ADSORPTION PROPERTIES OF HIGH-SILICA ZEOLITES FOR HIGH-TEMPERATURE CHEMICAL HEAT PUMPS

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To evaluate their usability as adsorbents in chemical heat pumps for high-temperature use (over 373 K), an accelerated aging test by steam was performed for various zeolites and the adsorption equilibria of selected zeolites were measured. From the high-temperature steaming test it was found that high-silica zeolites like *Na-mordenite*, *USY* (ultrastable Y) and *HY* had higher thermal stability than conventional A- or X-type zeolite. Further, measurements of isotherms of *Na-mordenite* and *USY* showed that they maintained adsorption capacity even at 473 K. Acquired isosters of each zeolite and water were approximated as straight lines in the range from room temperature to 473 K. On their charts, heat transformer (chemical heat pump) cycles that work at high temperatures could be generated. High-silica zeolites like *Na-mordenite* or *USY* are therefore expected to be usable as adsorbents of water for repeating chemical heat pump operations at high temperature, though their total adsorption capacities are smaller than those of A- or X-type zeolites.

Introduction

Research and development of heating and air-conditioning systems using porous adsorbents, such as zeolites (crystalline aluminosilicates) or silica gel with water as the working medium, has been widely studied.^{1-4,6)} Though these adsorption chemical heat pumps (CHPs) are solidgas systems, they are operated similarly to absorption heat pumps in principle, and

there is little fear of volume change of the material used. For most systems proposed, solar energy or waste heat at around 373 K as the highest operation temperature is used, along with *NaX* or *NaA* zeolites as adsorbents.

However, it is also important to make efficient use of heat at higher temperatures. A heat transformer is one of the key means and is a kind of CHP. It takes energy from an intermediate-temperature heat source and upgrades part of this energy to a process at a higher temperature. Under such high-tempera-

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ture conditions, however, conventional adsorbents such as those mentioned above may be low in thermal stability and may show a great decrease in adsorption capacity. Zeolites, for instance, are inherently in metastable phase thermodynamically. When exposed to high-temperature steam during repeated adsorption/desorption operations they may undergo crystal destruction or dealumination, leading to a gradual decrease in adsorption capacity or heat of adsorption. **Figure 1** illustrates the general tendency of adsorption equilibrium between water and typical adsorbents.⁵⁾ A- and X-type zeolites can adsorb water to almost their full adsorption capacity even at small relative pressure, while in the cases of silica gel, charcoal and activated alumina the amount of water adsorbed gradually increases with increasing relative pressure. Zeolites retain some adsorbed water even above 373 K, while silical gel and activated alumina show a sharp decrease in adsorption capacity, suggesting that they are not suitable for high-temperature use. These differences in properties may be attributed to the fact that zeolites have strong acidity associated with quarterly coordinated aluminum. There are various kinds of synthetic zeolites, differing in composition and structure. Generally, it is known that those with a low silica-alumina ratio ($\text{SiO}_2/\text{Al}_2\text{O}_3$), like A- or X-type, have high hydrophilicity but are low in thermal stability, while those with a high silica-alumina ratio, like L- and Y-type or mordenite, are high in thermal stability and high in hydrophobicity. (Here we define high-silica zeolites as those with a silica-alumina ratio of 5 or more.)

In the present study, accelerated aging tests under high-temperature steam were performed to evaluate various zeolites, some promising high-silica zeolites were selected, and adsorption equilibria with water were measured to determine their usability as adsorbents in CHPs for high-temperature use.

1. Experimental

1.1 Material used

High-silica zeolites, whose major properties are shown in **Table 1**, and *NaA*(A-4) and *NaX*(F-9) zeolites were supplied by Tosoh Corp. The silica-alumina ratio of *NaA* and *NaX* is about 2. These samples were press-molded without using a binder, followed by crushing and sieving to provide 12~24 mesh test specimens.

1.2 Aging test under high-temperature steam

A conventional fixed-bed reactor as shown in **Fig. 2** was used for steaming. Each sample of about 1 g was put into a silica tube of inner diameter 10 mm and kept at 473~773 K for 1~6 days in 100% steam atmosphere. Water was supplied at a rate of 3 ml/hour. The degree of relative crystallinity after steaming was determined from the ratio of the integrated peak

Fig. 1. General tendency of adsorption equilibrium between water and typical adsorbents at room temperature (RT) and under 3.2 kPa (vapor pressure at RT), respectively

Table 1. Characteristics of high-silica zeolites

Zeolite	$\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio [—]	Na/Al ratio [—]	Surface area [m^2/g]
<i>NaY</i>	5.5	1.02	700
<i>HY</i>	5.6	0.31	570
<i>USY</i>	6.1	0.01	600
<i>Na-Mordenite</i>	18.9	1.00	360
<i>H-Mordenite</i>	18.7	0.01	360

Fig. 2. Apparatus for steaming

intensity on X-ray diffraction charts measured by a Philips PW1700 system. A thermogravimetric (TG) analysis with a TA3000 system from Mettler Instrument Corp. was also made to determine the full adsorption capacity for water. Each sample, kept in saturated steam of 303 K for two days, was heated to 637 K at a rate of 10 K/min. Here, the amount of water desorbed from a sample was regarded as a

measure of adsorption capacity.

