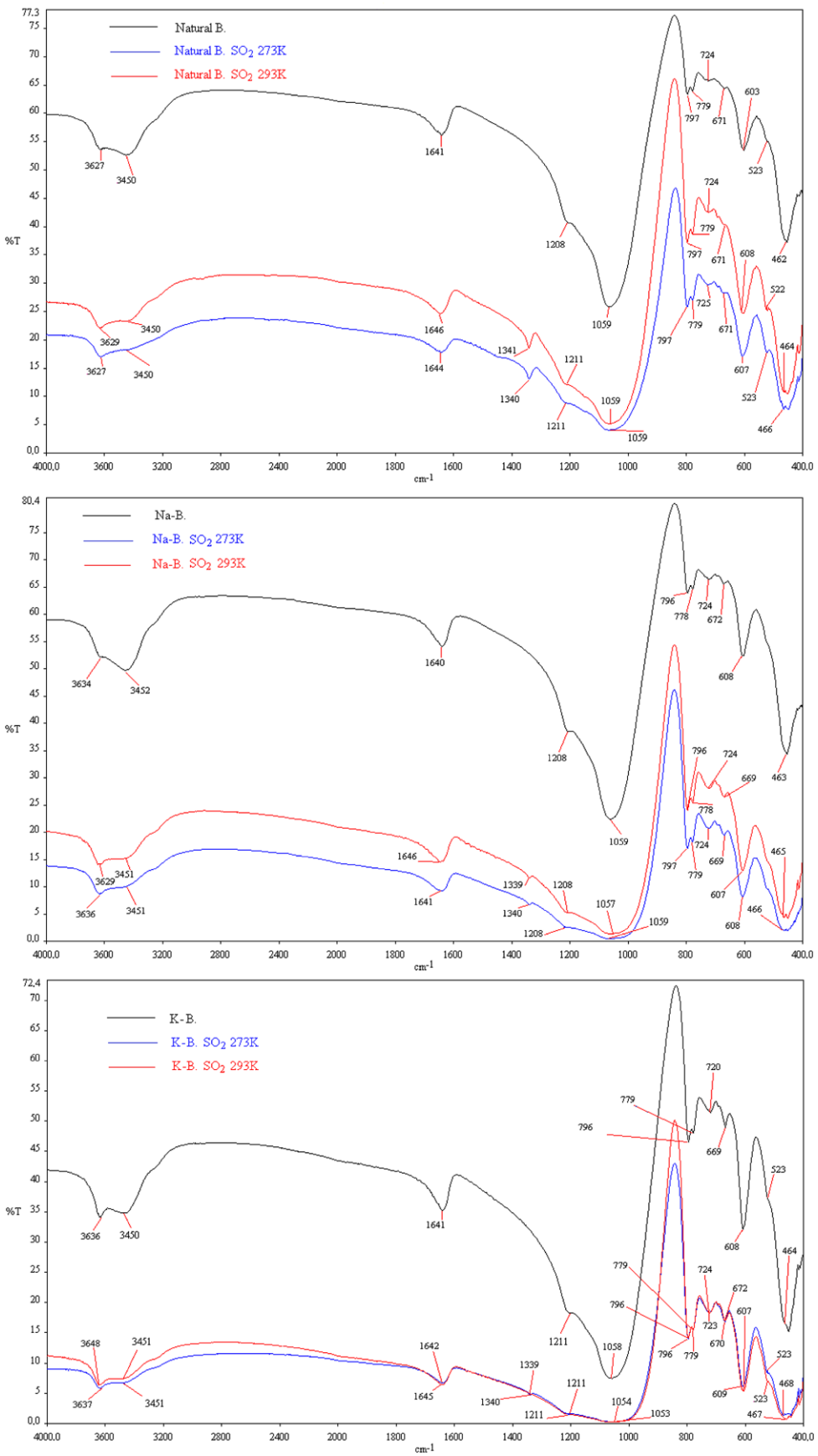

Fig. 4 FT-IR spectra of natural, Na- and K-forms of Bigadiç clinoptilolite

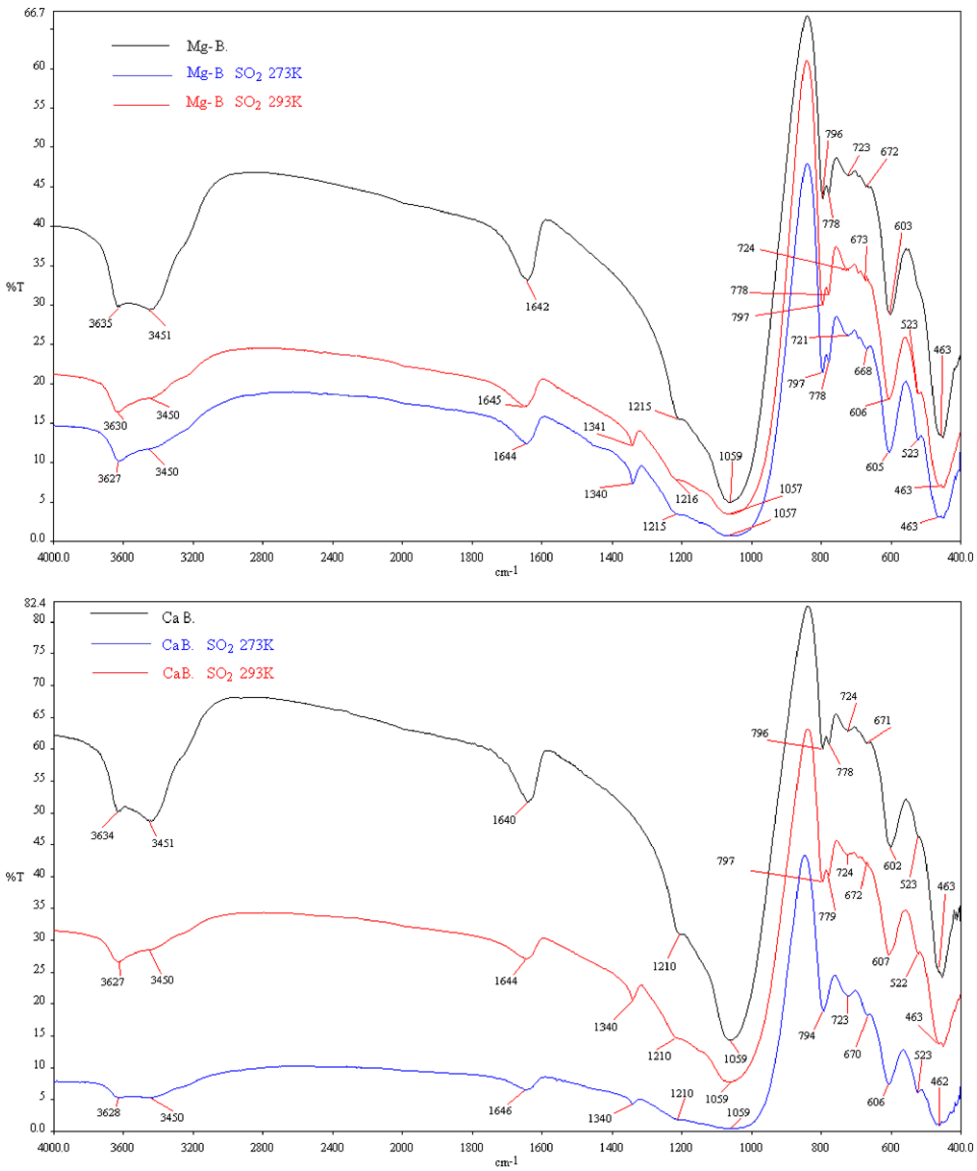

Fig. 5 FT-IR spectra of Mg- and Ca-forms of Bigadiç clinoptilolite

4 Conclusions

The SO_2 adsorption properties of natural and modified clinoptilolite samples were experimentally investigated by comparing the initial crystalline structure and SO_2 adsorption ability of the natural clinoptilolite samples to that of the samples after treatments with salt solutions. Among all the modified forms, it was found that the Na- forms of clinoptilolite sample has the most SO_2 adsorption capacity. It was found that SO_2 adsorption amounts of Na-B at 273 K, 293 K and 100 kPa were 2.967 mmol/g and 2.458 mmol/g, respectively. Uptake rates for SO_2 also varied considerably due to the effect of the different cations upon channel blockage. Ca-forms exhibited the lowest adsorption capacity at both temperatures and 100 kPa. Adsorption capacities of SO_2 were found to decrease considerably with increasing temperature. As expected according to electronegativity and ionization potential of the cations and their positions in clinoptilolite, it was observed that uptake of sulphur dioxide on Bigadiç zeolite at 273 K, 293 K and 100 kPa increases in the following sequence Ca-B < Natural-B < Mg-B < K-B < Na-B.

Acknowledgements Financial support by Anadolu University via Scientific Research Projects (No: AUAF 081009) is acknowledged. Special thanks to Dr. Matthias Thommes and Prof. Dr. Fahri Esenli for their helpful suggestions and corrections.

