

Alkali Treatment of Commercial Silicoaluminophosphate Molecular Sieves (SAPO-34) Enhances the Water Adsorption and Desorption Properties

Masahiro Katoh^{1*}, Kota Horiuchi², Ayaka Satoh², Kota Aoyagi², Shigeru Sugiyama¹

¹Department of Applied Chemistry, Graduate School of Technology, Industrial and Social Sciences, Tokushima University, Tokushima, Japan

²Department of Chemical Science and Technology, Tokushima University, Tokushima, Japan

Email: *katoh@tokushima-u.ac.jp

How to cite this paper: Katoh, M., Horiuchi, K., Satoh, A., Aoyagi, K. and Sugiyama, S. (2019) Alkali Treatment of Commercial Silicoaluminophosphate Molecular Sieves (SAPO-34) Enhances the Water Adsorption and Desorption Properties. *Journal of Encapsulation and Adsorption Sciences*, 9, 149-158.

<https://doi.org/10.4236/jeas.2019.94008>

Received: October 5, 2019

Accepted: December 3, 2019

Published: December 6, 2019

Copyright © 2019 by author(s) and Scientific Research Publishing Inc. This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

Commercial silicoaluminophosphate molecular sieves (SAPO-34) received alkali treatment with either NaOH (0.2, 0.01, 0.005, or 0.001 M) or NH₄OH (0.005 M). Treatment with NaOH (0.005 M) increased the water adsorption initial rate of SAPO-34 by 1.4-fold. The alkali treatment introduced Na⁺ adsorption sites into the SAPO-34. The desorption ratio (adsorption at 30°C and desorption at 100°C) was 88.2% higher than the original rate (84.3%). On the other hand, after alkali treatment of SAPO-34 using NH₄OH (0.005 M), calcination resulted in the highest desorption ratio at 91.3%. When combined with calcination, alkali treatment with NH₄OH introduced H⁺ adsorption sites into SAPO-34, H⁺ adsorption sites feature low levels of interaction with water, which enhanced the desorption ratio, but decreased the initial adsorption rate. These results indicate that treating commercial SAPO-34 with 0.005 M NaOH enhances both the adsorption and desorption behaviors.

Keywords

Alkali Treatment, Silicoaluminophosphate Molecular Sieves, Water, Adsorption, Desorption

1. Introduction

In 1984, a novel class of oxide molecular sieves with a crystalline microporous framework, silicoaluminophosphates, was synthesized [1] [2]. These new materials possess properties of both zeolites and aluminophosphates, which makes

them unique in many ways. The present study was focused on commercial silicoaluminophosphate molecular sieves (SAPO-34 (AQSOA-Z02,)) that were supplied by the Mitsubishi Chemical Corp. The water adsorption isotherm of AQSOA-Z02 revealed interesting behaviors [3]. The adsorbed amount of water increased rapidly at 10% relative humidity and the adsorbed amount of water corresponded to the amount that would saturate a Y type zeolite. The results of alkali treatment for both NaY zeolites [4] and ZSM-5 type zeolites [5] were reported previously. Water diffusivity was enhanced for NaY zeolites via alkali treatment with 1 M of a NaOH solution. This concentration was too high, however, for the alkali treatment of ZSM-5 zeolites, and the concentration was decreased to an optimum of 0.2 M.

In the present study, SAPO-34 was treated with either NaOH (0.2, 0.01, 0.005, or 0.001 M) [4] [5] or NH_4OH (0.005 M) with the goal of achieving a higher rate of water diffusivity. The modified SAPO-34 was characterized by XRD, SEM, XRF, IR, and nitrogen adsorption. The amount of water adsorbed onto zeolites under the recycled temperature conditions was estimated using the IR method [6]. The IR spectra of water adsorbed onto zeolites were measured under differential temperatures at a constant pressure. The water adsorption behavior was estimated by measuring the change of pressure under a constant volume [4] [5] [7].

2. Experimental Methods

All experiments were performed at Tokushima University from April, 2015 through September, 2019.

