Hydration enthalpy for synthetic and cation exchanged A-type zeolites with special reference to zeolite heat pump media

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Abstract

Na-A type zeolite has been synthesized from the waste solution with the red mud exhausted from the Bayer process. The heats of water-vapor absorption of the Na-A and cation exchanged zeolites were measured by means of an adiabatic water-vapor absorption calorimeter which had been devised for investigating heat pump effect of zeolites. The integrated hydration enthalpy of A-zeolite is in the same order as those of mordenite and clinoptilolite. However, A-zeolite shows twice the total heat amount obtainable from unit weight samples of a natural zeolite, because natural zeolites contain impurity phases, and their dehydration amount around 100°C is much smaller. Mg-exchanged A-zeolite dehydrated at 100°C showed the largest amount of hydration enthalpy of 65.1 kJ/mol, and a weight loss on dehydration of 14.7%. The Mg-A-zeolite will be the most efficient heat pump media of all zeolites dehydrated at 100°C in the present work.

Introduction

Dehydrated zeolites absorb water-vapor reversibly from about 15 up to 30 weight percent. Since the vaporization enthalpy of water is larger than that of any other common refrigerants, about 10 times larger than that of freons, the zeolite-water system may provide the most efficient system as a heat pump or a heat exchanger. Although other sorbents show almost linear H₂O absorption isotherms, the extremely nonlinear character of zeolites is essentially important for a zeolite solar system (Tchernev, 1978 and 1980). We have done basic research to use natural zeolites with the large hydration enthalpy. Dehydrated mordenite expels about 60 kJ of hydration heat when one mole of water vapor is absorbed at room temperature. Since the dehydration-hydration cycle of zeolites is reversible, the basic zeolite heat pump system could be illustrated (Fig. 1). During the day cycle, the solar heat warms up and dehydrates zeolite. The water-vapor expelled is transferred and condensed in a water-reservoir. The condensation heat should be removed from the condenser. During the night cycle, the cooled

FIG. 1. Schematic illustration of day and night cycle for zeolite-water heat pump system.

zeolite absorbs water-vapor even at low vapor pressure. This accelerates the evaporation of water at the surface of the water-reservoir and hence cools the surrounding area. The zeolite-water system must be evacuated beforehand to certify vapor-convection through the system via the pipe line. Tchernev succeeded in making ice by the zeolite solar-freezing system (Tchernev, 1978 and 1980). The solar refrigerator with an efficiency of 15% produces about 3.24MJ/h of cooling for each square meter of collector area for a solar input of 21.6MJ/h. The system has attractive points as follows: 1) The system can be operated by sun light or by exhaust heat, anywhere without electric power. 2) The system is composed mainly of pollution-free materials such as zeolite and water, and does not exhaust chemical pollutants such as freon during operation, nor after it is discarded. 3) The materials used for the system are all widely available and cheap. Although natural zeolites are available at low cost in large amounts, inevitable contaminations such as clay minerals, quartz and feldspar degrade the efficiency as a heat reservoir. The pure synthetic zeolites are useful especially for basic research without contamination effect.

The purposes of the present study are as follows; 1) simple zeolite synthesis at a reasonable price, 2) to find out optimum cation-exchanged zeolites for a heat pump system, 3) to compare abilities of heat pump media for the synthetic and natural zeolites.

The strongly alkalic waste solution with the red mud exhausted from the Bayer process

contains such a high amount of aluminum and sodium, that we attempted to synthesize zeolites by adding silica-component from reagents using a conventional autoclave as a reaction cell. We have already studied synthetic conditions such as synthetic duration and the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (n) of the starting mixture (Kasai *et al.*, 1993 and 1994). A special attention is focused on the relation between enthalpy of water-vapor absorption and the cation exchange of A-type zeolites for the application of a heat pump.

Experimental

Preparation of sample zeolites

Supernatant solution of red mud: Bauxite to alumina production wastes, the “red mud” which composed of the reddish solid and the strongly alkalic liquid. The alkali solution filtrated with Toyo 5C filter paper was analyzed chemically (Table 1) and was used for zeolite synthesis (Kasai *et al.*, 1993 and 1994).

Zeolite synthesis: Starting mixtures were prepared by mixing 100ml sample solution with various amounts of reagent-grade sodium silicate, from $n=1$ to 10. They were agitated at room temperature for 5h in a Teflon reaction bottle. The reaction-bottle was sealed in a conventional autoclave with pressure compensation water and heated at 105°C for various reaction periods. The products were filtrated, washed with deionized water, and then dried at 40°C for 24h. The phases and the crystallinity of the products were examined by X-ray powder diffraction.

