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Calorimetric investigation on zeolites, $AlPO_4$'s and $CaCl_2$ impregnated attapulgite for thermochemical storage of heat

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Abstract

The sorption properties of water in potential thermochemical storage materials such as low silica X zeolites, microporous aluminophosphates, SAPO-34 and $CaCl_2$ accommodated in the pores of attapulgite were investigated by thermogravimetry, differential scanning calorimetry, sorption isotherms and microcalorimetry.

Because of decreasing differential molar heats of sorption from LiLSX (100–70 kJ/mol) to SAPO-34 (90–65 kJ/mol) and to supported $CaCl_2$ (70–50 kJ/mol) the isotherms are shifted towards higher equilibrium pressure by about three orders of magnitude. The energy densities at 313 K and up to 20 mbar vapor pressure decrease in the same order from 1184 to 997 and 871 kJ/kg adsorbens. The average temperatures for the desorption of the water decreases as well from >450 to <400 K which classifies the silicoaluminophosphate between the common zeolites and the salt hydrates with regard to the properties as thermochemical storage material.

Keywords: Zeolite; SAPO; Salt hydrate; Water adsorption; Microcalorimetry; Thermochemical storage

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1. Introduction

Zeolites and zeolite-like materials such as $AlPO_4$- and SAPO molecular sieves as well as mesoporous materials such as aluminosilicates and silica gels are well known and partially since decades well established in catalysis and adsorption technologies. In the last two decades however, because of environmental reasons, zeolites and silica gels became subject of increasing interest for thermochemical storage of heat or heat pump applications [1–6]. Those materials with water as working agent for instance allow utilization of low temperature heat (like industrial waste heat and solar heat) for loss free storage or transportation of heat and heat transformation without refrigerants contributing to the global warming.

Mesoporous materials especially impregnated with hygroscopic salt hydrates [5] show a low charging temperature (<400 K for the desorption of the water) and high energy densities (high specific integral heats of adsorption) but have a very limited temperature lift. Zeolites on the other hand show a much higher temperature lift and a medium energy density but the charging temperature is high (>470 K). To close the gap between the properties of the zeolites and silica gel as storage material, we suggested in Ref. [7] to take in to account the mildly hydrophilic microporous aluminophosphates for thermochemical storage and heat pump applications. The $AlPO_4$ molecular sieves show a lower charging temperature, a medium storage density and a medium temperature lift. As well known, the incorporation of silicon into the AlPO structures modifies the adsorption properties of the so created SAPO molecular sieves and a "fine tuning" of the storage properties of those potential storage materials seems to be possible via the lattice chemistry.

The aim of this paper is, therefore, to integrate a SAPO molecular sieve into a comparison of the water adsorption properties of new low silica zeolites, microporous $AlPO_4$

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molecular sieve and an impregnated mesoporous aluminosilicate with regard to the thermochemical storage of low temperature heat. The results of the investigation of those materials in a lab-scaled thermochemical storage will be discussed elsewhere [8].

2. Experimental

2.1. Methods

The adsorption properties of water and the energy densities (integral heats of the water adsorption related to the amount of adsorbens) of different kinds of storage materials were investigated by means of isotherm measurements, microcalorimetry, thermogravimetry (TG) and differential scanning calorimetry (DSC).

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 experiment the water was adsorbed "offline" in a well evacuated desiccator at a relative water pressure of 0.3 at room temperature overnight. Then the samples were transferred into the apparatus.

Sorption isotherms of water were measured gravimetrically at 293, 313 and 333 K with a home-made McBain quartz spring balance equipped with two MKS Baratron pressure sensors (10^{-3} to 10 and 10^{-1} to 1000 mbar). The sensitivity of the quartz spring amounts to 4 mg/mm. The expansion of the spring were 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 623 K (zeolitic materials) and 523 K (impregnated material) for 2–3 h.

The differential molar heats of sorption were determined at 313 and 333 K using a SETARAM C 80 microcalorimeter of Calvet-type connected with a volumetric adsorption apparatus. The equilibrium pressure was measured also with a MKS Baraton sensor (10^{-2} to 100 mbar) and the adsorbed amount by a combination of a calibrated capillary (filled with carefully degassed water) and the kathetometer mentioned above. Prior to the measurements of the heat curves the zeolites (ca. 600 mg) were calcined over night in high vacuum ($<10^{-5}$ mbar) at 573 K and the impregnated material at 523 K. The accuracy of the adsorbed amount is about 2% and of the heat of adsorption 4–5%.

2.2. Samples

Powder of pure molecular sieves for the TG/DSC measurements and pelleted and powder samples of different types for the isotherms and microcalorimetry were used. The LiNaX, the aluminophosphates AlPO-18, AlPO-17 and AlPO-5 and SAPO-34 were pure powder samples and two types of low silica X-zeolites (LiLSX and NaLSX, Tricat GmbH, Bitterfeld, Germany) as well as attapulgite impregnated with 30% $CaCl_2$ were pelleted samples.

