THERMOCHEMICAL STORAGE OF LOW TEMPERATURE HEAT BY ZEOLITES; SAPO'S AND IMPREGNATED ACTIVE CARBON

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Abstract

The adsorption behaviour and storage properties of common and new microporous materials such as low silica X zeolites (LSX), SAPO and with $CaCl_2$ impregnated active carbon were investigated by means of TG/DSC, the measurements of adsorption isotherms and using a lab-scaled storages of 1.5 L volume. Tests of common zeolites and mesoporous materials (silica gel) in a lab-scaled storages showed that application of low temperature heat or solar heat for charging of those storage materials require new microporous materials which do not need a high charging temperature but have still a certain energy density and temperature lift. The present results show that special microporous silicoaluminophosphates and an impregnated active carbon are candidates for those applications with storage properties between the zeolites and the mesoporous materials.

Introduction

Increasing interest in the application of the thermochemical storage or adsorption heat pumps for utilization of industrial waste heat and solar heat stimulated several experimental and theoretical studies on short and long term heat storage (Tchernev, 2001, Mittelbach et al., 2000, Hauer et al.,1999) as well as heat driven heat pumps (Meunier,, 1986, Dieng, and Wang, 2001). However, less attention was paid to the properties of the porous materials such as common zeolites, silica gels or aluminosilicates which are mainly designed for catalysis and adsorption technologies but are not optimized for thermochemical heat storage applications.

In recent years some new storage materials were suggested and characterized such as the so called composite adsorbens (Levitskij et al., 1996, Jänchen et al., 2000) which have considerable high storage densities, a low charging temperature but their temperature lift is limited. Very recently (Jänchen, et al., 2002) we suggested the introduction of the $AlPO_4$'s for heat storage and heat transformation purposes. $AlPO_4$'s are zeolites-like microporous materials, which are mildly hydrophilic and may have the potential to close the gap between silica gels and zeolites in respect to the optimization of the adsorption strength of the water and the ability to be desorbed at mild conditions. Those microporous aluminophosphates can be modified by incorporation of some silicon into the lattice to tailor their adsorption properties with respect to the water adsorption/desorption properties.

Furthermore, we included into our studies microporous activated carbons beside meso- and macroporous supports as hosts for the hygroscopic salt hydrates ($CaCl_2$) to get informations about the influence of the pore size on the hydratation/dehydratation properties of the salt. The aim of this paper is, therefore, to give a progress report (since the 3rd workshop of the Annex 17 in Tokyo) about the results of the characterization of those new thermochemical storage systems. Both a special microporous silicoaluminophosphate and an impregnated activated carbon were subject of our extended investigations.

Experimental section

The samples used for the present study were new commercial low-silica zeolites, LiLSX and NaLSX (Tricat GmbH, Bitterfeld, Germany), own synthesis products of $AlPO_4$-5, $AlPO_4$-17, $AlPO_4$-18 and SAPO-34 as well as the with $CaCl_2$ impregnated silica gel, attapulgite and activated carbon, respectively, with different pore size distributions. The SAPO for the measurements on the kg-scale was a specially designed pelleted product for this purpose.