2.1. Materials

The SAPO-34 (AQSOA-Z02) used in this study was supplied by the Mitsubishi Chemical Corp. The Alkali treatment of AQSOA-Z02 was performed within an aqueous solution of either NaOH (0.2, 0.01, 0.005, or 0.001 M) or NH_4OH (0.005 M). Then, 1.0 g of AQSOA-Z02 was placed into a 100 mL of each aqueous solution and was kept at 95°C for 1 h. After a period of 1 h, the slurry was filtered using a filter media made of glass fiber with 0.3 μm pores. The filtered cake was dried overnight at 100°C in an air oven. After drying, the cake was crushed into powder, and the powder was rinsed with hot distilled water at 80°C for 2 h. After rinsing, the powder was filtered and dried to obtain either Z02-NaOH(X M) (X denoted the concentration of NaOH aqueous solution) or Z02- NH_4OH (0.005 M). As a reference, Z02- NH_4OH -C was obtained by calcination of Z02- NH_4OH (0.005 M) at 470°C for 4 h.

The crystalline structure of the samples was checked via X-ray diffraction microscopy (RINT2500-VHE; RIGAKU Corp.). SEM images were obtained using a JEOL JSM-6390HV microscope. The P/Al, Si/Al and Mg/Al ratios and Na content were measured by X-ray fluorescence analysis (JSM-3020M; JEOL Ltd.) The pore properties were determined by nitrogen adsorption at -196°C (BELSORP-max;

MicrotracBEL Corp.). The micropore and mesopore volumes were evaluated using the MP and BJH method, respectively.

2.2. Measurement of the Thermal Behavior of Water Adsorbed Onto Samples

The infrared (IR) spectra of the water-alkali treated SAPO-34 adsorption systems were obtained using the IR cell reports from other papers [4]-[10]. A sample disc that was 13 mm in diameter, approximately 8.5 mg in weight, and approximately 60 μm in thickness was pretreated in the cell at 350°C and 4.0×10^{-4} Torr for 2 h. The spectra were recorded on a FTX3000MX Bio-Rad Laboratories, Inc. spectrometer with a mercury-cadmium-telluride (MCT) detector at a resolution of 4 cm^{-1} . The spectra were recorded by increasing the temperature from 30°C to 200°C and under water pressure of 10 Torr. The IR integrated intensity of the peak around 1650 cm^{-1} , which was assigned to the bending vibration of adsorbed water, was normalized by the weight and diameter of the sample disc. The IR normalized intensity was equivalent to the amount of adsorbed water at a given temperature.

2.3. Measurement of the Water Adsorption and Desorption Behavior of Several Samples

Water adsorption was measured using a volumetric adsorption apparatus assembled in our laboratory [4] [5] [7]. The adsorbent was initially outgassed in a sample room at 350°C and 4.0×10^{-4} Torr for 2 h. Water was introduced to the sample room at a saturated water pressure and at room temperature. When water was adsorbed onto the samples in the sample room, the pressure was decreased by increasing the time under this constant volume. The amount of water adsorbed onto several samples was calculated from the pressure profile. This method revealed the behavior of water adsorption on the stronger adsorption sites, because the amount of water introduced into the sample room was limited. Only the slope of the adsorption initial behavior is discussed here.

3. Results and Discussion

3.1. Framework Structures and Nitrogen Adsorption Isotherms of Several Samples

Figure 1 shows the XRD patterns of Z02 (SAPO-34), alkali treated samples, and Z02-NH₄OH-C. Except for Z02-NaOH (0.2 M), these patterns are identical to that of a CHA structure in the literature [11]. These results indicated alkali treatment by the relatively lower NaOH concentration (<0.2 M) affected only the surface of SAPO-34, but the bulk of the structure was not changed by the treatment. This tendency agreed with the results of our previous studies [4] [5]. Previous papers showed that the alkali treatment of porous materials modified only the surface structure. SAPO-34 was also one of the porous materials. Only the surface was modified by the alkali treatment. In the XRD pattern for Z02-NaOH

(0.2 M), however, some peak shifts were observed at around 17 and 26 degrees and missing peaks were observed at around 31 degrees. This could suggest either a structural change, or a collapse in the CHA structure.

