Synthesis of Microporous Materials and Their Adsorptive Properties of H$_2$S for Dental Application

I. Kishida, H. Utaka, H. Morikawa, A. Nakamura, and Y. Yokogawa

Department of Mechanical and Physical Engineering, Graduate School of Engineering, Osaka City University, Osaka 558-8585, Japan

Address correspondence to Y. Yokogawa, yokogawa@imat.eng.osaka-cu.ac.jp

Received 11 November 2010; Accepted 2 December 2010

Abstract

The microporous materials, Zeolite A and ZSM-5 were hydrothermally synthesized and their H$_2$S adsorption was studied. The obtained samples were put into a separable glass flask filled with H$_2$S gas, and the change in concentrations of H$_2$S was measured for 1–48 h at rt. Then the samples were taken out and put into a pyrolysis plant attached to gas chromatography-mass spectroscopy to determine the amount of H$_2$S desorbed from samples. The amount of H$_2$S adsorbed on Zeolite A was found to be larger than that on ZSM-5. That is 46% of H$_2$S was desorbed from Zeolite A when heated at 400 °C, while 24% of H$_2$S was desorbed from ZSM-5. The adsorption/desorption behavior of H$_2$S from zeolite materials could be interpreted by the electrostatic interaction between H$_2$S and adsorbent.

Keywords

apatite; hydrogel; protein; release; cake; PBS

1 Introduction

Recently, it is reported that bad breath is caused by volatile sulfide compounds (VSC) such as hydrogen sulfide (H$_2$S), methyl mercaptan and dimethyl sulfide produced in mouth [3,4]. The VSC is also considered to make periodontal disease severe. Some oral (Gram-negative) bacteria produce VSC, which induces permeability of mucous membrane and oral malodor formation. Thus, the adsorbent which highly adsorbs VSC should be useful for health in mouth.

Zeolite has a three dimensional framework structure in which SiO$_4$ and AlO$_4$ tetrahedrons are bonded by sharing oxygen. Zeolite materials contain {AlO$_2$}– which is negatively charged in the structure, so that zeolite generally contains alkali metal or alkali-earth metal atoms as univalent or bivalent cations to compensate the negative charges originated from {AlO$_2$}–. This electrostatic effect results in the surface potential of zeolite materials [1,2], and may influence the adsorptive properties. Therefore, there can be a discussion about the surface potential of zeolite materials by the amount of Al, that is, Si/Al ratio, for the purpose of revealing the adsorptive property.

Here, we have synthesized two kinds of zeolite materials, Zeolite A and ZSM-5, which have different Si/Al ratios. Zeolite A, whose composition is Na$_2$(Al$_{12}$Si$_{12}$O$_{48}$)·27H$_2$O, has the smallest Si/Al ratio in zeolite materials. On the other hand, ZSM-5, whose composition is Na$_n$(Al$_n$Si$_{96-n}$O$_{192}$)·16H$_2$O (n < 27), has a high Si/Al ratio. Adsorption/desorption of the H$_2$S in/on Zeolite A and ZSM-5 were measured using H$_2$S gas detector and gas chromatography – mass spectrometer (GCMS QP-5000, Shimadzu) equipped with a pyrolysis device.

2 Materials and methods

Preparation of mesoporous materials. All chemicals used in this study were supplied by Wako Pure Chemical Industries and used without further purification. Zeolite A was synthesized as follows: 13.5 g of sodium aluminate and 25 g of sodium hydroxide were dissolved in 300 mL of Milli-Q water and the obtained aqueous solution was heated up to 90 °C. Then 14.2 g of sodium metasilicate nonahydrate was dissolved in 200 mL of Milli-Q water and heated up to 100 °C. The latter solution was added into stirring a former solution. The mixture was stirred at 90 °C for 5 h at 300 rpm. The products were filtered and washed with Milli-Q water, then dried at 110 °C for 1 h.