The micro-, meso- and macroporous materials (microporous active carbon, two types of silica gel with mesopores (1) and macropores (2) and attapulgite with small macropores or big mesopores) were impregnated (in all cases) with 30% $CaCl_2$. The salt was mainly accommodated in the pores. For the TG-experiments a LiNaX zeolite was used which was obtained by a Li-ion exchange of the Na-form of a commercial available X-zeolite (from CWK, Bad Köstritz, Germany).
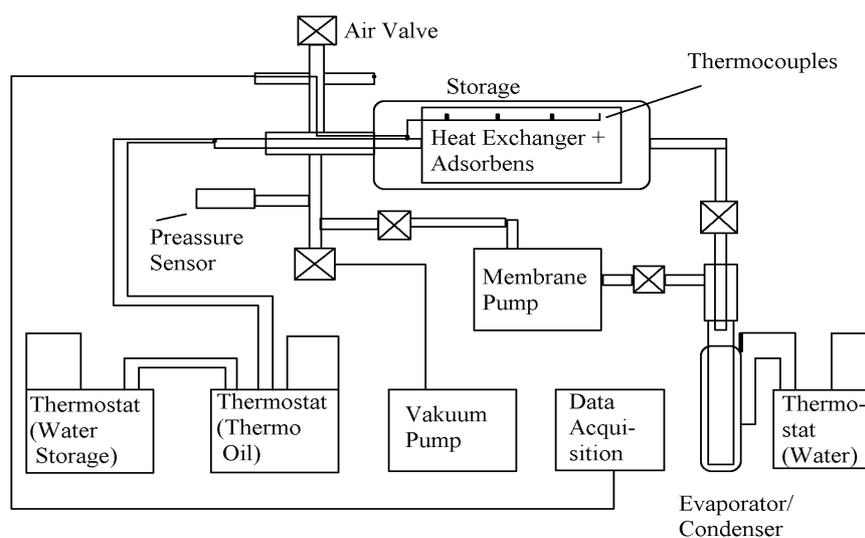
Figure 1   **Scheme of the 1.5 L thermochemical storage unit for 1 kg material.**
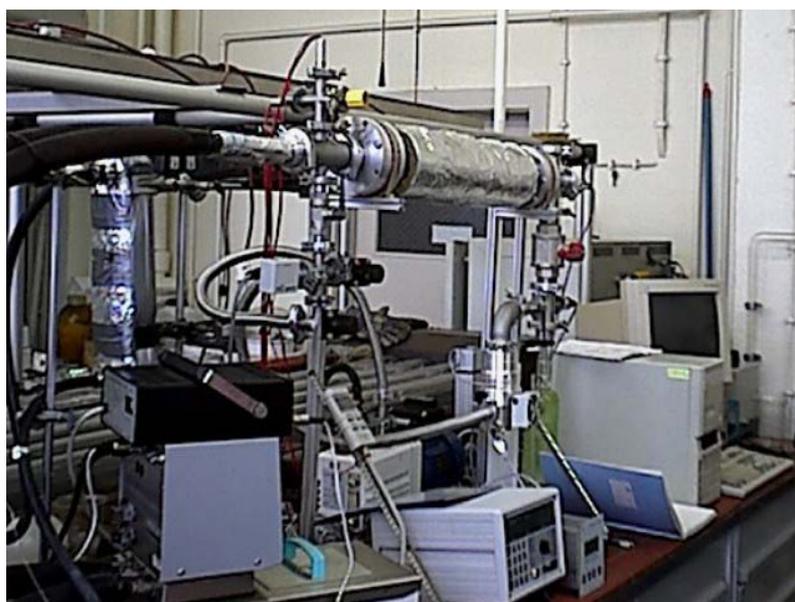
Figure 2   **Picture of the 1.5 L thermochemical storage unit for 1 kg material, the arrangement of the unit parts corresponds with the scheme in Figure 1.**

Thermogravimetry (TG), differential scanning calorimetry (DSC) and the measurements of water isotherms were applied to compare the adsorption- and desorption properties of the different kinds of porous storage materials. The TG and DSC measurements were performed on a SETARAM TG-DSC 111 equipment with a heating rate of 5 K/min to a temperature of 673 K in a nitrogen stream of 1 L/h. Prior to the desorption experiment the water was adsorbed "off-line" in a desiccator at a relative pressure of 0.3 at room temperature overnight. Then the samples were transferred into the apparatus. The sorption isotherms were measured gravimetrically at 313 K with a home-made McBain quartz spring balance equipped with MKS Baratron pressure sensors (10^{-3}-1000 mbar). The sensitivity of the quartz spring amounts to 4 mg/mm. The expansion of the spring was measured using a kathetometer with a resolution of 0.01 mm. Before application, the samples (150-200 mg) were calcined in high vacuum ($<10^{-5}$ mbar) at 573 K (zeolitic materials) and 523 K (impregnated material) for 2-3 h.

A storage unit with a volume of about 1.5 L was used for the tests on a larger scale (see Figures 1 and 2). It consists of an adsorber (storage, center upper part in Figures 1 and 2) filled with approximately 1 kg of storage material and equipped with a heat exchanger. The heat exchanger of the storage is connected to an thermostat/pump for heat transfer in charging and discharging mode. The storage is connected with an evaporator (for discharging), a condenser with chiller for charging (desorption of water) and a vacuum pump. A diaphragm vacuum pump between the exit of the storage on top the condenser and the entry on bottom support the water vapour stream storage-condenser during charging. The set-up is equipped with pressure sensors, thermocouples and data acquisition. The heat during discharging of the thermochemical storage was transferred via heat exchanger into a water reservoir of 7 L volume. The maximum charging temperature amounts to 473 K. The minimum temperature in the condenser was 274 K. For discharging of the storage the temperature of the evaporator was kept at about 293 K.