SEM images for Z02 (SAPO-34), alkali treated, and Z02-NH₄OH-C samples, are shown in **Figure 2**. These occurred mainly in a cubic structure. The morphological changes in Z02 during alkali treatment using a NaOH (0.2 M) solution were quite dramatic. Some grooves and voids that appeared on the surface of Z02 particles were caused by the alkali treatment with the NaOH (0.2 M) solution. Ogura *et al.* reported significant morphological changes in ZSM-5 zeolite during alkali treatment with NaOH (0.2 M) [12], and microporous SAPO-34

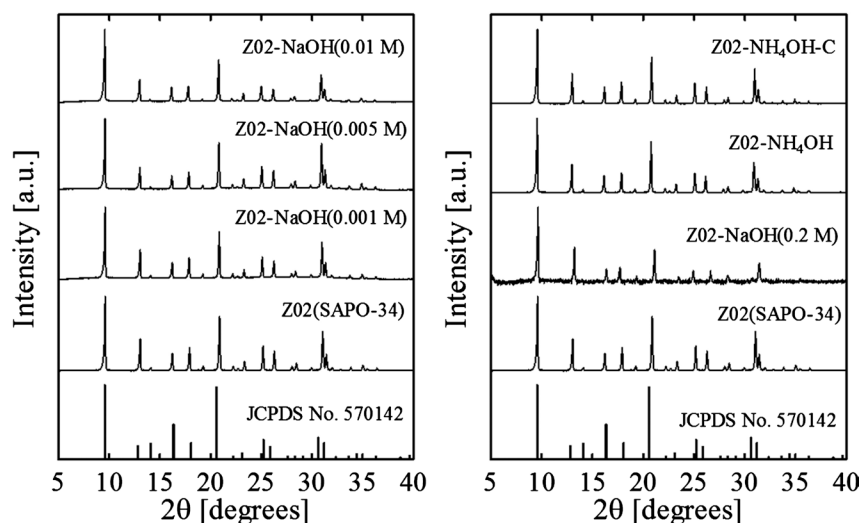


Figure 1. XRD patterns of several samples.

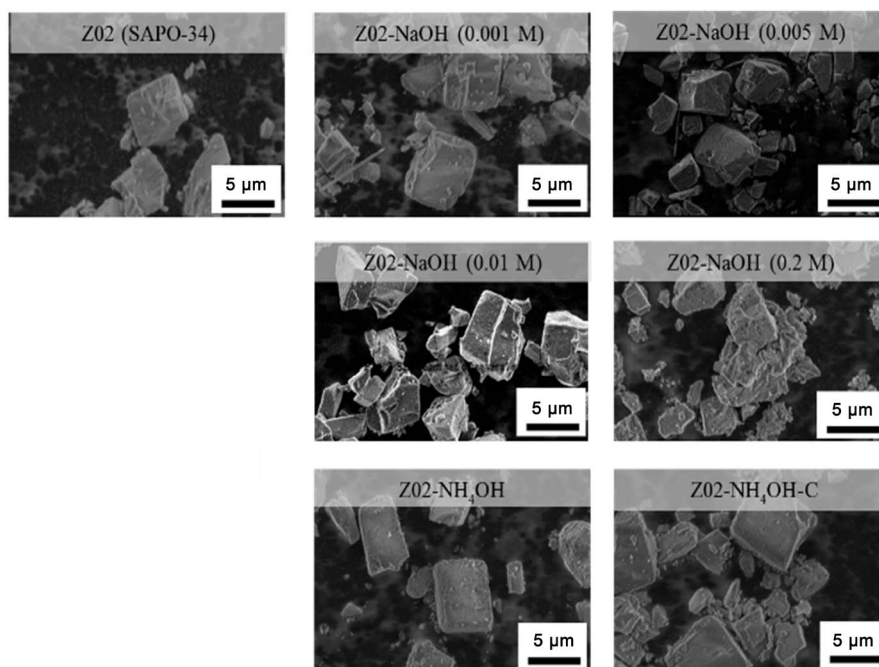


Figure 2. SEM iamges of several samples.

showed a similar tendency. No obvious differences were observed, however, for either the other alkali treated samples or for Z02-NH₄OH-C, which indicated that the obvious change in the surface morphology of Z02 was induced only by the relatively higher NaOH concentration (0.2 M).