1.3 Measurement of adsorption equilibrium with water

The adsorption equilibrium of *Na-mordenite* and *USY*, which were found to have good properties in the above tests, and *NaA* and *NaX* as references was measured at various temperatures. Figure 3 illustrates the apparatus for TG measurement supplied by Tanaka Scientific Instrument Co. The main measuring section is all included in the constant-temperature air bath (1). About 200 mg of zeolite was previously heated at 623 K for eight hours or more prior to putting it into a quartz basket. After confirming that the sample was at a specified temperature in dry nitrogen gas flow, the stream was changed to expose the sample to wet nitrogen gas (125~300 ml/min) at required constant water vapor pressure (humidity). The vapor pressure was adjusted by changing the water bath temperature (12) stepwise and was verified with the dew-point meter (5), a DP4-D from MBW Elektronik AG, located at the outlet of the measuring section. The maximum controllable vapor pressure was about 85 kPa, depending on the water bath's available temperature. The amount of adsorbed water was determined from changes in voltage detected by a differential transducer (3). The minimal detectable weight change (sensitivity) was 0.1 mg. When the sample temperature had to be set above 373 K, a tape heater (11) was additionally used.

2. Results and Discussion

2.1 Stability of zeolites under high-temperature steam

Table 2 shows changes in the amount of water desorbed from various zeolites before and after steaming. For unsteamed samples, the amount of desorbed water decreases in the following order: *NaY* > *HY* > *NaA* ~ *NaX* > *Na-mordenite* > *USY* > *H-mordenite*. This indicates that the total amount of adsorbable water increases as the silica-alumina ratio becomes lower. On the other hand, among zeolites of the same structure, H-type has a larger adsorption capacity than Na-type.

Comparing the ratio of each type of desorbed water individually, (water desorbed after steaming)/(water desorbed before steaming), *H-mordenite* > *Na-mordenite* > *USY* > *NaA* > *HY* > *NaY* > *NaX* is the order at 473 K for six days, while *Na-mordenite* ~ *USY* > *HY* > *NaY* > *NaA* > *H-mordenite* > *NaX* is the order at 773 K for five days. It appears that the capability of adsorption is reduced more markedly at higher steaming temperature, and that zeolites with higher silica-alumina ratio (high-silica zeolites) show higher thermal stability against steaming.

The time changes in relative crystallinity of *NaX* and *Na-mordenite* are illustrated in Figs. 4 and 5 respectively. The crystallinity of any zeolite decreased with steaming time more or less. This means that

Fig. 3. Apparatus for thermogravimetric measurement

Table 2. Change in amount of desorbed water from various zeolites by steaming

Steaming temp. [K]	—	473	573	673	773
period [days]	0	6	6	5	5
Zeolite	Amount of water desorbed [g/100 g-zeolite]				
<i>NaA</i>	24.8	22.8	22.3	20.3	14.1
<i>NaX</i>	24.2	13.3	11.9	10.7	2.2
<i>NaY</i>	31.9	26.9	21.1	20.8	20.0
<i>HY</i>	26.1	23.5	23.0	21.9	20.9
<i>USY</i>	13.1	12.3	11.8	11.1	10.8
<i>Na-Mordenite</i>	14.1	13.4	12.8	12.3	11.7
<i>H-Mordenite</i>	11.9	11.6	10.6	9.3	5.3

Fig. 4. Change in crystallinity of *NaX* by steaming

steaming causes destruction of the crystal structure, but it is clear that *Na-mordenite* is tougher than *NaX* under high-temperature steam conditions. On the other hand, after being kept in dry air at 773 K for six days, the relative crystallinity values of *NaX* and

Fig. 5. Change in crystallinity of *Na-mordenite* by steaming

Na-mordenite were 90 and 95 percent respectively. This suggests that crystal destruction occurs more rapidly in water vapor. Figures 6 and 7 illustrate the time course of relative amount of desorbed water for *NaX* and *Na-mordenite* (see Table 2). The changes of relative crystallinity almost coincide with those of relative amount of desorbed water, indicating that the decrease in desorption capacity is due mainly to crystal destruction. These findings show that such high-silica zeolites as *Na-mordenite*, *USY* and *HY* are more promising as adsorbents of water for high-temperature operation.