Results and Discussion

Investigation of the adsorption properties of the microporous and mesoporous storage materials

In the following part the results of the physico-chemical characterization of the adsorption behaviour of water in microporous aluminophosphates are discussed and compared with zeolites and mesoporous materials.
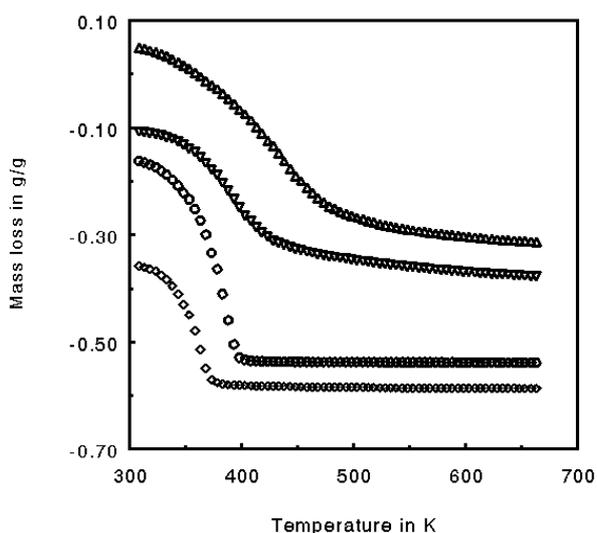
Figure 3   **Mass loss in a nitrogen flow between 300 and 670 K for LiNaX, SAPO-34, AlPO$_4$-18 and AlPO$_4$-17 (from top to bottom).**

Figure 3 shows the TG profiles for the desorption of water from LiNaX, as an example of a common zeolite with a high storage density and a high temperature lift, and the microporous aluminophosphates AlPO$_4$-17, AlPO$_4$-18 and the SAPO-34. As can be seen, at about 400 K the main part of the water is removed from the AlPO$_4$ and SAPO samples different to the zeolite. The first derivative of the curves shows that the main part of the water from AlPO$_4$-5 is desorbed at about 370 K, from AlPO$_4$-17 at 380 K and from AlPO$_4$-18 at about 390 K. Incorporation of Si into the AlPO$_4$-structure increases the maximum of the desorption curve to about 400 K (SAPO-34) and the shape of the curve becomes more similar to the X zeolite. For the LiNaX the main peak is shifted to about 450 K and it takes another 200 K to achieve complete desorption. So, step by step modification of the molecular sieves as storage material seams to be possible to optimize their desorption properties with respect to the temperature level available for the charging of the storage.

The position of the water isotherms of the low silica X zeolites on one hand and the SAPO-34 on the other hand support the findings given above (see Figure 4). The isotherms of LiLSX and NaLSX are, compared to the SAPO, shifted by two orders of magnitude towards lower equilibrium pressure. Also the shape of the isotherm, which rise more steeply between 3-5 mbar due to a hydratation of the SAPO (see Jänchen et al., 1993), differs from the common zeolites. Accordingly, the differential molar heats of sorption decreases from LiLSX (100-70 kJ/mol) to SAPO-34 (90-65 kJ/mol) and finally to the CaCl$_2$/attapulgite system (70-50 kJ/mol water) significantly.

