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HYDRATION HEATS OF ZEOLITES FOR EVALUATION OF HEAT EXCHANGERS

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Abstract

The enthalpy of hydration of purified clinoptilolite from Beli Plast, Bulgaria, and various cation-exchanged types such as Na-, K-, Ca- and Mg-clinoptilolite was determined by the adiabatic water-vapor absorption calorimeter. The hydration enthalpy becomes more exothermic in the sequence K, Na, Ca, Mg depending on hydration energy values of exchanged cations. Na-clinoptilolite would be an efficient heat exchanger in a wide temperature range of dehydration, 180–300°C, while Mg-clinoptilolite in higher temperatures, 300–350°C.

Keywords: calorimetry, clinoptilolite, enthalpy, heat-exchanger, hydration heat

Introduction

Zeolites belong to a series compounds of hydrated aluminosilicates with open porous structure capable of absorbing large quantities of water molecules in the vicinity of room temperature even at low pressures. The non-linear relations in the isotherms of zeolites characterize zeolite-water vapor system [1, 2]. This unique property of zeolites was realized in the heat-pump system. Attractive point of the system is the ability of using the solar energy or waste heat.

Thermodynamic data of hydration processes of zeolites are essential to evaluate zeolites as heat exchangers. Enthalpies of hydration of zeolites have been obtained by using different calorimetric methods: immersion calorimetry [3, 4]; HF solution calorimetry [5, 6]; transposed temperature drop calorimetry [7, 8] and adiabatic water-vapor calorimetry [9, 10].

Many studies have shown that the nature of the dehydration/hydration process of zeolites is largely controlled by the hydration energy of extra-framework cations [4, 8, 11] and structural variation during dehydration [12].

In the present study calorimetric measurements for water absorption were made to determine the integral molar enthalpy of hydration on purified clinoptilolite, and K-, Na-, Ca- and Mg-exchanged clinoptilolite. From this data it was possible to clar-

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ify the influence of hydration energy of exchanged cations on enthalpy values, and to identify suitable clinoptilolite forms to use as heat exchangers.

Experimental

Sample preparation

Clinoptilolite tuff from Beli Plast, Eastern Rhodopes, Bulgaria, containing about 75 mass% clinoptilolite was used in this study. This material was purified by the following procedure:

(1) removal of the clay minerals and crystobalite by decanting the fraction under 2 μm size in water, and (2) separation of the heavy minerals by centrifuge in a mixture of bromoform and acetone with the density of 2.2 g cm^{-3}, followed by washing and drying at room temperature. Almost 98 mass% purification was obtained as no other minerals have been detected by the X-ray powder diffraction. A portion of the purified material was cation exchanged with 1 M Na-, K-, Ca- or Mg-chloride solution by shaking for three days at 60°C changing the solution each day, and finally washed and dried at 40°C. The cation-exchanged samples were rehydrated in a water-vapor atmosphere equilibrated with the saturated solution of ammonium chloride at 25°C. The chemical compositions of these forms were determined by the flame photometry for Na and K, and by the atomic absorption spectroscopy for other elements and are as follows:

As purified:	$(Na_{0.61}K_{1.90}Ca_{1.32}Mg_{0.35})(Al_{5.83}Fe_{0.06}Si_{30.12})O_{72}\cdot 24.1H_2O$
Na-exchanged:	$(Na_{4.65}K_{1.05}Ca_{0.06}Mg_{0.18})(Al_{5.53}Fe_{0.06}Si_{30.27})O_{72}\cdot 21.8H_2O$
K-exchanged:	$(Na_{0.64}K_{5.39}Ca_{0.04}Mg_{0.13})(Al_{5.76}Fe_{0.05}Si_{30.05})O_{72}\cdot 17.3H_2O$
Ca-exchanged:	$(Na_{0.35}K_{0.94}Ca_{2.15}Mg_{0.29})(Al_{5.95}Fe_{0.05}Si_{29.96})O_{72}\cdot 23.9H_2O$
Mg-exchanged:	$(Na_{0.05}K_{1.40}Ca_{0.48}Mg_{1.52})(Al_{5.97}Fe_{0.07}Si_{30.12})O_{72}\cdot 23.8H_2O$

On the charge basis, the cation-exchanges of the above formula correspond to 75.2 for Na, 84.8 for K, 69.8 for Ca and 55.9% for Mg. The water content of the clinoptilolite samples was determined by TG heated to 800°C.