ZSM-5 was synthesized as follows: 2.8 g of sodium hydroxide was dissolved in 300 mL of Milli-Q water. The solution was added into stirring another solution that contains 30.8 g of tetraethyl orthosilicate in 100 mL of 1 mol/L nitric acid. The mixture was added into another mixture of solutions, 100 mL of solution containing 0.36 g of sodium aluminate and 100 mL of solution containing 4.00 g of tetrabutyl ammonium bromide. After stirring at room temperature for 12 h, hydrothermal process at 180 °C for 36 h was conducted. The products were filtered and washed with Milli-Q water, then dried at 110 °C for 1 h.

Characterization. The crystal phases of the synthesized materials were each examined by an X-ray powder diffraction method using an X-ray diffractometer at 40 KV
and 20 mA with CoKα radiation (RINT2200, Rigaku Co., Japan). Identification of the phases was achieved by comparing the diffraction patterns with ICDD (JCPDS) standards using JADE6 (Rigaku Co., Japan). A fourier transform infrared (FT-IR) analysis using KBr was done. The TG/DTA of the as-dried powders was conducted using a thermal analyzer (Seiko Instrument, SSC5100) from room temperature to 800 °C at 5 °C/min under an air flux of 100 mL/min. The Ca/P molar ratio of the synthesized powder was determined by ICP (Shimadzu, ICPS-2000). The specimens were dissolved in a teflon container with HF and HNO3 in microwave oven. The average particle diameter of the synthesized powder was calculated by a centrifugal sedimentation method with a 0.2% solution of sodium pyrophosphate as a dispersion medium using LA-920 from Horiba Co. The specific surface area of the powders was determined by the Brunauer-Emmett-Teller method using a surface area analyzer (Uasa Ionics, Autosorb-1).

Gas adsorption/desorption. Adsorption treatment of H2S was done as follows. The samples were put in an oven for 12 h at 150 °C to remove the adsorptive water. Then 500 mg of dry sample was enclosed in a 10 L polymer bag with H2S gas which is initially adjusted to 20 ppm with nitrogen gas. Kitagawa-type H2S gas detector tube no. 120 SE and Kitagawa-type gas sampler AP-20 were used to adjust the initial concentration and to measure the changes in concentration. Concentrations of H2S with a zeolite sample in polymer bag were measured at 0.5, 1, 2, and 4 h. Concentrations without a zeolite sample were also measured to evaluate the amount of adsorption onto polymer bag wall.

Gas chromatography - mass spectrometer (GCMS QP-5000, Shimadzu) equipped with a pyrolysis device (PYR-4A, Shimadzu Co., Japan) was used to measure the amount of H2S adsorbed in the samples. The samples of zeolites that were exposed and not exposed in H2S were put in a pyrolysis plant by 3 mg and heated at 100 °C, 200 °C, 300 °C, 400 °C, 500 °C and 600 °C. Mass chromatograms, the variations in ion strength of H2S molecules against time, were obtained on molecules whose molecular weight equals to 18, which is that of H2S. Calibration curve was constructed at 300 °C to determine the amount of H2S absorbed in zeolite. H2S gas which was adjusted to 200 ppm and 1000 ppm with nitrogen gas was used as standard material and 0.5 mL of the gases was injected to gas chromatography mass spectrometer using micro-syringe. Therefore, the injected gas should contain 1 μL and 5 μL of H2S, respectively. The calibration curve was obtained by a least-squares method. The amount of H2S adsorbed in zeolite was determined by the area of mass chromatogram using calibration curve obtained at 300 °C.

### Table 1: ICP-derived Si, Al, Na wt% of prepared materials.

| Material | Si (wt%) | Al (mol%) | Na (mol%) | Al/Si ratio |
|----------|----------|-----------|-----------|-------------|
| Zeolite A | 16.5     | 16.7      | 13.9      | 1.02        |
| ZSM-5    | 39.3     | 1.54      | 0.96      | 0.039       |

### 3 Results and discussion

Table 1 is the ICP-derived wt% of Si, Al, Na of prepared materials. The Si/Al molar ratio of Zeolite A is 0.95 and that of ZSM-5 is 24.9, which is in accord with the typical compositions of zeolite materials. Zeolite A contains much amount of Na compared to ZSM-5.