The attapulgite had a BET surface area of 98 m^2/g and, estimated by mercury intrusion, an average pore diameter of 64 nm with a surface area of 86 m^2/g. By comparison of the texture data of the pure and impregnated samples it could be concluded that the salt was accommodated inside the pores of the attapulgite [9]. Because the pore diameter is close to the border of meso- and macropores (IUPAC definition 50 nm) attapulgite will be still called to be "mesoporous".

For zeolites a high pore volume or a low lattice density is important to achieve high storage densities [3,7]. Therefore, mainly molecular sieves of the faujasite-, erionite- and chabasite type were selected. LiNaX (95.5% ion exchange degree) was prepared by a standard ion exchange procedure with LiCl (based on common NaX, CWK, Bad Köstritz, Germany). The $AlPO_4$ and SAPO materials were synthesized hydrothermally according to the patent literature [10–12] using organic template molecules: AlPO-5 with tetrapropyl ammonium hydroxide, AlPO-17 with cyclohexyl amine and AlPO-18/SAPO-34 with tetraethyl ammonium hydroxide. The SAPO-34 contains 3 Si/u.c. according to the chemical composition. All $AlPO_4$ and SAPO samples were checked by XRD measurements to be highly crystalline and pure.

3. Results and discussion

First in TG experiments the differences in the desorption behaviour of water from the molecular sieves were compared. Fig. 1 gives the results of those thermogravimetric investigations. Fig. 1a shows the mass loss of water in g/g as function of the temperature and Fig. 1b (for more clarity) the first deviation of the TG profiles. As can be seen the water from the $AlPO_4$-5 and $AlPO_4$-18 is desorbed at significant lower temperatures as for LiNaX is observed. The SAPO-34 can be found in between. The desorption peaks of the $AlPO_4$'s in Fig. 1b are very narrow in accordance with the steep course of the water isotherms of $AlPO_4$ molecular sieves (see for instance [13]). Thus it is possible to desorb the main part of the water from $AlPO_4$-5 at about 370 K and of $AlPO_4$-18 at about 390 K. Incorporation of Si into the $AlPO_4$-structure increases the maximum of the desorption curve to about 400 K 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.

Table 1
Results of the TG/DSC measurements: adsorbed amounts (a, at 296 K and $p/p_s = 0.3$) and integral molar heats of desorption (Q_{int})

Sample	a (g/g)	Q_{int} (kJ/mol water)
LiNaX	0.375	61.7
SAPO-34	0.279	54.8
AlPO-5	0.237	53.4
AlPO-17	0.283	55.4
AlPO-18	0.388	55.3
Attapulgite/$CaCl_2$	0.395	48.7

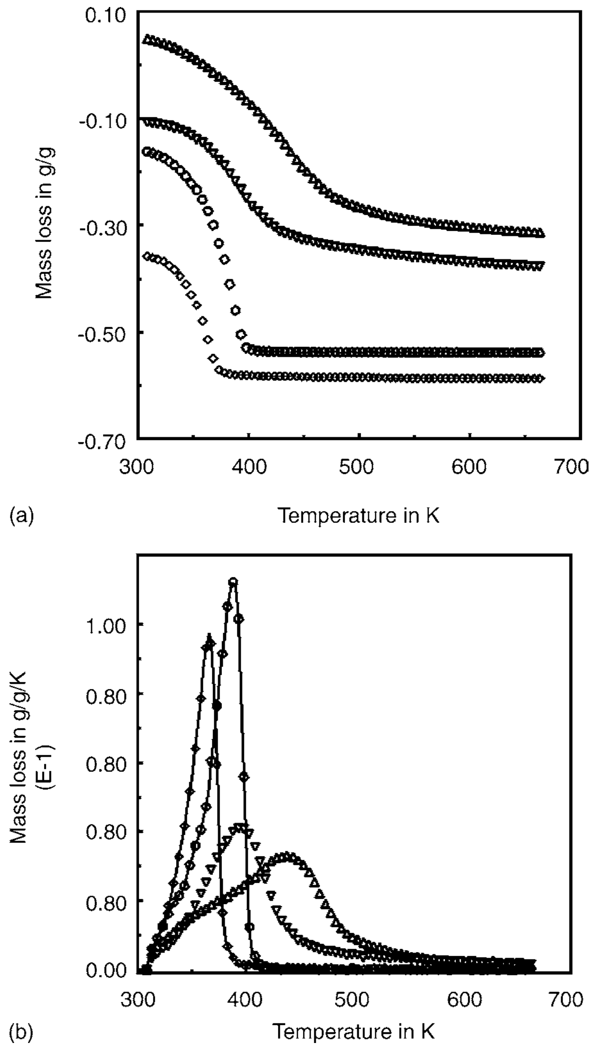

Fig. 1. (a) TG-curves for the desorption of water from LiNaX, SAPO-34, AlPO-18 and AlPO-5 (from top to bottom) and (b) DTG-curves (differential mass loss) of the same samples.