Calorimetry

Heats of absorption of water-vapor were measured with the adiabatic water-vapor absorption calorimeter [9]. A 0.25 g of zeolite sample placed in a glass flask was dehydrated in evacuation (10^{-3}–10^{-4} torr) and heated at various temperatures such as 80, 100, 120, 140, 180 and 300°C, for 1 h. The hydration amount was determined as mass-difference for the sample before and after the hydration in the calorimeter. The calorimeter is composed of a heater for supplying calibration heat, a high resolution (10^{-4} K) thermistor-thermometer, an agitator and the sample flask, all of which are immersed in 0.4 dm^3 of water in a vacuum jar. All data, including resistivity and voltage values for the heat supply, were acquired by a micro-computer system through the digital multimeter (Yokogawa 7561). Water vapor was introduced from a water reservoir to the sample through a glass tube. The heat values were calculated based on the linear relation between temperature elevation due to the hydration and the electric power supplied. Temperature increments were determined by the conventional method of interpolating the aperture between lower and higher steps [9]. The experiments were provided at room temperature and no special temperature control was implemented for the system.

Results and discussion

Hydration enthalpy

The results from the calorimetric investigation for the as purified, Na-, K-, Ca- and Mg-clinoptilolite samples are listed in Table 1. The measured heat of water vapor absorption is expressed as the integral molar enthalpy of hydration (ΔH_h) of absorbed water vapor. Statistical errors of hydration enthalpies are estimated as ‘mean error’: $r=(1/n)\sum|d_i|$ in case of two or three experimental points and ‘standard error’: $\sigma_m \approx (5/4)r/\sqrt{(n-1)}$ in case of five or seven data, where n is the number of measurements, ‘i’ – change from 1 to n, d_i is the remainder of the ‘i’-measurement, $d_i=\Delta H_{h(i)}-\Delta H_{h(mean)}$. Table 1 summarizes other data such as: dehydration ($W_{dehyd.}$) and hydration amount ($W_{hyd.}$) of water, mass%; amount of water hydrated (Δm_h), mmol g^{-1} zeolite; heat of hydration (q), normalized to the zeolite mass, J g^{-1} . The q-value is introduced for evaluating heat exchange ability of the zeolite. The increase of dehydration temperature leads to increase of both the amount of water dehydrated/hydrated and the enthalpy of hydration, and resulted in greater heat value evolved from 1 g of zeolite (q).

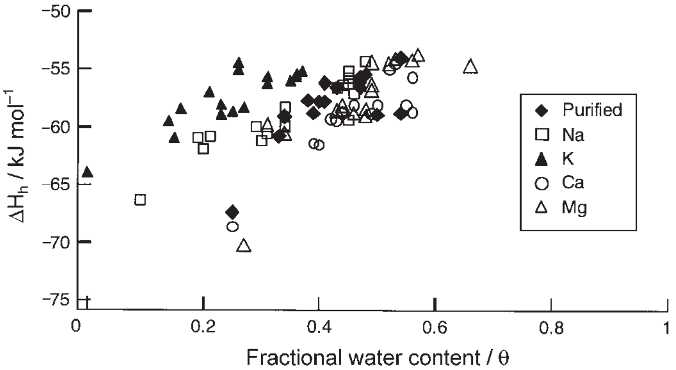

Fig. 1 Plots of integral molar enthalpy of hydration (ΔH_h) as a function of fractional water content (θ) at the dehydrated state for clinoptilolite samples

Dependence of values of ΔH_h on fractional water content (θ) is presented in Fig. 1, where θ is a ratio between the hydration amount of water and the full saturated water content for each sample. According to hydration characteristics of exchanged

Table 1 Dehydration and hydration amount ($W_{dehyd.}$ and $W_{hyd.}$), amount of water hydrated (Δm_h), heat of hydration (q) and hydration enthalpy (ΔH_h) of purified, Na-, K-, Ca- and Mg-exchanged clinoptilolite samples dehydrated at different temperatures (r – mean error; σ_m – standard error of hydration enthalpy measurements)

