

Development of absorbents for solid-absorbent-type heat-pump system

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Microporous materials should be considered as potential absorbents for energy saving. Heat exchange capacities and integral molar hydration enthalpies have been measured as functions of dehydration temperature by means of the adiabatic vapor hydration calorimeter. As the maximum heat exchange capacity reported so far attained to 1MJ/kg for the Mg89-A synthetic zeolite dehydrated at 200°C, chabazite and clinoptilolite, both naturally occurring zeolites, as well as their cation exchanged types has been investigated as the high temperature-type-absorbents. Low temperature-type-absorbents usable at around 60-80°C are desirable however for using waste heat from fuel cell systems, which are promised to be popular as one of the main sources for electricity in near future. Calorimetric measurements show that various microporous materials such as zeolites with larger voids with 12-membered rings, meso-porous silica, etc. will be the prospective absorbents for the low temperature heat sources.

Key words: zeolite, heat pump, mesoporous silica, hydration enthalpy, heat exchange capacity

1. INTRODUCTION

Energy saving is the most serious and global issue to maintain the sustainable environment on the earth surface. Conventional trend of energy conservation has been placed on using high temperature heat sources to improve efficiency of most mechanisms. Although temperatures on the earth surface are kept at around 20°C, enormous amount of waste heat at high temperatures has eventually been exposed from many mechanisms. We can easily point out an example on the cement kiln, the surface temperature of which is around 400°C. We have still been innocent enough to use low temperature heat sources below 100°C except for the direct use of hot water.

Microporous or nanoporous absorbents including zeolites have been considered as key materials to use such low temperature heat wasted widely in the world. Tchernev (1978, 1980) [1, 2] proposed a heat pump system for refrigeration or air-conditioning by using the solar heat as an essential heat source and natural zeolite as the heat absorbent. Despite efforts by many workers since then, the real system appeared on commercial bases has been only the beer cooling system named "Self-cooling Keg" developed by Zeo-Tech Co., Germany

(http://www.zeotech.de/htm/e/e_keg.htm).

Many kinds of zeolites have been investigated in order to develop absorbents for water-vapor with high capability in the heat effect. The ion exchange zeolites with higher valence cations increases water content due to the creation of space for water molecules in the voids[3,4]. Thus, Mg89-A zeolite was found having the heat exchange capacity over 1MJ/kg, when it was dehydrated at 200°C[4]. The fuel cell systems and the micro-gas-turbine systems

will govern the electric source environment for dispersed consumers of moderate to small scale, but the high efficiency of both electric generators however would be attained only when their exhausting heat was used effectively. Although the main focus may be on the temperature range around 60-80°C for fuel cells, various absorbents including those for higher temperatures will be necessary to fit discharged energies from many mechanisms. The present paper deals mainly with several kinds of absorbents of which hydration characters were measured by means of the adiabatic vapor hydration calorimeter[3,4,7].

2. EXPERIMENTAL

2.1 Samples

K-CHA, K-type chabazite, was supplied from Tosoh Co. Ltd. The K-CHA powder samples were treated with various chloride solutions at elevated temperatures for ion-exchange to prepare Mg²⁺, Na⁺, or Ca²⁺-exchanged K-CHA zeolites.

Faujasite(FAU) type zeolites, X and Y types, and the β-zeolite, disordered BEA type, were supplied also from Tosoh Co. Ltd.

Three types of mesoporous silica samples were from Mitsui Chemical Co. Ltd. The pore size distribution

Table 1 Characteristics of mesoporous silica samples

Sample	Specific Surface Area	Water cont.%*	
		RH50%	RH 100%
A	970	20	37
B	1030	2	39
C	870	26	31

*Water content is based on saturated water state of the sample

and the water contents at two humidity levels were shown in the table 1. These characters were adjusted on syntheses by using templates of organic surfactants.

The water content in percent for each sample in the present work is given based on the saturated hydration state, which is attained by keeping a specimen for a sufficient duration on the saturated aqueous solution of ammonium chloride of the relative humidity of 80% at 25°C.

