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Review Article

Synthesis of Microporous Materials and Their Adsorptive Properties of H_2S for Dental Application

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Abstract The microporous materials, Zeolite A and ZSM-5 were hydrothermally synthesized and their H_2S adsorption was studied. The obtained samples were put into a separable glass flask filled with H_2S gas, and the change in concentrations of H_2S 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_2S desorbed from samples. The amount of H_2S adsorbed on Zeolite A was found to be larger than that on ZSM-5. That is 46% of H_2S was desorbed from Zeolite A when heated at 400 °C, while 24% of H_2S was desorbed from ZSM-5. The adsorption/desorption behavior of H_2S from zeolite materials could be interpreted by the electrostatic interaction between H_2S 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_2S), methyl mercaptan and dimethyl sulfide produced in mouth [3,4]. The VSC is also considered to make periodonatal 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 $Na_2(Al_{12}Si_{12}O_{48})\cdot 27H_2O$, has the smallest Si/Al ratio in zeolite materials. On the other hand, ZSM-5, whose composition is $Na_n(Al_nSi_{96-n}O_{192})\cdot 16H_2O$ ($n < 27$), has a high Si/Al ratio. Adsorption/desorption of the H_2S in/on Zeolite A and ZSM-5 were measured using H_2S 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 tetrapropyl ammonium bromide. After stirring at room temperature for 12 h, hydrothermal process at 180 °C for 36 h was conducted. The products were filleted and rinsed with Milli-Q water, then dried at 110 °C for 10 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

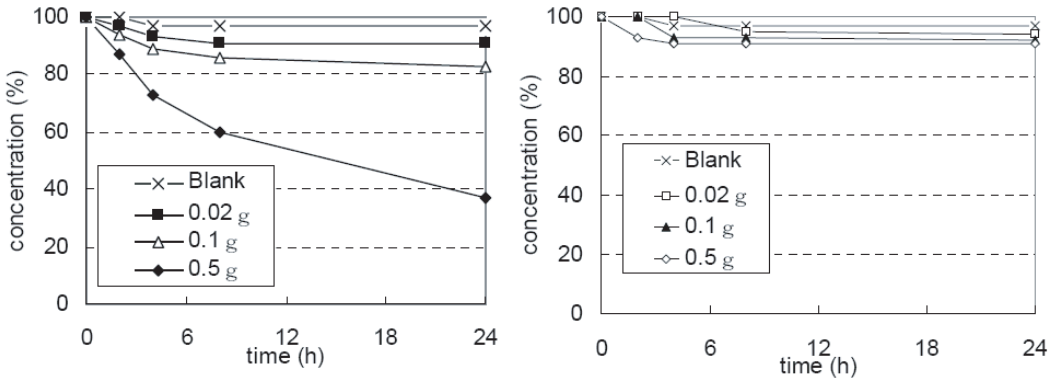

Figure 1: The change in concentration of H2S in polymer bag with various amount of Zeolite A (left) and ZSM-5 (right) as a function of adsorption time.

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 HNO_3 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 H_2S 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 H_2S gas which is initially adjusted to 20 ppm with nitrogen gas. Kitagawa-type H_2S 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 H_2S 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 H_2S adsorbed in the samples. The samples of zeolites that were exposed and not exposed in H_2S 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 H_2S molecules against time, were obtained on molecules whose molecular weight equals to 18, which is that of H_2S.

	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

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

Calibration curve was constructed at 300 °C to determine the amount of H_2S absorbed in zeolite. H_2S 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 H_2S, respectively. The calibration curve was obtained by a least-squares method. The amount of H_2S adsorbed in zeolite was determined by the area of mass chromatogram using calibration curve obtained at 300 °C.

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 H_2S 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 H_2S 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

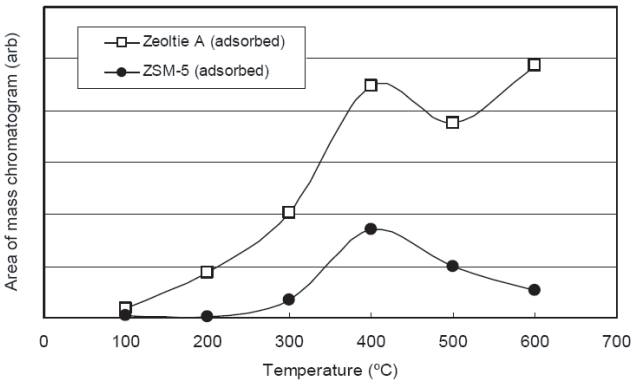

Figure 2: Area of mass chromatogram of molecular weight of 18.

	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_2S adsorbed for 24 h and desorbed at 400 °C.

of Zeolite A, the concentration was falling with time. The fall of concentration of H_2S 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_2S, at every 100 °C between 100 °C and 600 °C. Zeolite A seems to commence to release H_2S at 200 °C, but ZSM-5 at 300 °C. The maximum value of desorbed H_2S 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_2S 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_2S onto Zeolite A was larger that onto ZSM-5. The difference in the amount of adsorbed H_2S 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_2S 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_2S 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_2S 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_2S was studied. The amount of H_2S adsorbed on zeolite A was found to be larger than that on ZSM-5. But 46% of H_2S on zeolite A was released when heated at 400 °C, while 24% of H_2S 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.

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