Sample	T_d/°C	W_{dehyd}/%	W_{hyd}/%	Δm_h/mmol g^{-1}	$-q$/J g^{-1}	$-\Delta H_h$/kJ mol^{-1}	$-\Delta H_h$(mean)/kJ mol^{-1}	r	σ_m
Purified	80	6.99	7.02	3.90	211	54.1	54.05	0.05	
clinoptilolite		7.17	7.09	3.94	213	54.0	(2)		
	100	8.08	7.11	3.95	233	58.8	56.9	1.2	0.6
		8.20	7.61	4.23	250	58.9	(7)		
		8.52	7.95	4.42	245	55.4			
		8.11	8.13	4.52	253	56.1			
		8.64	8.19	4.55	253	55.7			
		8.47	8.22	4.56	258	56.6			
		8.81	8.76	4.87	275	56.6			
	120	9.26	9.06	5.03	283	56.2	57.2	0.7	
		8.95	9.18	5.10	295	57.8	(3)		
		9.13	9.36	5.20	300	57.7			
	140	9.16	9.04	5.02	290	57.8	58.3	0.5	
		9.35	9.44	5.25	309	58.9	(2)		
	180	10.73	10.17	5.65	334	59.2	60.0	0.8	
		10.78	10.25	5.70	347	60.8	(2)		
	300	13.00	11.44	6.36	429	67.4			
		15.36	15.36	8.54	nd*	nd*			
Na-clinoptilolite	80	7.13	7.35	4.08	221	54.3	55.5	1.1	
		7.04	7.51	4.17	238	57.1	(3)		
		7.40	7.65	4.25	234	55.1			

Table 1 Continued

Sample	T_d/°C	W_{dehyd}/%	W_{hyd}/%	Δm_h/mmol g^{-1}	$-q$/J g^{-1}	$-\Delta H_h$/kJ mol^{-1}	$-\Delta H_h$(mean)/kJ mol^{-1}	r	σ_m
Na-clinoptilolite	100	8.37	7.72	4.29	254	59.4	56.8	1.0	0.7
		8.60	7.77	4.31	243	56.2	(5)		
		8.97	7.78	4.32	241	55.7			
		8.52	7.83	4.35	245	56.3			
		8.46	8.04	4.46	253	56.6			
	120	9.22	9.20	5.11	306	59.9	59.3	0.7	
		9.60	9.30	5.17	301	58.3	(3)		
		9.34	9.31	5.17	309	59.8			
	140	10.0	9.70	5.38	326	60.6	60.5	0.4	
		9.81	9.78	5.43	332	61.1	(3)		
		10.02	9.97	5.57	334	60.0			
	180	11.61	11.04	6.13	373	60.8	61.2	0.5	
		11.60	11.27	6.26	387	61.9	(3)		
		11.45	11.36	6.31	384	60.9			
	300	13.42	12.74	7.07	469	66.3			
		14.01	14.01	7.80	nd*	nd*			
K-clinoptilolite	80	7.30	7.29	4.05	223	55.1	55.4	0.2	
		7.25	7.38	4.10	227	55.4	(3)		
		7.12	7.48	4.16	231	55.6			
	100	9.13	7.51	4.17	234	56.0	55.5	0.6	0.4
		8.64	7.99	4.43	249	56.2	(5)		
		9.14	8.07	4.48	249	55.6			

Table 1 Continued

Sample	T_d/°C	W_{dehyd}/%	W_{hyd}/%	Δm_h/mmol g^{-1}	$-q$/J g^{-1}	$-\Delta H_h$/kJ mol^{-1}	$-\Delta H_h$(mean)/kJ mol^{-1}	r	σ_m
K-clinoptilolite	100	8.82	8.62	4.79	261	54.4			
		8.57	8.62	4.79	264	55.0			
	120	8.79	8.46	4.70	274	58.2	57.6	0.6	
		9.13	9.13	5.08	289	57.0	(2)		
	140	9.22	8.71	4.84	284	58.7	58.5	0.4	
		9.00	8.91	4.95	292	58.9	(3)		
		9.05	8.98	4.99	289	58.0			
	180	9.80	9.75	5.43	317	58.4	59.6	0.9	
		10.30	9.83	5.47	333	60.9	(3)		
		10.09	9.98	5.55	330	59.5			
	300	11.65	11.60	6.44	412	64.0			
Ca-clinoptilolite	80	6.78	6.79	3.78	211	55.7	55.1	0.4	
		6.90	7.25	4.03	220	54.5	(3)		
		6.93	7.38	4.10	226	55.0			
	100	8.06	6.79	3.77	221	58.7	58.4	0.3	0.2
		7.82	6.95	3.86	225	58.2	(5)		
		8.42	7.79	4.33	252	58.1			
		8.03	7.99	4.43	261	58.8			
		8.40	8.38	4.65	270	58.1			
	120	8.69	8.64	4.80	282	58.8	58.7	0.2	
		9.01	8.62	4.80	281	58.6	(2)		
	140	8.76	8.78	4.88	290	59.4	59.35	0.05	
		9.26	9.08	5.04	299	59.3	(2)		