2.2 HYDRATION CALORIMETRY

Hydration heats were measured by means of the adiabatic vapor hydration calorimeter to obtain hydration enthalpies and heat exchange capacities. Details of measurement have already been described[4,6]. About 0.25g of each sample was used for the measurement. Hydration heat q (J) was obtained directly from the calorimetric measurement for hydration. The value is expressed to be negative in general in accordance with the evolving hydration heat. The hydration amount Δm_w (g) was brought from the direct weighing of the sample with the flask before and after the hydration. Thus the integral molar hydration enthalpy (hydration enthalpy hereafter) is calculated as follows:

$$\Delta H_h = \frac{q \times 18.015}{1000 \cdot \Delta m_w} \quad (\text{kJ/mol}) \quad (1).$$

The heat exchange capacity Q is expressed with the sample weight of fully hydrated state, m (g), as:

$$Q = \frac{-q}{m} \quad (\text{kJ/kg}) \quad (2).$$

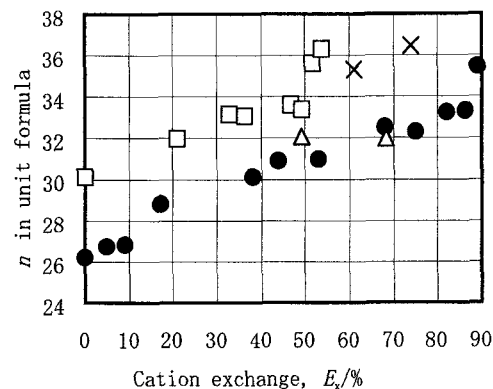
The Q -value shows the specific hydration energy value reservable in the zeolite of 1kg (hydrated basis). The value is recognized to be the direct measure for energy reserve of the absorbent.

3. RESULTS AND DISCUSSIONS

3.1 Cation Exchange

Cation-exchange with smaller size and/or higher valence ions is favorable in general for any heat absorbents with exchangeable cations due to the increase of space for water molecules in voids[4,5]. The water content number n of Mg-exchanged A type, $M^{+}_{12}(H_2O)_n[Al_{12}Si_{12}O_{48}]$, is compared with that of Mg, Na and Ca-exchanged K-CHA, $K_{11}(H_2O)_n[Al_{11}Si_{25}O_{72}]$ (Fig. 1). The minimum water content is 17.3% for K-CHA and the maximum one 21.3% for Ca74-K-CHA. The notation such as Ca74-K-CHA expresses that the 74% of valence charge of K^+ in K-CHA is exchanged with that of Ca^{2+} . The water content does not always increase linearly with increasing amount of Mg exchanged for A-types, but somewhat stepwise as seen in the figure 1. The maximum exchange ratios obtained for K-CHA were 53.8, 68.2 and 73.8% for Mg^{2+} , Na^+ and Ca^{2+} , respectively. The cation size and valence effects mentioned above are also concordant to the water content in the case of CHA.

The Mg-exchange and the DTG(differential thermal



gravimetry) effects are shown in figure 2, and are comparable with those for Mg-Na-A[5,6]. The DTG profiles reveal characteristic effect on dehydration of