Further, Figure 4 compares the isotherms of the zeolite-like materials with those of the impregnated active carbon and the attapulgite. Whereas the isotherm of the hydratation of the CaCl$_2$ in the microporous active carbon is comparable with the hydratation of the SAPO, the CaCl$_2$/attapulgite isotherm is again shifted towards higher equilibrium pressure in accordance with the decreasing heat of sorption. Obviously, there is an influence of the pore architecture on the hydatation process of the hygroscopic salt. To discuss this phenomenon in more detail Figure 5 and Table 1 summarize the results of the TG/DSC measurements for the impregnated storage materials with different pore size distributions.
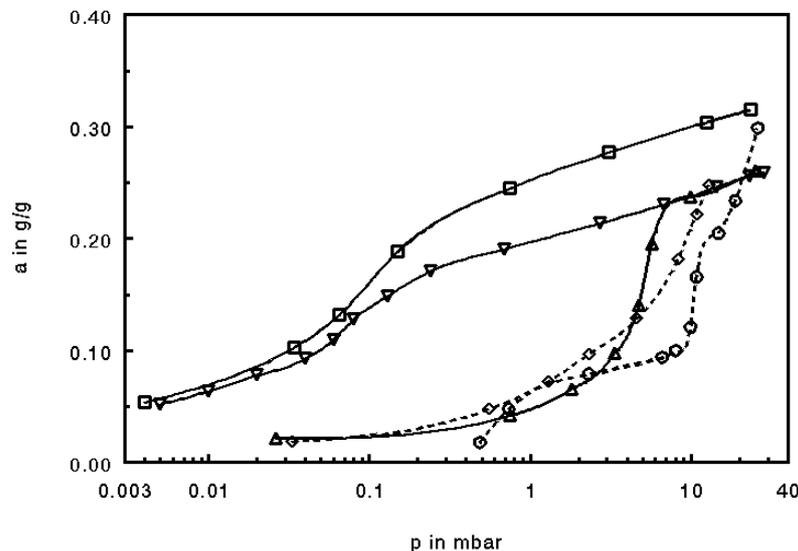
Figure 4 **Adsorption isotherms of water at 313 K for LiLSX, NaLSX and SAPO-34 (molecular sieves, solid lines) as well as active carbon/CaCl$_2$ and the CaCl$_2$ impregnated attapulgite (dashed lines), from left to right.**
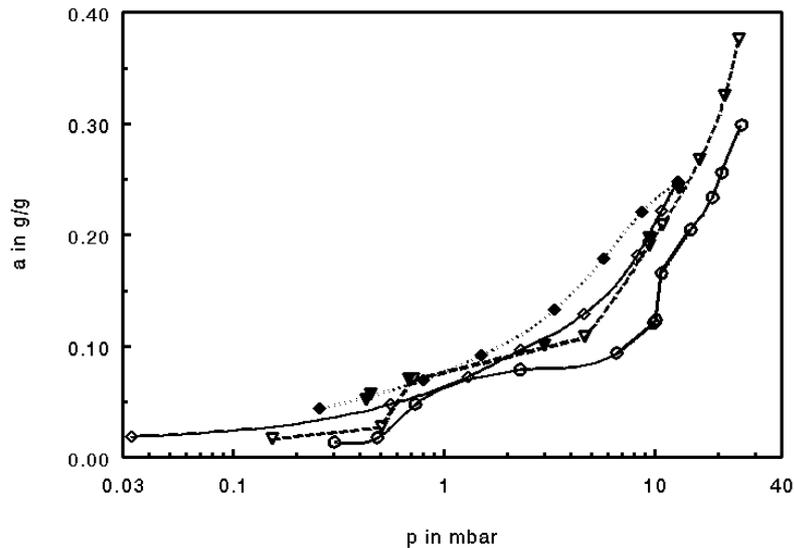
Figure 5 **Adsorption isotherms of water at 313 K for active carbon/CaCl$_2$ (filled points desorption), silica gel 1/CaCl$_2$ and the CaCl$_2$ impregnated attapulgite (from left to right),.**

As can be seen the shape and position of the isotherms, the integral molar heats of sorption (hydratation) and the storage densities are influenced by the pore architecture of the hosting material. Whereas in the meso- and macroporous supports the pores are big enough (20-60 nm in diameter) to form one after the other the dihydrate (first step at 0.1 g/g in Figure 5), the tetrahydrate (step at 0.2 g/g) and at higher equilibrium pressures the hexahydrate (see Jänchen et al., 2000). However, the isotherm of the active carbon do not show a stepwise course in accordance with XRD measurements and has a hysteresis loop different to the other materials (for a <0.1 g/g). In the XRD no diffraction pattern for any hydrate can be observed different to the other materials with bigger pores. Obviously, no defined hydrates can be created in the small micropores with a diameter of <4 nm.

Table 1 **Results of the TG/DSC measurements: sorbed amounts of water, integral molar heats of sorption of the water and energy densities for impregnated materials with different pore size distribution**

| Material	Kind of porosity of the host	Sorbed amount in g/g	Q$_{int}$ in kJ/mol	ρ$_Q$ in Wh/g
Active carbon/ CaCl$_2$	microporous	0.385	53.4	0.317
Silica gel 1/CaCl$_2$	mesoporous	0.395	50.6	0.299
Attapulgite/ CaCl$_2$	small macropores	0.395	48.7	0.297
Silica gel 2/ CaCl$_2$	macroporous	0.490	50.7	0.382

