

## Water Sorption of $\text{CaCl}_2$ -Containing Materials as Heat Storage Media

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(Received December 2, 2003; CL-031171)

The water sorption behavior of  $\text{CaCl}_2$ -containing materials as heat transfer media was studied. Amount of the water sorption on  $\text{CaCl}_2$ -containing materials was higher than those on the zeolites at the higher humidity region. Heat storage capacity of 33 wt %  $\text{CaCl}_2$ /FSM16 ( $1200 \text{ MJ m}^{-3}$ ) was 3.5 times as high as Na form Y-zeolite at 18.7 Torr of water vapor.

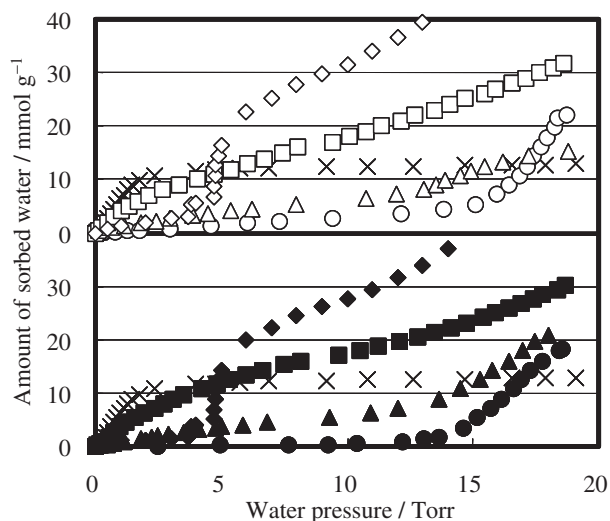
In recent years, the technologies of chemical heat pump and chemical heat storage are widely studied for the reduction of energy consumption and  $\text{CO}_2$  emission. If unutilized energy such as industrial waste heat (e.g. the heat around 473 K from the disposal furnaces) can be transferred and utilized at an urban residence area, it will contribute to solve these problems. Thus, the heat storage material suitable for the heat transfer system should be developed. In view of environmental impact and the temperature of heat source, water sorption on solid material is a promising reaction among the various chemical heat pump systems and the chemical heat storage materials.<sup>1-3</sup> The reaction heat of water vapor occlusion into metal halides are generally higher than those of water adsorption on the typical adsorbent such as zeolites. However, hydrated metal halides may cause the corrosion of the reaction vessel, thus metal halides cannot be used for this purpose without some modification. Recently, the hydration and the dehydration reactions of metal halide with porous matrix have been reported for the chemical heat pump.<sup>4-8</sup> In this work,  $\text{CaCl}_2$  was bared on high surface area materials, and the water sorption and desorption behavior were studied. The possibility of these materials as heat storage media was discussed.

Two types of samples,  $\text{CaCl}_2$ -containing materials and conventional zeolite (Na form Y-zeolite (Na-Y;  $670 \text{ m}^2 \text{ g}^{-1}$ ; JRC-Y-4.8) and molecular sieves 5A (MS-5A;  $406 \text{ m}^2 \text{ g}^{-1}$ )) as reference, were used as water sorbent. For  $\text{CaCl}_2$ -containing materials, active carbon (AC;  $1265 \text{ m}^2 \text{ g}^{-1}$ ) and mesoporous silica (FSM16;  $1055 \text{ m}^2 \text{ g}^{-1}$ )<sup>9</sup> were used as support materials. Support materials were impregnated with  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  aqueous solution, evaporated at 343 K, dried at 383 K, and finally calcined at 823 K in He flow for 3 h. In case of FSM16, it has been reported that water treatment affects the water sorption behavior.<sup>10</sup> Here, water-treated FSM16 (FSM16-w) without  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  was also prepared by the same procedure as  $\text{CaCl}_2$ /FSM16.