Cation exchange: Na-A type synthetic zeolite was served for the cation exchange experiments. The method of cation exchange was the same and common for all cation solutions: 1.0mol/l of aqueous solutions of KCl, AgNO_3 , MgCl_2 , CaCl_2 , $\text{Sr}(\text{NO}_3)_2$, CoSO_4 , NiCl_2 or CuSO_4 . The 100ml of each solution was poured onto 2g of the Na-A zeolite powder. The slurries were shaken at 40°C for 3h. Solid-liquid separation was done by a centrifuge. The samples were washed with deionized water and dried at 40°C for 24h. The cation-exchanged

TABLE 1. Chemical composition of two kinds of supernatant solutions of red mud.

Element	Concentration / ppm	
	Sample 1	Sample 2
Na	7110	15100
Al	1900	5620
Mo	390	---
Si	47	7.0
Fe	40	---
Ca	16	0.90
Mg	0.3	0.04

samples were then rehydrated in a water-vapor atmosphere equilibrated with the saturated ammonium chloride solution at 25°C. The chemical compositions of cation-exchanged zeolites were analyzed by the flame photometry for Na and K and by the atomic absorption method for other elements, using a HITACHI 170-50A atomic absorption spectrophotometer. Specimens for the analyses were prepared by dissolving into fluoboric-boric acid (Bernas, 1968; Buckley and Cranston, 1971) for samples containing K, Mg, Co, Ni or Cu. The hydrochloric acid was used for Ca or Sr-exchanged samples, and the nitric acid was used for Ag-exchanged samples. X-ray powder diffraction patterns were obtained by the automated powder diffraction system with monochromated Cu-K α radiation (MAC Science MXP³).

Hydration calorimetry

Heat of water-vapor absorption was measured with an adiabatic water-vapor absorption calorimeter which had been devised for investigating heat pump effect of zeolites. The calorimeter (Fig. 2) is composed of a high resolution (10^{-4} K) thermistor-thermometer (1) with a digital multimeter (YOKOGAWA 7561), a heater for supplying calibration heat (2), an adiabatic vessel with 400ml of water (3), a sample tube with a grease-less valve and a personal

FIG. 2. Schematic view of the adiabatic calorimeter for measuring heat of absorption of water vapor with the automatic data acquisition and calibration heat-input system.

computer system, NEC PC-8801, for data acquisition and for heat-supply control.

A 0.25g of zeolite sample was dehydrated by evacuating at 100°C for 1h in the sample tube. The amount of dehydration was obtained as the weight difference before and after the

FIG. 3. An example of measurement of water vapor absorption calorimetry.

a: Temperature-time trace of the measurement, three steps by calibration heat input and a temperature elevation on hydration. b: Calibration line obtained from the measurement shown in the figure a. c: Explanation of data processing of the calorimeter system.

dehydration by correcting evacuated air weight. The sample tube was set in the calorimeter. It takes several hours to settle the initial fluctuation in temperature before starting the calorimetric measurement.

To explain the method of data analysis, a temperature-time trace through the measurement is shown in Fig. 3a. Relatively flat traces such as AB, CD, EF, GH and IJ mean the temperature equilibrium (Fig. 3c). Steps such as BC, FG and HI show the temperature elevation by the input of calibration heat. The trace DE indicates the effect of the heat evolved by hydration of zeolite. The temperature change (ΔT) for each step was obtained from the extrapolated values, such as B'C', D'E', F'G' and H'I'. For example, D'E' is defined at a middle point between T1 and T2 on the time axis. The heat of water-vapor absorption was calculated from the relations between ΔT and calibration-heat (Fig. 3b).

We also measured the heat of hydration (ΔH_w) in liquid water-zeolite system to evaluate the consistency of the heat cycle, water/vapor/zeolitic-water. The zeolite sample was dehydrated by heating in vacuum, and then sealed in an ampoule. The ampoule was crushed in water of the adiabatic calorimeter to measure the hydration heat. The heat of evaporation (ΔH_e) available from a database gives self-consistent relation among ΔH_v , ΔH_w and ΔH_e as follows: $\Delta H_v = \Delta H_w - \Delta H_e$.