The P/Al, Si/Al, and Mg/Al ratios, along with the Na content, are summarized in **Table 1**. With the exception of Z02-NaOH (0.2 M), the P/Al and Si/Al ratios approximated that of Z02 (SAPO-34). Although the P/Al and Si/Al ratios were maintained by treatment with a lower concentration of alkali solution, P and Al were removed from SAPO-34 under treatment with a 0.2 M alkali solution. For NaOH treatment, however, the Mg/Al ratio was maintained. These results indicated that neither the Mg²⁺ nor the Mg(OH)⁺ ions were not changed by the Na⁺ in NaOH treatments [4]. The Na content was increased with an increase in the NaOH concentration. These results indicated that the H⁺ was changed by Na⁺. These results were supported by IR measurement (**Figure 3**).

Figure 3 shows the IR spectra of pretreated samples. This spectra shows that the original SAPO-34 had several OH peaks, which were decreased by the alkali treatment (0.001 M to 0.01 M), and these disappeared following 0.2 M of NaOH treatment. Conversely, with NH₄OH treatment, the Mg/Al ratio was decreased. This result indicated that some portion of Mg²⁺ was changed by the NH₄⁺ in the NH₄OH treatment, and that the NH₄⁺ was changed to H⁺ by calcination.

Table 1. P/Al, Si/Al, Mg/Al ratios and Na content of several samples.

Sample	P/Al ratio [-]	Si/Al ratio [-]	Mg/Al ratio [-]	Na [mol %]
Z02 (SAPO-34)	0.94	0.18	0.04	-
Z02-NaOH (0.001 M)	0.91	0.18	0.04	0.11
Z02-NaOH (0.005 M)	0.94	0.18	0.04	0.93
Z02-NaOH (0.01 M)	0.91	0.17	0.04	1.68
Z02-NaOH (0.2 M)	0.77	0.24	0.04	6.45
Z02-NH ₄ OH	0.90	0.18	0.03	-
Z02-NH ₄ OH-C	0.93	0.18	0.03	-

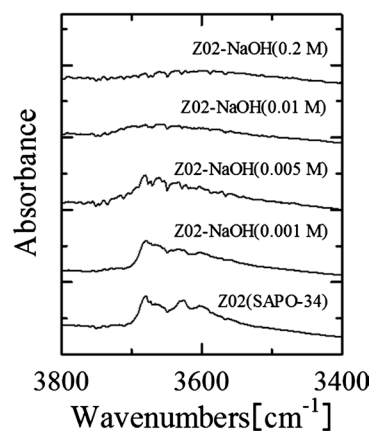


Figure 3. IR spectra of pretreated samples.

Figure 4 shows the adsorption isotherms of nitrogen for several samples. **Table 2** shows the Brunauer-Emmett-Teller (BET) specific surface area, the micropore volume, and the mesopore volume. Except for Z02-NaOH (0.005 M), both the BET surface area and the micropore volume of alkali-treated SAPO-34 were decreased. When SAPO-34 was alkali-treated with the 0.2 M NaOH solution, the CHA structure was changed in the XRD pattern (**Figure 1**), the SEM image showed a collapse of the surface structure, and the N₂ adsorption isotherm showed that the pore structures had been damaged. The micropore volume was drastically decreased and the mesopore volume was increased. The pore structure of the ZSM-5 was unchanged by alkali treatment with the 0.2 M NaOH solution. The concentration of NaOH (0.2 M), however, was too high for alkali treatment of SAPO-34. The results indicated that with alkali treatment the structure of SAPO-34 was weaker than that of ZSM-5. For NaOH, 0.005 M solution proved to be the best concentration for the enhancement of nitrogen adsorption properties. The highest BET surface area was induced in the micropores of SAPO-34 that were created by an alkali treatment using the optimum NaOH concentration of 0.005 M. The enhancement of water adsorption and desorption properties was also expected. On the other hand, the pore structure of SAPO-34 treated using 0.005 M of NH₄OH solution was not substantially changed, but both the BET surface area and the micropore volume were decreased by calcination.