Figure 1 shows the changes in concentration of H2S in polymer bag during the adsorption process. The initial concentration was 20 ppm. In the case of no sample used, the concentration fell to 19 ppm for the first 4 h of this process. It may indicate that a little amount of H2S adsorbed onto the inner wall of polymer bag. In the case of ZSM-5, the concentration fell to 19 ppm for the first 4 h, but little change of the concentration was observed after that and an equilibrium was attained for 8 h. On the other hand, in the case...
Figure 2: Area of mass chromatogram on molecules whose molecular weight is equal to 18.

|                | Adsorption (µL/g) | Desorption (µL/g) | Ratio of desorption/adsorption (%) |
|----------------|-------------------|-------------------|-----------------------------------|
| Zeolite A      | 450               | 206               | 46                                |
| ZSM-5          | 300               | 72                | 24                                |

Table 2: Amount of H$_2$S adsorbed for 24 h and desorbed at 400 °C.

of Zeolite A, the concentration was falling with time. The fall of concentration of H$_2$S in the polymer bag increased with an increase of amount of Zeolite A in the polymer bag. When 0.5 g of Zeolite A was applied, the equilibrium did not seem to reach even for 24 h.

Figure 2 shows the result of mass chromatogram on molecules whose molecular weight is equal to 18 of H$_2$S, at every 100 °C between 100 °C and 600 °C. Zeolite A seems to commence to release H$_2$S at 200 °C, but ZSM-5 at 300 °C. The maximum value of desorbed H$_2$S was observed at 400 °C and at higher temperature that was decreased, which may be due to the new products formed. The ZSM-5 samples heated at over 500 °C changed to be blackened from sulfuration.

Table 2 shows the amount of H$_2$S adsorbed onto 0.02 g of zeolite samples at rt for 24 h, and that released at 400 °C which was determined by the area of mass chromatogram on a quantitative analysis using calibration curve obtained at 400 °C. The amount of adsorbed H$_2$S onto Zeolite A was larger that onto ZSM-5. The difference in the amount of adsorbed H$_2$S between two types of zeolites can be explained by the surface potential. Polarity of zeolites depends on their Si/Al ratio.

The released amount of H$_2$S from Zeolite A was larger than that from ZSM-5. Zeolite A contains many Na ions, which are located outside of Zeolite crystals. And so H$_2$S may tend to adsorb onto the surface of Zeolite A crystal. ZSM-5, which has a large Si/Al ratio, is the opposite case, as reported that the surface potential of ZSM-5 is low when the Si/Al ratio is extremely large [1]. H$_2$S may enter inside micropores of ZSM-5. So the ratio of desorption/adsorption of Zeolite A is larger than that of ZSM-5.

4 Conclusion

We attempted to develop the material that adsorbs volatile sulfides selectively. Two kinds of zeolites, Zeolite A and ZSM-5, were synthesized and their adsorptive property of the H$_2$S was studied. The amount of H$_2$S adsorbed on zeolite A was found to be larger than that on ZSM-5. But 46% of H$_2$S on zeolite A was released when heated at 400 °C, while 24% of H$_2$S was desorbed from ZSM5. This suggests that adsorptive property of zeolites depends on their Si/Al ratio. By optimizing Si/Al ratio, it is expected to develop an adsorbent material, which highly adsorbs VSC, useful for health in mouth.

Acknowledgment The authors are grateful to Dr. T. Inamura for carrying out FT-IR spectrometry, ICP analysis, particle size analysis at Technology Research Institute of Osaka Prefecture.

References

[1] U. Messow, K. Quitzsch, and H. Herden, *Heats of immersion of ZSM-5 zeolite in n-alkanes, 1-alkenes and 1-alcohols at 30 °C*, Zeolites, 4 (1984), p. 255.
[2] D. H. Olson, W. O. Haag, and R. M. Lago, *Chemical and physical properties of the ZSM-5 substitutional series*, J Catalysis, 61 (1980), pp. 390–396.
[3] J. Tonzetich, *Oral malodour: an indicator of health status and oral cleanliness*, Int Dent J, 28 (1978), pp. 309–319.
[4] K. Tsutsumi and H. Takahashi, *Study of the nature of active sites on zeolites by the measurement of heat of immersion. I. Electrostatic field of calcium-substituted Y zeolite*, J Phys Chem, 74 (1970), pp. 2710–2713.