Results

Zeolite sample preparation

X-ray diffraction measurements indicated that Na-A zeolites are obtained for $1 \leq n \leq 3$ and Na-X zeolite for $3 \leq n \leq 6$ (Kasai *et al.*, 1994; Ciric, 1968; Lechert and Kacirek, 1991) (Table 2). Relative amounts of zeolite-components were estimated semi-quantitatively from peak heights of X-ray diffraction patterns and shown as circle size in the figure. Almost pure analcime was synthesized for $n \geq 6$. Small amount of phillipsite is found to crystallize at any

TABLE 2. Change of synthesized phases with $n = \text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio in starting mixtures. Hydrothermally treated for 10 days at 105°C.

Zeolite phase	$n = \text{SiO}_2/\text{Al}_2\text{O}_3$ ratio									
	1	2	3	4	5	6	7	8	9	10
Zeolite Na-A	●	●								
Zeolite Na-X			●	●	●					
Phillipsite	●	●	●	●	●					
Analcime						●	●	●	●	●

Circle diameter indicates the semi-quantitative amount of zeolite contained.

compositions. The amount of phillipsite was not reproducible and was fluctuated at random. Under the present synthetic conditions, the largest amount of Na-A zeolite was obtained at $n=1$. Samples synthesized at $n=1$ were used for the cation-exchange and calorimetric studies.

SEM photomicrographs (Fig. 4) of synthesized zeolites show cubic form of Na-A, octahedral crystals of Na-X (Morris *et al.*, 1993), trapezohedral crystals of analcime with twin-traces and spherical aggregates of phillipsite (Morris *et al.*, 1993; Hansen *et al.*, 1993), respectively. The spherical aggregate of phillipsite was observable in all products. Some spherical aggregates encapsulate Na-A cubes.

Cation exchange experiments show that Na^+ is completely exchanged with Ag^+ , whereas Ni^{2+} shows only 17 percent of the exchange. Other cations range from 51 to 85 percent in exchange in the present experiment (Table 3). Although the degree of exchange was variable for cations, the obtained zeolites were supplied for the hydration calorimetry. The weight loss

FIG. 4. SEM photomicrographs of products from supernatant solution of red mud.

TABLE 3. Chemical compositions of synthesized Na-A and the cation exchanged zeolites, denoted as oxide molar ratio in the formula of $a(M_2^+, M^{2+})O \cdot bNa_2O \cdot cAl_2O_3 \cdot dSiO_2 \cdot nH_2O$, and loss of weight on heating.

Cations	Oxide ratio (O=8)				Ratio of cation exchange / %	Loss of weight on heating / %			
	a	b	c	d		Under vacuum 25~100°C	25~100°C	25~500°C	25~800°C
Na ⁺	0.00	1.03	1.00	2.00	0	14.0	3.72	20.1	21.6
K ⁺	0.83	0.15	0.99	1.93	85	9.12	2.69	16.9	17.8
Ag ⁺	1.09	0.00	1.09	2.54	100	11.7	2.51	11.6	14.2
Mg ²⁺	0.49	0.48	1.00	1.99	51	14.7	7.19	22.8	25.9
Ca ²⁺	0.82	0.22	1.01	2.01	78	9.41	3.55	20.3	21.6
Sr ²⁺	0.73	0.22	1.09	2.67	77	9.94	3.68	20.4	22.1
Co ²⁺	0.50	0.46	0.98	1.92	52	11.8	8.19	23.4	25.2
Ni ²⁺	0.13	0.62	0.94	1.78	17	20.8	4.76	23.0	24.5
Cu ²⁺ *	2.36	0.05	1.20	2.73	98	---	10.4	25.9	34.7

* : Na-A zeolite is completely decomposed by Cu²⁺-exchange.

on heating depends on individual cation type. Unusually high weight loss is observed for Cu²⁺ exchanged sample. X-ray diffraction pattern of each sample coincides with that of A-type zeolite except Cu-exchanged one (Fig. 5). This indicates that the Cu-exchange decomposes zeolite structure and forms copper sulfate hydroxide, Cu₄SO₄(OH)₆.

Hydration calorimetry

The integrated heat of absorption per 1 mole of absorbed water-vapor (ΔH_v) was calculated from the hydration heat and the weight difference between samples before and after hydration. The values of ΔH_v for Na-A and cation exchanged samples range from 60 to 66 kJ/mol (Table 4). Reproducibility of the enthalpy values is within ± 1.5 kJ/mol in this study.