References

Ackley, M.W., Giese, R.F., Yang, R.T.: Clinoptilolite: an untapped potential for kinetic gas separations. Zeolites **12**, 780–787 (1992)

Asenov, A., Ivanova, E., Kostova, M.: Adsorption of sulfur dioxide with natural zeolites. Khim. Prom. **10**, 612–614 (1984)

Axente, D., Abrudean, M., Baldea, A.: Adsorption of Romanian natural clinoptilolite. Zeolites **3**, 259–260 (1983)

Baerlocher, Ch., Meier, W.M., Olson, D.H.: Atlas of Zeolite Framework Types, 5th edn. Elsevier, Amsterdam (2001)

Balmes, J.R., Fine, J.M., Sheppard, D.: Symptomatic bronchoconstriction after short-term inhalation of sulphur dioxide. Am. Rev. Respir. Dis. **136**, 1117–1121 (1987)

Breck, D.W.: Zeolite Molecular Sieves: Structure, Chemistry, and Use. Wiley, New York (1974)

Breck, D.W.: Chem. Eng. Prog. **73**, 44–48 (1977)

Caputo, D., De Gennaro, B., Liguori, B., Pansini, M., Colella, C.: Adsorption properties of clinoptilolite-rich tuff from Thrace, NE Greece. In: Gamba, A., Colella, C., Coluccia, S. (eds.) Studies in Surface Science and Catalysis, pp. 121–129. Elsevier, Amsterdam (2001)

Castaldi, P., Santona, L., Cozza, C., Giuliano, V., Abbruzzese, C., Nastro, V., Melis, P.: Thermal and spectroscopic studies of zeolites exchanged with metal cations. J. Mol. Struct. **734**, 99–105 (2005)

Daulo, M., Ioannou, A., Dimirkou, A.: Copper adsorption and Si, Al, Ca, Mg and Na release from clinoptilolite. J. Colloid Interface Sci. **245**, 237–250 (2002)

Demirtaş, A.: Adsorption of sulfur dioxide from coal combustion gases on natural zeolite. Energy Source A **28**, 1329–1335 (2006)

Deng, S.G., Lin, Y.S.: Sulfur dioxide sorption properties and thermal stability of hydrophobic zeolites. Ind. Eng. Chem. Res. **34**, 4063–4070 (1995)

Dong, J., Wang, X., Xu, H., Zhao, Q., Li, J.: Hydrogen storage in several microporous zeolites. Int. J. Hydrog. Energy **32**, 4998–5004 (2007)

Elaiopoulos, K., Perraki, Th., Grigoropoulou, E.: Mineralogical study and porosimetry measurements of zeolites from Scaloma area, Thrace, Greece. Microporous Mesoporous Mater. **112**, 441–449 (2008)

Erdoğan, B., Sakızcı, M., Yörükoğulları, E.: Characterization and ethylene adsorption of natural and modified clinoptilolites. Appl. Surf. Sci. **254**, 2450–2457 (2008)

Erdoğan Alver, B., Sakızcı, M., Yörükoğulları, E.: Investigation of clinoptilolite rich natural zeolites from Turkey: a combined XRF, TG/DTG, DTA and DSC study. J. Therm. Anal. Calorim. **100**, 19–26 (2010)

Esenli, F., Sirkecioğlu, A.: The relationship between zeolite (heulandite-clinoptilolite) content and the ammonium-exchange capacity of pyrodastic rocks in Gordes, Turkey. Clay Miner. **40**, 557–564 (2005)

Gupta, A., Gaur, V., Verma, N.: Breakthrough analysis for adsorption of sulfur-dioxide over zeolites. Chem. Eng. Process. **43**, 9–22 (2004)

Hayhurst, D.T.: Gas adsorption by some natural zeolites. Chem. Eng. Commun. **4**, 729–735 (1980)

Hernandez-Huesca, R., Diaz, L., Aguilar-Armenta, G.: Adsorption equilibria and kinetics of CO_2, CH_4 and N_2 in natural zeolites. Sep. Purif. Technol. **15**, 163–173 (1999)

Ivanova, E., Koumanova, B.: Adsorption of dulfur dioxide on natural clinoptilolite chemically modified with salt solutions. J. Hazard. Mater. **167**, 306–312 (2009)

Kallo, D., Papp, J., Valyon, J.: Adsorption and catalytic properties of sedimentary clinoptilolite and mordenite from the Tokaj Hills, Hungary. Zeolites **2**, 13–16 (1982)

Kopaç, T.: Non-isobaric adsorption analysis of SO_2 on molecular sieve 13X and activated carbon by dynamic technique. Chem. Eng. Process. **38**, 45–53 (1999)

Korkuna, O., Leboda, R., Skubiszewska-Zeiba, J., Vrublevska, T., Gunko, V.M., Ryczkowski, J.: Structural and physicochemical properties of natural zeolites: clinoptilolite and mordenite. Microporous Mesoporous Mater. **87**, 243–254 (2006)

Koyama, K., Takeuchi, Y.: Clinoptilolite: the distribution of potassium atoms and its role in thermal analysis. Z. Kristallogr. **145**, 216–239 (1977)

Lee, K.T., Bhatia, S., Mohamed, A.R.: Preparation and characterization of CaO/$CaSO_4$/Coal fly ash sorbent for sulfur dioxide removal: Part I. Energy Source A **28**, 1241–1249 (2006)