Table 1 Continued

Sample	T_d/°C	W_{dehyd}/%	W_{hyd}/%	Δm_h/mmol g^{-1}	$-q$/J g^{-1}	$-\Delta H_h$/kJ mol^{-1}	$-\Delta H_h$(mean)/kJ mol^{-1}	r	σ_m
Ca-clinoptilolite	180	10.11	9.39	5.23	322	61.5	61.5	0.0	
		10.04	9.53	5.30	326	61.5	(2)		
	300	12.40	11.66	6.48	444	68.6			
		15.53	15.53	8.64	nd*	nd*			
Mg-clinoptilolite	80	7.59	5.46	3.03	165	54.6	54.2	0.3	
		6.91	6.97	3.87	210	54.2	(3)		
		7.77	6.90	3.88	209	53.7			
	100	7.69	7.58	4.21	228	54.1	55.2	1.1	0.7
		8.01	7.69	4.27	233	54.5	(5)		
		7.94	8.18	4.54	247	54.4			
		8.14	8.18	4.54	258	56.8			
		8.18	8.21	4.55	257	56.3			
	120	9.44	8.29	4.60	271	59.0	58.7	0.2	
		9.43	8.32	4.62	270	58.4	(3)		
		8.21	8.58	4.77	280	58.8			
	140	10.0	8.90	4.95	288	58.2	58.4	0.2	
		10.06	9.03	5.02	294	58.6	(2)		
	180	11.14	10.56	5.87	355	60.5	60.2	0.4	
		11.27	10.99	6.27	375	59.8	(2)		
	300	12.57	11.71	6.50	456	70.2			
		15.95	15.95	8.85	nd*	nd*			

[*] nd – calorimetric measurement was not done, only dehydration/hydration amount is determined

cations the hydration enthalpy for different forms becomes less exothermic in the sequence Mg, Ca, Na, K at low θ, but converge to similar values at high θ. The K-clinoptilolite completely dehydrates at 300°C to θ=0.00 and completely hydrates to θ=1.00 at the room temperature, while other forms show insufficient dehydration/hydration characters (for dehydration of Na-clinoptilolite θ=0.09; as purified clinoptilolite θ=0.25, Ca-clinoptilolite: θ=0.25 and Mg-clinoptilolite θ=0.27). Zeolite forms with cations of high-hydration energy, such as Mg^{2+} and Ca^{2+} contain significantly more H_2O than those with cations such as K^+ and Na^+ of low-hydration energy, and forms with Mg^{2+} or Ca^{2+} retain their H_2O to higher temperature, as stated by Bish [11].

Values of q for all forms as a function of θ are presented in Fig. 2. As seen in the figure, a lower θ for Na-clinoptilolite (θ=0.09) determines a higher exothermic q value, –469 J g^{-1} comparing with Ca- and Mg-clinoptilolite, –444 and –456 J g^{-1}, even if both of them have θ of about 0.25. In the same figure a fitting procedure to obtain hydration heat for complete dehydration state at θ=0.0 is shown using polynomial equation: $q=k_1+k_2\theta+k_3\theta^2$. The q-values for complete heat of hydration are obtained for K-clinoptilolite, –413, and for Na-clinoptilolite, –524 J g^{-1}, and the hydration molar enthalpy values are respectively, –64.0 and –67.2 kJ mol^{-1}. This fitting procedure is not always applicable for as purified, Ca-, and Mg-clinoptilolite, as calculated values of the complete hydration enthalpy are higher than –80 kJ mol^{-1} due to the lack of experimental data at low θ.

The molar enthalpy values for K- and Na-clinoptilolite in this study compare well with data determined by other authors for K-clinoptilolite, –66.4 kJ mol^{-1} [3] and Na-clinoptilolite, –67.4 [3]; –66.1 [4]; –67.4 kJ mol^{-1} [5].