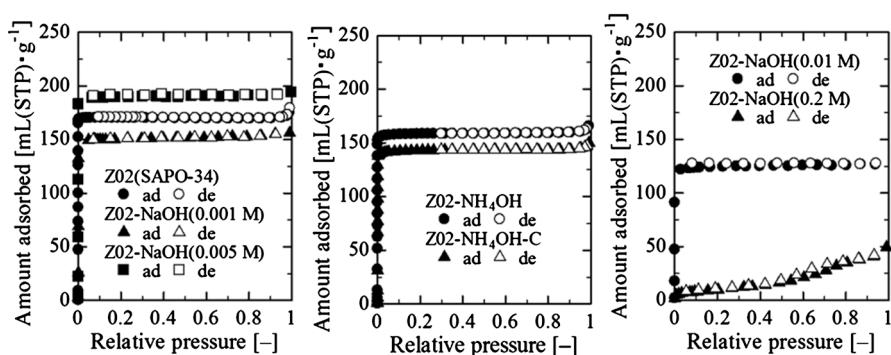


Figure 4. Nitrogen adsorption isotherms of several samples.

Table 2. Summary of physicochemical properties of several samples.

Sample	BET surface area [m ² /g]	Micropore volume [cm ³ /g]	Mesopore volume [cm ³ /g]
Z02 (SAPO-34)	716	0.28	0.02
Z02-NaOH (0.001 M)	621	0.25	0.01
Z02-NaOH (0.005 M)	770	0.32	0.01
Z02-NaOH (0.01 M)	517	0.20	0.01
Z02-NaOH (0.2 M)	36	0.03	0.08
Z02-NH ₄ OH	672	0.27	0.02
Z02-NH ₄ OH-C	606	0.25	0.02

3.2. Water Adsorption and Desorption Behavior

Figure 5 shows the normalized IR integrated intensity for several samples. The IR integrated intensity at 30 °C and the desorption ratios (adsorption at 30 °C and desorption at 80 °C or 100 °C) are summarized in **Table 3**. The temperature behavior was changed by the alkali treatment. After NaOH treatment, Z02-NaOH (0.005 M) had the highest IR integrated intensity of 30 °C. The best concentration for NaOH treatment was 0.005 M. These results were supported by the enhancement of N₂ adsorption properties. Alkali treatment with higher concentrations of NaOH solution tended to damage the pore structure, but treatment with a lower concentration did not sufficiently affect the pore structure to increase micropore volume. Also, introducing the optimum amount of Na⁺ exchanged by alkali treatment was also important. The desorption ratio of Z02-NaOH (0.01 M) was smaller than that of Z02-NaOH (0.005 M). These results indicated that although a higher NaOH concentration can introduce a sufficient amount of Na⁺ into SAPO-34, the desorption ratios (adsorption at 30 °C and desorption at 80 °C or 100 °C) were decreased. Strong interaction between Na⁺ and water prevented the release of water from SAPO-34. On the other hand, with NH₄OH treatment, Z02-NH₄OH had a higher IR integrated intensity at 30 °C and Z02-NH₄OH-C

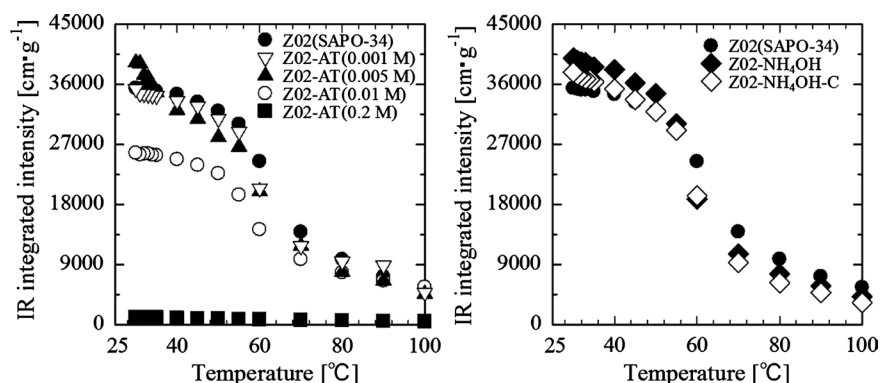


Figure 5. IR integrated intensity of adsorbed water at 10 Torr of several samples.