2.2 Adsorption isotherms and isosters

Figures 8, 9 and 10 show the adsorption isotherms of *NaX*, *Na-mordenite* and *USY* at various temperatures. Figure 11 compares the isotherms of *NaX*, *NaA*, *USY* and *Na-mordenite* at 373 K. Water is still absorbed even at 473 K with increasing water vapor pressure, but the water-adsorption capacity of high-silica zeolites is lower than that of *NaA* or *NaX*. Figures 12 and 13 show the amount of water adsorbed on *Na-mordenite* and *USY* plotted against the relative pressure (humidity) in the range from 303 to 473 K. For both zeolites it appears that each point correlated by relative pressure falls roughly on a common curve. Comparing these curves with those in Fig. 1, the manner of adsorption of *Na-mordenite* is ordinary "zeolite type," like *NaX* and *NaA*, while that of *USY* is "activated alumina type" or "silica gel type." The reason was thought to be that *USY* contains some imperfections in crystal structure, formed during its production. This was confirmed by the fact that six-coordinated aluminum was detected by high-resolution solid-state NMR analysis.

From the above isotherms, adsorption isosters of each zeolite and water were obtained and are shown in as Figs. 14 and 15, which are convenient for the study of CHP cycles. Each isoster can be approximated as a straight line. The magnitude of incline of each line corresponds to the isosteric heat of adsorption. In the case of the *Na-mordenite*-water system, the

Fig. 6. Change in amount of desorbed water from *NaX* by steaming

Fig. 7. Change in amount of desorbed water from *Na-mordenite* by steaming

Fig. 8. Adsorption isotherms of water on *NaX*

calculated values increase from 42.3 to 43.5 kJ/mol·H₂O gradually as the adsorbed water varies from 0.12 to 0.03 g/g·ads. Similarly, in the case of the *USY*-water system, they change from 42.6 to 56.3 kJ/mol·H₂O, which correspond to 0.16 and 0.03 g/g·ads.

2.3 Application to chemical heat pump

Simple examples of three single-step heat transformer cycles using the *Na-mordenite*-water system are shown in Fig. 16. (The region above 100 kPa is

Fig. 9. Adsorption isotherms of water on *Na-mordenite*

Fig. 12. Adsorption isotherms of water on *Na-mordenite* correlated by relative pressure

Fig. 10. Adsorption isotherms of water on *USY*

Fig. 13. Adsorption isotherms of water on *USY* correlated by relative pressure

Fig. 11. Adsorption isotherms of water at 373 K

extrapolated.) In principle, each cycle can upgrade heat-source temperature from 373 K to 453 K or 433 K with a 293 K heat sink, or from 423 K to 513 K with a 308 K heat sink, respectively. Figure 17 is the case of *USY*. Similar heat transformer cycles are possible. The thermal energy received from heat source at 373 or 413 K can be enhanced up to 423 or 483 K with heat sink of 293 or 313 K, respectively. Owing to low adsorption capacity, movable water per unit weight of adsorbent during adsorption and desorption could be rather small. Roughly estimating from Figs. 16 and

Fig. 14. Isosters of *Na-mordenite* and water

17 and the adsorption isosters of *NaX*,¹⁾ the amount of movable water of *Na-mordenite* or *USY* is about half that of *NaX*, a typical low-silica zeolite, under similar

Fig. 15. Isosters of USY and water

Fig. 16. Examples of three single-step heat transformer cycles using Na-mordenite and water

conditions. As the heat capacity of a chemical heat pump depends on the amount of water moved, about double the quantity of high-silica adsorbents will be required for obtaining a specified energy output. So, for example, if one adopted a fixed bed of specified particle depth in an adsorber/desorber, the bed area should be about doubled in size if using high-silica zeolites, and accordingly the volume of the adsorber/desorber would be larger than in the case of using low-silica zeolites. Therefore, thermal stability (*i.e.* application to high temperature) and heat capacity of equipment could be a trade-off.

Conclusion

From a high-temperature steaming test, it was found that high-silica zeolites like Na-mordenite, USY

Fig. 17. Examples of two single-step heat transformer cycles using USY and water

and HY had higher thermal stability than conventional A- or X-type zeolite. Further, through measurements of isotherms of Na-mordenite and USY, it was found that they maintained adsorption capacity even at 473 K, and isosters obtained for each zeolite and water were approximated as straight lines in the range from room temperature to 473 K. They can generate heat transformer (chemical heat pump) cycles that work at high temperatures. Consequently, high-silica zeolites like Na-mordenite and USY are promising as adsorbents of water for chemical heat pump systems that operate at high temperatures, though their total adsorption capacities are smaller than those A- or X-type zeolites.

Nomenclature

P	= vapor pressure of water	[kPa]
P_s	= saturated vapor pressure of water	[kPa]
T	= temperature	[K]
HY	= Y-type zeolite with H^+ as cation	
H-mordenite	= mordenite with H^+ as cation	
NaA	= A-type zeolite with Na as cation	
Na-mordenite	= mordenite with Na as cation	
NaX	= X-type zeolite with Na as cation	
NaY	= Y-type zeolite with Na as cation	
USY	= Y-type zeolite with H^+ as cation (Ultrastable Y)	
-X, -Y	= X or Y-type zeolite of same structure as faujasite	

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