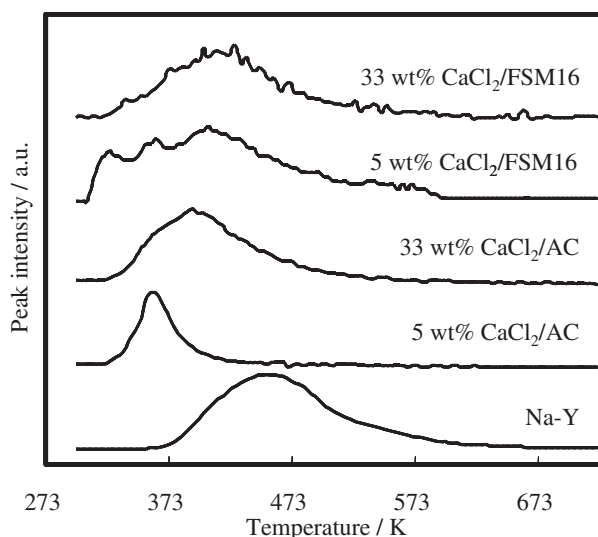
Water sorption isotherms were measured between 0 and 19 Torr at 298 K after evacuation at 723 K as the pretreatment. The measurements were carried out by OMNISORP 100CX (Beckman Coulter). Amount of sorbed water was calculated from the pressure change. When the pressure change in 30 sec becomes smaller than 0.015 Torr, the sorption was regarded to be in equilibrium. The water desorption temperature was characterized by TPD (Temperature Programmed Desorption) method.

The sample was evacuated at 723 K for 1 h, and cooled down to the room temperature. After water pre-sorption at 5 Torr for 30 min, the excess water was flushed out by  $\text{N}_2$  flow. Water TPD was carried out in  $\text{N}_2$  flow with  $5 \text{ K min}^{-1}$  of temperature increasing rate from the room temperature to 723 K. The integral heat of water sorption at 18.7 Torr of samples was measured at 298 K for 3 h, after evacuation at 723 K. The measurements were carried out by MMC-5111 (Tokyo Riko Co. Ltd.).

The water sorption isotherms of  $\text{CaCl}_2$ -containing materials and Na-Y are shown in Figure 1, together with calculated isotherm (described as “-calcd” in the caption) assuming that water is sorbed independently on the support and  $\text{CaCl}_2$ . Amount of water sorbed on Na-Y was sharply increased below 2 Torr, and reached to  $12.8 \text{ mmol g}^{-1}$  at 18.7 Torr. Amount of water sorbed on AC was almost zero below 12 Torr and that was sharply increased at above 12 Torr due to the capillary condensation into the pore of AC, and reached to  $18.4 \text{ mmol g}^{-1}$  at 18.7 Torr. By the  $\text{CaCl}_2$  addition to AC, amount of water sorption was increased with the amount of added  $\text{CaCl}_2$  and reached to  $30.0 \text{ mmol g}^{-1}$  for 33 wt %  $\text{CaCl}_2$ /AC at 18.7 Torr. In case of FSM16, amount of water sorption was increased almost linearly with water pressure up to 15 Torr, and the slope increased more above 15 Torr due to the capillary condensation into the pore of FSM16. Amount of the water sorption on 33 wt %  $\text{CaCl}_2$ /FSM16 was quite high ( $31.9 \text{ mmol g}^{-1}$ ) at 18.7 Torr. It is thought that hydration and deliquescence of dispersed  $\text{CaCl}_2$  on the sur-



**Figure 1.** Water sorption isotherms of  $\text{CaCl}_2$ -containing materials and Na-Y. (●) AC, (▲) 5 wt %  $\text{CaCl}_2$ /AC, (■) 33 wt %  $\text{CaCl}_2$ /AC, (◆) 33 wt %  $\text{CaCl}_2$ /AC-calcd, (○) FSM16, (△) 5 wt %  $\text{CaCl}_2$ /FSM16, (□) 33 wt %  $\text{CaCl}_2$ /FSM16, (◇) 33 wt %  $\text{CaCl}_2$ /FSM16-calcd, and (×) Na-Y.



