ADSORPTION OF WATER VAPOR ON SEPIOLITE FOR CHEMICAL HEAT PUMPS

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Key Words: Adsorption, Sepiolite, Adsorption Isobar, Adsorption Isoster, Chemical Heat Pump, Heat Transformer, Energy Saving

Introduction

Research and development of heat pump systems using various adsorbents, such as zeolites or silica gel with water as working medium, have been proposed^{2,3,5}. They are operated similarly to absorption heat pumps in principle. Though most of these adsorption chemical heat pumps (CHPs) are usually intended to apply to air-conditioning, some have the potential for extension to use at higher temperatures³.

Sepiolite is a kind of nonporous crystalline adsorbent, and is known as a crystalline magnesium silicate^{1,4,6}, $\text{Si}_{12}\text{Mg}_8\text{O}_{30}(\text{OH})_4(\text{OH}_2)_4 \cdot n\text{H}_2\text{O}$ ($n=6-8$). As much as 300,000 tons per year⁴ is yielded as a natural resource. The internal structural channels give sepiolite large surface areas. Under the condition of relatively low temperature to about 473–523 K, zeolitic (free) water, $n\text{H}_2\text{O}$, adsorbs/desorbs on/from sepiolite reversibly.

In the present paper, the adsorption properties of the sepiolite-water system and its availability for CHP systems are described.

1. Experiments

1.1 Material used

Sepiolite was obtained as “Aid Plus” from Takeda Chemical Industries Ltd. The powdered samples were heated at 473 K for eight hours or more prior to measuring their properties.

1.2 Measurement of adsorption equilibrium

Thermal analyses by TG and DSC were first made by using a TA3000 system from Mettler for confirming sepiolite's basic characteristics such as thermal stability and relative amount of heat of adsorption of zeolitic water. **Figure 1** illustrates the apparatus for adsorption equilibrium measurement, where a quartz spring and a sample basket are suspended in the vessel. The weight change is detected by differential transformer. The water vapor pressure was kept constant during an experiment by controlling the bath temperature and regulator valves. Whole lines are kept

warm by tape heater to avoid the condensation of water. About 500 mg of sepiolite was put into the basket, previously heated to 473 K. After evacuating the air in the system and confirming the sample to be dry enough, *i.e.* having no weight change, by heating at 473 K again, the sample was exposed to steam with required constant vapor pressure. The sample was retained stepwise at from 473 K to about 5 K above the water bath temperature, which had been kept at a specified value between 303 K and 368 K. After each equilibrium was obtained, the next one was made by decreasing or increasing the sample temperature. It took about 60 min for each measurement. The adsorption isobars are developed through those procedures.

2. Results and Discussions

2.1 Adsorption isobars and isosters

Figure 2 shows the schematic DSC and TG chart for the sepiolite used. It was confirmed that the amount of released water till around 473 K almost agreed with the calculated value of the zeolitic water (about 11 weight percent when $n=8$), and its could be completely desorbed under dry environment at 473 K. The second endothermic peak around 573 K corresponds to the

Fig. 1. Apparatus for thermogravimetric measurement for adsorption of water on sepiolite

Received December 19, 1991. Correspondence concerning this article should be addressed to I. Fujiwara.

Fig. 2. Schematic chart of DSC and TG of sepiolite (10 K/min.)

Fig. 3. Adsorption isobars of water on sepiolite

release of crystal water^{4,6}). Therefore, it is concluded that when sepiolite adsorbs or desorbs water below about 523 K, only zeolitic water is concerned.

Adsorption isobars at various water vapor pressures are shown in Fig. 3, where the ordinate is the amount of water adsorbed on dry adsorbent (*i.e.* sepiolite) based at 473 K. From the above isobars, the adsorption isosters shown in Fig. 4 were obtained according to the same procedures as described in the previous report³). The calculated isosteric heat of adsorption changes from 50.6 to 42.6 kJ/mol·H₂O as the adsorbed water increases from 10 to 100 mg/g·ads. No expansion or contraction of sepiolite itself by adsorbing or desorbing water was observed during the experiments.

2.2 Application to chemical heat pump

Using the above isosters, it is possible to construct some CHP cycles with various temperature conditions. Especially, heat transformer (a kind of CHP) cycles which work at high temperatures are available. Simple examples of two single-step cycles are shown in Fig. 5. In each cycle, the thermal energy received from the heat source at 385 K can be upgraded to 465 or 446 K with a heat sink of 306 or 313 K, respectively, which

Fig. 4. Adsorption isosters of water on sepiolite

Fig. 5. Examples of two single-step heat transformer (CHP) cycles using sepiolite and water

are near environmental temperatures. Although movable water per a sepiolite's weight in such high-temperature CHP cycles becomes rather small owing to its low adsorption capacity, sepiolite has some advantages for use as a material for CHP systems⁴); They 1) need no binders for forming various shapes such as particles or pellets (*i.e.* there is no decrease of energy density); 2) pose no fear of cracking during repeated sorption operation, unlike silica gel; and 3) are stable at high temperature. Sepiolite can thus be considered as a candidate water adsorbent for a chemical heat pump system which can operate at high temperatures.

Acknowledgement

The authors wish to thank Mr. S. Matsuyama, who was a student of Tokyo Science University, for his contribution to the experimental work.

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