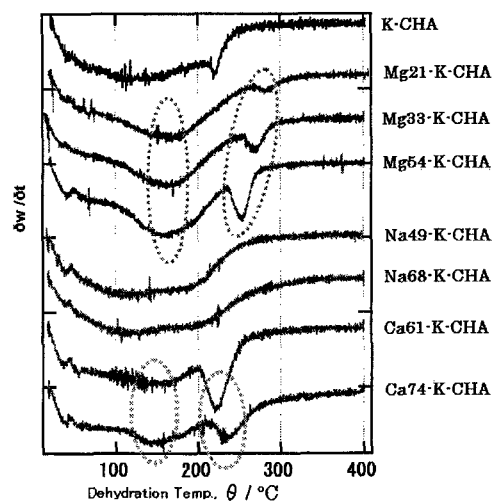


Fig. 2 DTG curves for Mg, Na and Ca-exchanged K-CHA

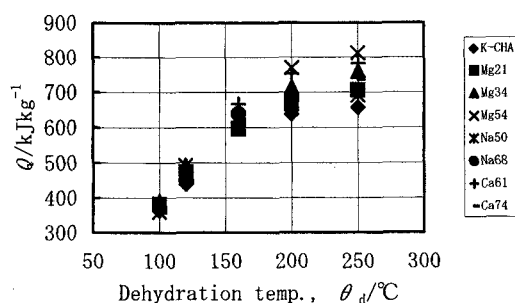


Fig. 3 Hydration enthalpies for variously cation-exchanged CHA

ion-exchanged K-CHA exchanged with cations such as Mg^{2+} , Na^+ and Ca^{2+} -ions (Fig. 2). The DTG pattern of K-CHA shows a wide and shallow area of dehydration between 50 and 250°C, with a sharp peak at 230°C. The peak at 230°C was disappeared for both Na49-K-CHA and Na68-K-CHA. Various Mg-exchanged K-CHA shows broad peak at around 160°C and a relatively sharp peak at the higher temperature range from 250°C to 270°C. The former peak temperature falls down with the increase of exchange amount of Mg^{2+} . Ca61-K-CHA and Ca74-K-CHA show similar patterns with those of Mg-K-CHA, but the higher temperature peaks are at 220-230°C, which are in a little lower temperature range than those of Mg-exchanged K-CHA. This means the stronger Mg^{2+} -water interaction, that is, large hydration energy of magnesium than that of calcium.

3.2 Hydration Calorimetry

High temperature type absorbent: The K-CHA and the cation exchanged types are considered to be the high temperature type useful above 150°C. Hydration enthalpies of these materials range from -64kJ/mol at the dehydration temperature of 100°C to -70kJ/mol at 200°C (Fig. 3). The heat exchange capacity of Mg54-K-CHA exceeds 800kJ/kg, when it is dehydrated at 250°C (Fig. 4).

FAU: The faujasite (FAU) type zeolite, $M^+_x(H_2O)_n[Al_xSi_{192-x}O_{384}]$, have been used widely as catalysts in various chemical industries because of the relatively large window (0.7-0.8nm) with stable structure and the variety of Al/Si-ratio adjustable. Here we measured two types of FAU: zeolite X (Si/Al=1-1.5) and zeolite Y (Si/Al=1.5-3). The adiabatic calorimetry results are shown in the figures 5 and 6 for various types. The large 12-membered ring suggests that it is favorable as the relatively low temperature type zeolite. The Al-poor type Y is more hydrophobic that the type may be useful for the lower temperature type absorbent.

BEA: Zeolite beta corresponds to a disordered BEA, $Na_7(H_2O)_n[Al_7Si_{57}O_{128}]$, which has large 12-membered rings forming straight tunnels in the structure with lower Al-content, which suggests easy hydration by heating or the smaller dehydration energy-value than 55kJ/mol (Fig. 5), in the absolute value, for water in the tunnels. This indicates that the zeolite is usable also in relatively lower dehydration temperatures as seen in the figure 6. We really succeeded in making ice by using 4kg of the β -zeolite as a heat pump absorbent dehydrated at 100°C.

Mesoporous Silica: Three kinds of mesoporous silica samples shown in table 1 were investigated by means of the hydration calorimeter. These materials are composed of only SiO_2 , and have relatively larger pores (meso-pores) in comparison with zeolites. The hydrophilic natures were adjusted by making silanol-radicals on the defects. The hydration enthalpies ranges from -50 to -55kJ/mol for samples

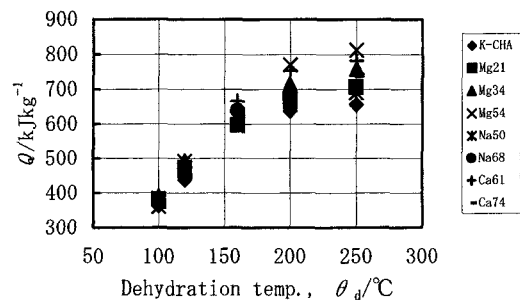


Fig. 4 Heat exchange capacities for variously cation-exchanged CHA

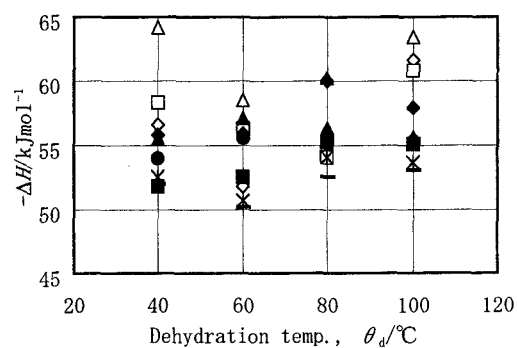


Fig. 5 Hydration enthalpies for FAU and BEA-type zeolites, \diamond Na-X, \square Ca-X, \triangle Mg-X, \blacklozenge NaY, \blacksquare H-Y, \blacktriangle RE-Y, \bullet Y-Y, \times B1, $-$ B2