Ma, Y.H., Lee, T.Y.: Sorption and diffusion properties of natural zeolites. In: Sand, L.B., Mumpton, F.A. (eds.) Natural Zeolites, Natural Zeolites, Occurrence, Properties, Use, pp. 487–493. Pergamon Press, Oxford (1978)

Ma, Y.H., Byron, R.J., Feltre, P., Lee, T.Y.: Effects of presorbed water vapor upon the sorption and diffusion of sulfur dioxide in natural mordenite. AIChE Symp. Ser. **74**, 8–52 (1978)

Marcu, I.C., Săndulescu, I.: Study of sulfur dioxide adsorption on Y zeolite. J. Serb. Chem. Soc. **69**, 563–569 (2004)

Merkle, A.B., Slaughter, M.: Determination and refinement of the structure of heulandites. Am. Mineral. **53**, 1120–1138 (1968)

Mihaila, G., Barbu, H.C., Lutic, D., Sava, M.I.: Adsorption of sulphur dioxide on clinoptilolite volcanic tuff. In: Kirov, G., Filizova, L., Petrov, O. (eds.) Natural Zeolites-Sofia '95, pp. 146–152. Bulgaria (1997)

Mozgawa, W.: The influence of some heavy metal cations on the FTIR spectra of zeolites. J. Mol. Struct. **555**, 299–304 (2000)

Munson, R.A.: Properties of natural zeolites. U.S. Bureau of Mines Report of Investigation, 7744 (1973)

Perraki, Th., Orfanoudaki, A.: Mineralogical study of zeolites from Pentalofos area, Thrace, Greece. Appl. Clay Sci. **25**, 9–16 (2004)

Petrov, O.E.: Cation exchange in clinoptilolite: an X-ray powder diffraction analysis. In: Ming, D.W., Mumpton, F.A. (eds.) Natural Zeolites'93. Int. Comm. Natural Zeolites, pp. 271–279. Brockport, New York (1995)

Rodriguez-Fuentes, G., Ruiz-Salvador, A.R., Mir, M., Picazo, O., Quintana, G., Delgado, M.: Thermal and cation influence on IR vibrations of modified natural clinoptilolite. Microporous Mesoporous Mater. **20**, 269–281 (1998)

Roux, A., Huang, A.A., Ma, Y.H., Zwiebel, I.: Sulfur dioxide adsorption on mordenites. AIChE Symp. Ser. **69**, 46–53 (1973)

Ruiz-Serrano, D., Flores-Acosta, M., Conde-Barajas, E., Ramírez-Rosales, D., Yáñez-Limón, J.M., Ramírez-Bon, R.: Study by XPS of different conditioning processes to improve the cation exchange in clinoptilolite. J. Mol. Struct. **980**, 149–155 (2010)

Ruthven, D.M.: Zeolites as Selective Adsorbents. Chem. Eng. Prog. **84**, 42–50 (1988)

Sharonova, O.M., Dubkov, A.A., Kirik, S.D., Dubkova, S.A., Anshits, A.G.: Study of the adsorption of sulfur dioxide on dealuminated zeolites Y by thermal desorption and powder X-ray diffraction. Phys. Chem. **40**, 459–464 (1991)

Sirkecioğlu, A., Altav, Y., Erdem-Şenatalar, A.: Adsorption of H_2S and SO_2 on bigadiç clinoptilolite. Sep. Sci. Technol. **30**, 2747–2762 (1995)

Srinivasan, A., Grutzeck, M.W.: The adsorption of SO_2 by zeolites synthesized from fly ash. Environ. Sci. Technol. **33**, 1464–1469 (1999)

Srivastava, R.K.: Controlling SO_2 Emissions: A Review of Technologies. Nova Science, Hauppauge (2003)

Sun, Y., Liu, C., Su, W., Zhou, Y., Zhou, L.: Principles of methane adsorption and natural gas storage. Adsorption **15**, 133–137 (2009)

Triebe, R.W., Tezel, F.H., Knulbe, K.C.: Adsorption of methane, ethane and ethylene on molecular sieve zeolites. Gas Sep. Purif. **10**, 81–84 (1996)

Tsitsishvili, G.V., Andronikashvili, T.G., Kvernadze, T.K., Okugava, N.G.: Natural Zeolites. Ellis Horwood, Chichester (1992)

Valyon, J., Papp, J., Czaran, E.: Study of the adsorption properties of a natural Hungarian mordenite and its ion-exchanged derivatives. React. Kinet. Catal. Lett. **5**, 21–28 (1976)

Weast, R.C., Astle, M.J., Beyer, W.H.: CRC Handbook of Chemistry and Physics, 66th edn. CRC Press, Boca Raton (1985)