Table 3. IR integrated intensity at 30 °C and desorption ratio (adsorption at 30 °C and desorption at 80 °C or 100 °C) of several samples.

Sample	IR integrated intensity at 30 °C [cm ² ·g ⁻¹]	Desorption ratio (adsorption at 30 °C and desorption at 80 °C or 100 °C) [%]	
		80 °C	100 °C
Z02 (SAPO-34)	35,400	72.3	84.3
Z02-NaOH (0.001 M)	35,300	73.2	86.4
Z02-NaOH (0.005 M)	39,300	79.9	88.2
Z02-NaOH (0.01 M)	25,700	69.5	78.0
Z02-NaOH (0.2 M)	1100	43.2	55.3
Z02-NH ₄ OH	40,000	81.1	89.6
Z02-NH ₄ OH-C	37,800	83.5	91.3

had a higher desorption ratio. As **Figure 5** shows, NH_4OH treatment decreased the amount of adsorbed water at higher temperatures (80°C and 100°C). These results were supported by the change of Mg^{2+} to NH_4^+ and H^+ . Lower interaction between water and either NH_4^+ or H^+ decreased the amount of water adsorbed at higher temperatures.

Figure 6 showed the adsorption behavior of water. The slope of the adsorption initial behavior determined the adsorption initial rate [4], which is summarized in **Table 4**. Z02-NaOH (0.005 M) had the highest rate of water adsorption. The increase in the micropore volume and introduction of an optimum amount of Na^+ sites induced the highest rate of water adsorption. These results indicated that treatment of SAPO-34 using an optimum concentration (0.005 M) of NaOH enhanced both the amount of water adsorbed and the water adsorption rate. On the other hand, the treatment with NH_4OH decreased the adsorption rate. This effect was explained by the low interaction between water and either NH_4^+ or H^+ .

4. Conclusions

The present study examined the effects that alkali treatment (NaOH or NH_4OH) exerts on commercial silicoaluminophosphate molecular sieves (SAPO-34).

1) XRD patterns showed that, except for 0.2 M NaOH treatment, the other alkali treatments produced effects to SAPO-34 that were identical to that of CHA.

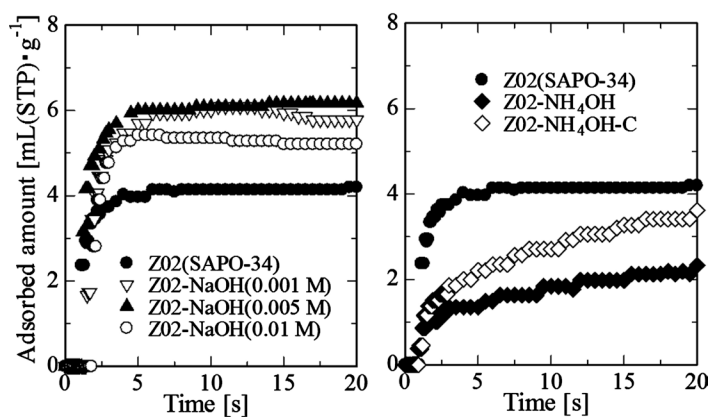


Figure 6. Adsorption behavior of water onto several samples 30°C .

Table 4. Adsorption initial rate of several samples at 30°C .

Sample	Adsorption initial rate [$\text{mL (STP)}\cdot\text{g}^{-1}\cdot\text{s}^{-1}$]
Z02 (SAPO-34)	2.7
Z02-NaOH (0.001 M)	3.5
Z02-NaOH (0.005 M)	3.9
Z02-NaOH (0.01 M)	3.5
Z02- NH_4OH	1.2
Z02- $\text{NH}_4\text{OH-C}$	1.4

2) SEM images of all treated materials showed mainly in a cubic structure. Obvious changes to the surface morphology of SAPO-34 were induced only by a relatively higher NaOH concentration (0.2 M).

3) SAPO-34 samples treated with 0.005 M NaOH showed the highest amount of adsorbed water at 30 °C as well as the highest adsorption capacities (adsorption at 30 °C and desorption at 80 or 100 °C).