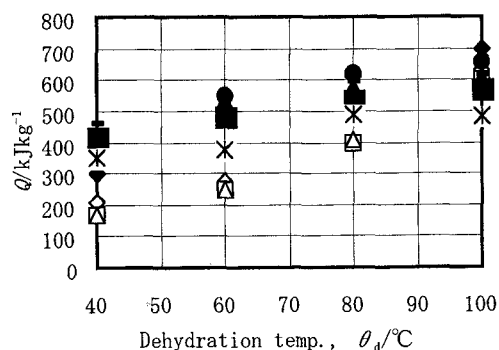


Fig. 6 Heat exchange capacities for various low temperature type zeolite. Data marks are the same as those in figure 5.

dehydrated at room temperatures to 100°C in vacuum. The absolute value of the enthalpy is the smallest of the other materials treated in the present work. Dehydration/hydration cycle for materials were irreversible experimentally, because considerable amount of dehydrated vapor was not absorbed on hydration during the calorimetric experiment. This indicates that the hydration enthalpy values of considerable part of water in the void are the same level of that of liquid water or the vapor pressure is

almost comparable to that of free water. The heat exchange capacities attain 700kJ/kg for the A-sample dehydrated at temperatures around 60 °C. The mesoporous silica may be one of the prospective candidates as the absorbent useful in low temperatures.

Allophane and Imogolite: These materials have been recognized traditionally to be the kinds of clay minerals, because these occur in soil of volcanic origin, and to belong to the alumino-silicate with amorphous structure. According to the recent results of both the high resolution TEM observation and the computer simulation, the structure of allophane is explained as spherical large molecule with windows made of defect structures. Imogolite also belongs to alumino-silicate with nano-tube structure which is similar to that of the carbon-nano-tube. Suzuki et al. (2000)[8] measured the hydration nature in the calorimetry giving that these materials show prospective absorbent useful for the low temperature heat sources far below 100°C. These materials may also be relatively low temperature type absorbents of vapor, but details of the hydration natures are now under investigation.

4. CONCLUSION

Various types of vapor-absorbent have been investigated calorimetrically by means of the adiabatic hydration calorimeter. Various cation-exchanged K-CHA zeolites were examined to correlate the cation-type, the TG-pattern and the calorimetric nature on hydration. Suitable absorbents should be selected and used effectively corresponding to the temperature range of the heat sources. The higher most waste heat temperature is about 400°C for surface temperature of conventional cement kilns, and is not only sufficiently high as dehydration temperatures for any zeolite, but also too high to maintain the structures for many zeolites. The maximum heat exchange capacity obtained for Mg-exchanged K-CHA is 813kJ/kg at the dehydration temperature of 250°C and 770kJ/kg at 200°C for Mg54-K-CHA. The values correspond to almost 80% of the heat exchange capacity of Mg89-A[4], and have special meaning for CHA as the naturally occurring zeolite when they are adoptable for 200°C or higher temperature heat sources. Hydration enthalpy values have intimate correlation with the pore sizes. The larger enthalpy of hydration in absolute value corresponds to the smaller void and results in the higher dehydration temperatures. The cation-species give significant influences for the dehydration temperatures according to the hydration energy of the ion. Omitting the precise influences to cation-species present in zeolites, the enthalpy values of three types of zeolite dehydrated at around 100°C for CHA, FAU and BEA are in ranges of about -65kJ/mol, -56kJ/mol and -54kJ/mol, respectively. The enthalpy values of mesoporous silica are in a range of -50kJ/mol, which is smaller in absolute values than those of zeolites.

Even the fuel cell-system could not attain the sufficient efficiency of about 80% without using the waste heat. To use the low temperature heat sources,

the dehydration enthalpy values of absorbents will need to be smaller in absolute value than 55kJ/mol. Mesoporous silica may therefore be the most prospective candidate thermally, but the toughness or the durability in long term use in steam may be the heavy issue to be cleared up. Many kinds of materials such as clay minerals, oxides, salts, inorganic or organic complex compounds, polymers etc. may be the possible candidates as heat absorbents, when they will be used at low temperatures below 80°C.

ACKNOWLEDGEMENT

The authors would like to express their thanks to Drs. K. Itabashi of Tosoh Co. Ltd. and M. Murakami of Mitsui Chem. Co. Ltd for donating test samples.

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(Received December 24, 2004; Accepted March 22, 2005)