Investigation of the micro- and mesoporous materials in the lab-scaled storage

Table 2 and Figure 6 show the results for selected micro- and mesoporous storage materials obtained by measurements with the lab-scaled storage. As can be seen the new low silica X-type zeolite (in the Li- and Na form) gives the highest values for the adsorbed amounts of water, the storage densities and the maximum temperature which could be achieved in the storage (see also Figure 6). In the case of the SAPO, the impregnated microporous active carbon and the mesoporous materials (common silica gel and an impregnated attapulgite) the desorption (charging) temperature can be lower as for LSX but the

maximum temperature in the storage in discharging mode is lower as well. As it is known those mesoporous materials are suitable for application of solar heat (Mittelbach et al. 2000) but with a limited temperature lift. However, Figure 6 shows that those limits are less pronounced for the SAPO. The temperature profile of the latter is between the zeolites and the mesoporous materials. Next to the SAPO follows the impregnated active carbon followed by the silica gel at the lowest temperature. The flat course of the temperature profile of the SAPO from the beginning at a medium temperature in the storage is in accordance with the thermodynamic behaviour discussed above.

Table 2 **Desorption temperatures, adsorbed amounts of adsorbed water, energy densities and maximum temperature in the storage for zeolites, SAPO, pure silica gel and impregnated materials**

Material	Desorption temperature in K	(Ad)sorbed amount water in kg/kg	Energy density in Wh/kg	Max. temperature in the storage in K
LiLSX	473	0.24	225	380
NaLSX	473	0.23	185	370
SAPO	373, 423	0.23	154	345
Active carb./CaCl$_2$	393	0.223	161	350
Attapulgite/CaCl$_2$	393	0.18	177	336
Silica gel	393	0.18	123	335
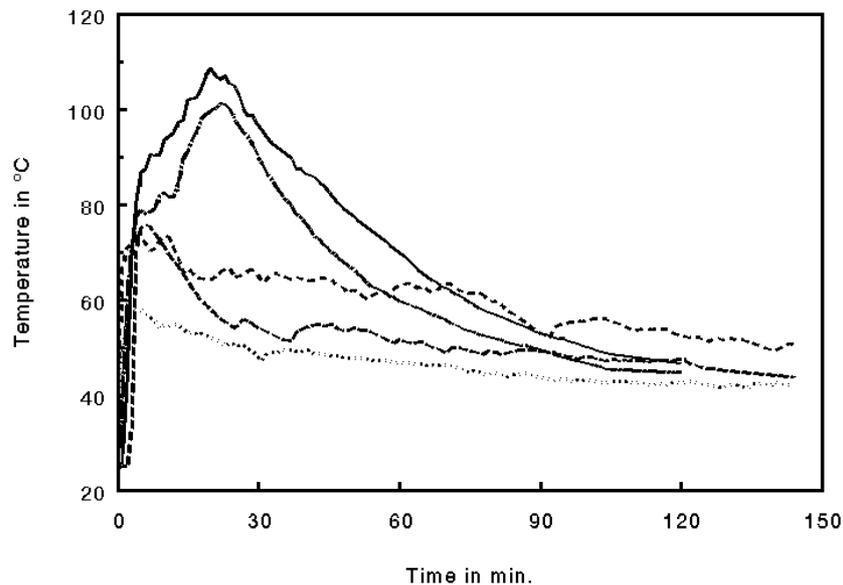
Figure 6 **Temperature profiles of different storage materials inside the storage vs. time: LiLSX, NaLSX, SAPO, active carbon/CaCl$_2$ and pure silica gel (from top to bottom).**

Conclusions

It was shown that zeolites of different types show a higher temperature lift during discharging of a thermochemical storage. However, the charging temperature of those materials exceed 473 K which is practically not easy to achieve by common solar collectors. Silica gel or impregnated mesoporous materials show a high storage density and need a lower charging temperature, about 393 K, but the

temperature lift is low. The impregnation of porous hosts with different pore architecture results in different storage properties.

Water from microporous aluminophosphates and silicoaluminophosphates can be desorbed almost completely at temperatures <420 K. The storage density is comparable with zeolites and the differential molar heats of adsorption of water are between those of zeolites and impregnated storage materials. The results of the measurements in the lab-scaled storage show that the temperature lift is in between as well. Thus, it can be expected that microporous SAPO's and AlPO$_4$'s have the potential of zeolite like storage properties, however, with a lower charging temperature and, hence, meet the conditions for solar application.

Acknowledgement

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