4) For NH₄OH treated samples, the amount of adsorbed water at 30 °C and the effective adsorption capacities (adsorption at 30 °C and desorption at 80 °C or 100 °C) were higher than for NaOH-treated samples, but the adsorption initial rate was less than half that of the NaOH treated samples due to the low interaction between water and either NH₄⁺ or H⁺.

5) When SAPO-34 was treated with 0.005 M NaOH, the initial rate of water adsorption at 30 °C was about 1.4 times that of the original rate, which represented a higher amount of adsorbed water and a higher effective adsorption capacity than that of other alkali treatments of SAPO-34 by NaOH solutions. These results indicated that treatment of commercial SAPO-34 with 0.005 M NaOH produced the most advantageous conditions for water adsorbancy.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Lok, B. M., Messina, C.A., Patton, R.L., Gajek, R.T., Cannan, T. R. and Flanigen, E.M. (1984) Crystalline Silicoaluminophosphates. US Patent 4440871.
- [2] Lok, B.M., Messina, C.A., Patton, R.L., Gajek, R.T., Cannan, T.R. and Flanigen, E.M. (1984) Silicoaluminophosphate Molecular Sieves: Another New Class of Microporous Crystalline Inorganic Solids. *Journal of the American Chemical Society*, **106**, 6092-6093. <https://doi.org/10.1021/ja00332a063>
- [3] Kubokawa, S. (2011) Development of New Product Using AQSOA. *Adsorption News*, **25**, 6-11.
- [4] Katoh, M., Kimura, M., Sugino, M., Horikawa, T., Nakagawa, K. and Sugiyama, S. (2015) Modification of Commercial NaY Zeolite to Give High Water Diffusivity and Adsorb a Large Amount of Water. *Journal of Colloid and Interface Science*, **455**, 220-225. <https://doi.org/10.1016/j.jcis.2015.05.050>
- [5] Katoh, M., Satoh, A., Horikawa, T., Nakagawa, K. and Sugiyama, S. (2016) The Effects of Created Mesopores in ZSM-5 Zeolites by an Alkali Treatment on Water Adsorption. *Journal of Chemical Engineering of Japan*, **49**, 120-125.
- [6] Katoh, M., Koide, R., Yamada, K., Yoshida, T. and Horikawa, T. (2012) IR Spectroscopic Analysis of Thermal Behavior of Adsorbed Water on Y-type Zeolite. *International Journal of Modern Physics. Conference Series*, **6**, 437-442. <https://doi.org/10.1142/S2010194512003571>
- [7] Katoh, M., Satoh, A., Kimura, M. and Sugiyama, S. (2019) Enhancement of Water Adsorption-desorption Performance of Aluminophosphate Molecular Sieves (ALPO-5) Substituted with Several Metals. *Journal of Chemical Engineering of Japan*, **52**, 210-214.

- [8] Yamazaki, T., Watanuki, I., Ozawa, S. and Ogino, Y. (1987) An IR Study on Methane Adsorbed on ZSM-5 Type Zeolites. *Nippon Kagaku Kaishi*, **1987**, 1535-1540.
- [9] Yamazaki, T., Watanuki, I., Ozawa, S. and Ogino, Y. (1988) Infrared Spectra of Methane Adsorbed by Ion-Exchanged ZSM-5 Zeolites. *Langmuir*, **4**, 433-438.
<https://doi.org/10.1021/la00080a031>
- [10] Katoh, M., Yoshikawa, T., Tomonari, T., Katayama, K. and Tomida, T. (2000) Adsorption Characterization of Ion-Exchanged ZSM-5 Zeolites for CO₂/N₂ Mixtures. *Journal of Colloid and Interface Science*, **226**, 145-150.
<https://doi.org/10.1006/jcis.2000.6795>
- [11] Digital Data Management Corp. (1997) PCPDFWIN, Version 1.30, JCPDS-ICDD, File 570142.
- [12] Ogura, M., Shinomiya, S. Tateno, J., Nara, Y., Nomura, M., Kikuchi, E. and Matsukata, M. (2000) Formation of Uniform Mesopores in ZSM-5 Zeolite through Treatment in Alkaline Solution. *Chemistry Letters*, **29**, 882-883.
<https://doi.org/10.1246/cl.2000.882>