**Figure 2.** H<sub>2</sub>O-TPD profiles of CaCl<sub>2</sub>-containing materials and Na-Y.

face of support material is the cause of the increase of water sorption amount. For each 33 wt % CaCl<sub>2</sub>-added samples, observed isotherm is not same as the calculated isotherm. This indicates that the behavior of hydration and deliquescence of CaCl<sub>2</sub> in these samples is different from the authentic CaCl<sub>2</sub>. Deliquescence of CaCl<sub>2</sub> was detected visibly for CaCl<sub>2</sub>/AC after water sorption measurement; however, that was not detected visibly for CaCl<sub>2</sub>/FSM16.

The water desorption behavior of CaCl<sub>2</sub>-containing materials and Na-Y are shown in Figure 2. The temperature at peak top for CaCl<sub>2</sub> containing materials (391 K for 33 wt % CaCl<sub>2</sub>/AC and 425 K for 33 wt % CaCl<sub>2</sub>/FSM16) were lower than that for Na-Y (454 K), therefore these CaCl<sub>2</sub>-containing materials were more suitable for the use of waste heat (at 473 K) than Na-Y. For CaCl<sub>2</sub>-containing materials, 80–95 % of water was desorbed below 473 K; however, Na-Y was able to desorb only 60 % of water at this temperature. In case of AC, water desorption by this TPD measurement was negligibly small and the amount of sorbed water at 5 Torr was very low (Figure 1). Thus, the water desorption from CaCl<sub>2</sub>/AC is considered to be the dehydration of hydrated CaCl<sub>2</sub> (on AC). The peak top temperature for CaCl<sub>2</sub>/AC was decreased with the decrease of CaCl<sub>2</sub> loading (391 K for 33 wt % sample and 360 K for 5 wt % sample). This indicates that for low CaCl<sub>2</sub>-loaded sample (5 wt % CaCl<sub>2</sub>/AC), CaCl<sub>2</sub> is well dispersed on the AC surface and that the hydration becomes weak due to the small cluster of CaCl<sub>2</sub>.

The heat storage capacity of CaCl<sub>2</sub>-containing materials and zeolites are summarized in Table 1, together with that for authentic CaCl<sub>2</sub>. Here, the heat storage capacity is defined as the

**Table 1.** Integrated heat of water sorption for CaCl<sub>2</sub>-containing materials and zeolites at 298 K, 18.7 Torr

Sample	Heat storage capacity	
	/ kJ g <sup>-1</sup>	/ MJ m <sup>-3</sup>
Na-Y	1.08	345
MS-5A	0.81	456
AC	1.15	654
5 wt % CaCl <sub>2</sub> /AC	1.11	663
33 wt % CaCl <sub>2</sub> /AC	2.47	2110
FSM16	1.82	731
FSM16-w	1.25	431
5 wt % CaCl <sub>2</sub> /FSM16	0.91	361
33 wt % CaCl <sub>2</sub> /FSM16	2.10	1200
CaCl <sub>2</sub> <sup>a</sup>	7.64	16400

<sup>a</sup> Density of CaCl<sub>2</sub> assumed as 2.15 g cm<sup>-3</sup>

integral heat of water sorption at 18.7 Torr. The heat storage capacity of AC (654 MJ m<sup>-3</sup>) and FSM16-w (431 MJ m<sup>-3</sup>) were higher than that of Na-Y (345 MJ m<sup>-3</sup>). By addition of 33 wt % of CaCl<sub>2</sub> to AC and FSM16, the heat storage capacity was increased to 2110 MJ m<sup>-3</sup> and 1200 MJ m<sup>-3</sup>, respectively. Thus, CaCl<sub>2</sub> addition is effective on any high surface area materials for increase of the heat storage capacity.

It is concluded that CaCl<sub>2</sub>-containing materials are more suitable for chemical heat storage media with water sorption than the zeolite studied here. The sample stability against multiple operation of water sorption–desorption cycle under practical condition should be studied for the practical use in the future.

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