Both the large hydration amount and the large molar heat of absorption of water-vapor are favorable for the application of zeolite as a heat pump media. Total heat amount (Q) obtainable from 1 kg of zeolite sample was calculated (Table 4) for this purpose. The maximum Q value was 531 kJ/kg for Mg²⁺ exchange zeolite, when it was dehydrated at 100°C. This value is about 9 percent greater than that of the Na-A, 488 kJ/kg. This indicates that Mg²⁺ exchanged zeolite is the most suitable heat reservoir among all samples treated in the present study. Table 5 shows the ΔH_v and Q values for mordenite samples from Koromogawa, Iwate prefecture, Japan, and from Cikalong, west Java, and for clinoptilolite from Bogor, west Java, Indonesia. The ΔH_v value of natural zeolite, such as mordenite and clinoptilolite, was of the same order to that of zeolite A samples. However, the Q values were smaller than those of zeolite A samples, because the natural zeolites include impurity phases such as clay minerals and quartz; and show relatively low dehydration amounts at low temperatures around 100°C.

The mordenite sample from Koromogawa showed the ΔH_w value of -18.5 kJ/mol and the ΔH_v value of -60.0 kJ/mol, when it was dehydrated at 120°C. These values give the evaporation

FIG. 5. X-ray diffraction patterns of synthesized Na-A zeolite and cation exchanged zeolites. C: Copper sulfate hydroxide, $\text{Cu}_4\text{SO}_4(\text{OH})_6$.

TABLE 4. Integrated molar enthalpy of water vapor absorption and the ratio of rehydration of type A zeolite and of cation exchanged zeolites. ΔH_v : integrated heat of absorption of H_2O (g) at 23–25°C. Q : heat of water vapor absorption per 1 kg of zeolite.

Guest cation	Rehydration / %	$-\Delta H_v / \text{kJ} \cdot \text{mol}^{-1}$	$Q / \text{kJ} \cdot \text{kg}^{-1}$
Na^+*	102	63.0	488
K^+	86.2	65.1	330
Ag^+	88.1	59.6	342
Mg^{2+}	87.4	65.1	531
Ca^{2+}	102	66.2	345
Sr^{2+}	108	65.7	362
Co^{2+}	70.1	63.3	413
Ni^{2+}	66.4	65.6	489

* : Original Na-A zeolite

TABLE 5. Integrated molar enthalpy of water vapor absorption (ΔH_v) of natural zeolites from Koromogawa, Iwate Pref. Japan, and Cikalong and Bogor, west Java Indonesia measured at 23–25°C. Q : heat of water vapor absorption per 1kg of zeolite.

Temperature of dehydration / °C	Sampling locality	Main component	$-\Delta H_v / \text{kJ} \cdot \text{mol}^{-1}$	$Q / \text{kJ} \cdot \text{kg}^{-1}$
100	Koromogawa	Mordenite	58.8	237
	Cikalong	Mordenite	63.4	222
	Bogor	Clinoptilolite	61.1	197
120	Koromogawa	Mordenite	60.0	257

enthalpy to be $-18.5 - (-60.0) = 41.5 \text{ kJ/mol}$ by using the self-consistency relation, $\Delta H_e = \Delta H_w - \Delta H_v$. Since the true value of ΔH_e is quoted to be 44.0 kJ/mol at 25°C , the mismatch of 2.5 kJ , will be due to the error of measurements of either ΔH_v or ΔH_w .

Conclusions

Several kinds of zeolites have been synthesized hydrothermally at 105°C from the waste solutions of red mud exhausted in the Bayer process in an alumina production industry by adding sodium silicate as a silica component. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios (n) for the starting mixture significantly influenced the kind of product-phases. Main products were of Na-A zeolite at $n=1$ and 2, Na-X zeolite at $n=3-5$ and analcime at $n=6-10$. Phillipsite was crystallized in the same condition in which Na-A or Na-X zeolite was synthesized. The amount of phillipsite was not reproducible in the present syntheses.

The hydration enthalpy of Na-A type and the cation exchanged zeolites ranges from 60 to 66 kJ/mol (H_2O). The maximum value of total heat amount (Q) obtainable from 1kg of zeolite was 531 kJ/kg for Mg^{2+} exchanged A-zeolite. This value is about 9 percent greater than that of the Na-A, 488 kJ/kg . The Mg^{2+} exchanged A-zeolite is the most suitable heat reservoir among all the samples treated in the present study.

Integrated hydration enthalpy of natural zeolites, such as mordenite and clinoptilolite, was almost the same as that of A-zeolite. But the Q -values of natural zeolites were about half of that of A-zeolite samples because of the presence of impurity phases, and the insufficient dehydration characters at the relatively low temperature region around 100°C .

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