Evaluation of clinoptilolite as a heat exchanger

To search for zeolites as heat exchangers, it is necessary to take into consideration energetic data for the hydration process as well as structural changes during dehydration. Four cation sites were resolved in the fully hydrated natural clinoptilolite sample

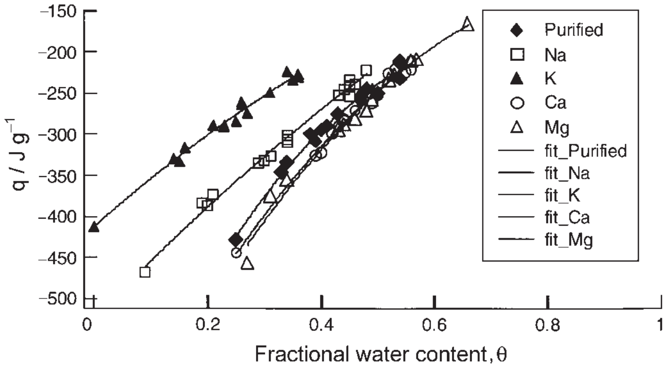

Fig. 2 Heat of hydration (q) *vs*. fractional water content (θ) at the dehydrated state for clinoptilolite samples. Solid lines indicate polynomial fitting for plot-data

[13, 12] namely Na1 within the 10-member ring (coordinated by five H_2O molecules and two O atoms), Ca2 within the 8-member ring (surrounded by five H_2O molecules and three O atoms), K3 at the edge of the 10-member ring (coordinated by three H_2O molecules and six O atoms), and Mg4 in the center of the 10-member ring (coordinated only by six H_2O molecules). Structural studies [12] of the clinoptilolite with 25, 7 and 5-H_2O per 72 O-atoms proposed distinct order of the hydration steps. The model is applicable to our observations on dehydration for various forms of clinoptilolite as follows. Dehydrating the sample to 7 H_2O molecules ($\theta=0.3$ in our study for as purified, Ca-, and Mg-clinoptilolite) results in loss of water molecules and migration of Na1, Ca2, and Mg4 towards K3. The clinoptilolite with 5-H_2O molecules ($\theta=0.2$ in this study for as purified, Ca-, and Mg-clinoptilolite) characterizes by further migration of Na1 and Ca2 to K3 and compression of the channel system. The large cation such as K^+ [13] prevents the structure from collapsing, while the smaller one such as Ca^{2+} is too small to keep the channel shape.

In order to evaluate the zeolite heat exchanger Mizota *et al.* [10] were concerned with the partial dehydration at relatively low temperature, 80–120°C, of synthetic A-type and some natural zeolites. The highest exothermic q-value was founded to be -531 J g^{-1} for Mg-exchanged A zeolite dehydrated at 100°C. Our measurements for all clinoptilolite samples show q-values between -230 and -270 J g^{-1}, which are comparable to that of mordenite sample, -233 J g^{-1} [10]. The q-value for Na-clinoptilolite attains -469 J g^{-1}, when it is dehydrated at 300°C (Table 1, Fig. 2), and shows -524 J g^{-1} for the complete dehydration. The Mg-A type zeolite is thus preferable for a solar-powered system while clinoptilolite will be applicable in the system operated at relatively higher temperature of waste heat sources: Na-clinoptilolite exchanges water most effectively of all the cation-exchanged types in a wide temperature interval, especially between 180 and 300°C, while Mg-clinoptilolite is preferable at higher temperature, namely 300–350°C ($\theta=0.3$–0.2), which supports the structural considerations.

Conclusions

1. The enthalpy of hydration has been determined by means of the water-vapor absorption calorimeter for as purified, K-, Na-, Ca- and Mg-exchanged clinoptilolite. For all samples, both the molar enthalpy of hydration and the heat of hydration become more exothermic when the sample is dehydrated to lower water contents (θ). Polynomial fitting of the q *vs*. θ plots provides complete molar enthalpy of hydration for K-clinoptilolite, -64.0 and Na-clinoptilolite, -67.2 kJ mol^{-1}.
2. Zeolites concerned become more exothermic in hydration with increasing hydration energy of exchanged cation-sequence: K<Na<Ca<Mg, at smaller θ, but converge to similar hydration enthalpy values at larger θ.
3. Na-clinoptilolite will be a suitable heat-exchanger in a wide temperature interval of dehydration (180–300°C), while Mg-clinoptilolite, as well as purified and Ca-clinoptilolite, will have higher q-values if they are dehydrated above 300°C. The natural zeolites thus have prospects for use as heat exchangers.

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