Table 1 gives already an indication of the reason of this behaviour beside possible kinetic effects in the comparison between $AlPO_4$-18 and SAPO-34. The last column shows the integral molar heats of desorption (DSC results) for the samples under discussion. The heat of desorption decreases from LiNaX to the $AlPO_4$, and the SAPO molecular sieves from 62 kJ/mol to about 55 kJ/mol. In the last line of Table 1 also values for the mesoporous attapulgite impregnated with $CaCl_2$ (as hygroscopic salt) are given. The integral heat of sorption (or hydratation) of the $CaCl_2$ in the pores of the almost hydrophobic host is the lowest and the desorption temperature is comparable to the $AlPO_4$'s (not shown in Fig. 1). The table compares also the adsorbed amounts of water at 296 K and a relative pressure of 0.3. The highest value of the microporous materials is found for the $AlPO_4$-18. However, the uptake of the impregnated material is even higher which may overcompensate the lower heat of hydratation with respect to the total heat of sorption related to the amount of adsorbens [9].

In the following part the adsorption properties (isotherms and differential molar heat curves) of the low silica X zeolites, the SAPO-34 and the impregnated material, selected for further investigations in a lab-scaled storage, will be discussed. The isotherms at 313 K (a typical inlet temperature for modern space heating systems) are depicted in Fig. 2.

The isotherm of LiLSX is typical S-shaped as well known for zeolites of the faujasite type. Most of the water is already adsorbed in a very low range of equilibrium pressure (10^{-3} to 1 mbar). The isotherm of the other zeolitic material, SAPO-34, is shifted to significant higher equilibrium pressures and the main part of the water is adsorbed between 0.1 and 6 mbar. And, finally, an even higher vapour pressure is necessary for the water uptake of the impregnated attapulgite. This behaviour is related, to a large extent, to the energetics of sorption as will be shown later.

Whereas the isotherm of LiLSX is reversible (not show in Fig. 2) the isotherm of the SAPO-34 is not (compare filled points in Fig. 2). A small difference between the ad- and desorption branch of the water isotherm is a known phenomenon of aluminophosphate molecular sieves [13,14]. From ^{27}Al DOR NMR studies on AlPO-18 in [14] for instance it is known that polar molecules such as methanol, ammonia and water turn the coordination number of lattice Al-atoms from four to fife or six. A direct interaction of the adsorbate molecules with the lattice Al is the reason which also causes the small difference in ad- and desorption mode. According to this phenomenon the very steep part of the SAPO isotherm in Fig. 2 from $a \approx 0.05$ to 0.25 g/g and in the pressure range of 2–5 mbar should be explained in terms of the formation of a hydrate.

A similar approach can be used to explain the stepwise and steep course of the water isotherm of $CaCl_2$/attapulgite. The water uptake of this sample is mainly due to the formation of hydrates of this hygroscopic salt. The first step of its isotherm in Fig. 2 (from 0.5 to 10 mbar) is due to the formation of the dihydrate (0.099 g/g) and the following sec-

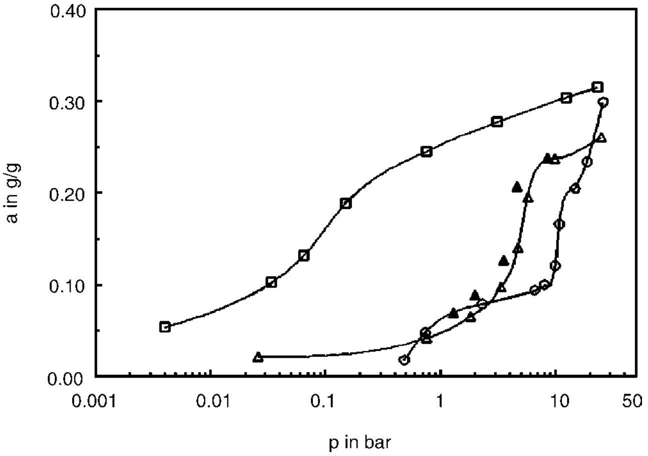

Fig. 2. Sorption isotherms of water at 313 K for LiLSX, SAPO-34 and $CaCl_2$/attapulgite (from left to right, filled points desorption).

ond step and steep part to the formation of the tetrahydrate (0.198 g/g) of $CaCl_2$ which is confirmed by XRD measurements. A continued pressure increase allows the formation of the hexahydrate and of even higher hydrates [5].

Fig. 3 compares the heat curves also at 313 K of the same samples. As can easily be seen the curves of LiLSX, SAPO-34 and the $CaCl_2$ impregnated attapulgite are shifted down to lower heats of sorption in the same order as the isotherms are, indicating energetic reasons for the considerable differences in the sorption behaviour of those materials.

Striking is for all three curves a more or less steep downswing for low loadings followed by a nearly constant horizontal part till an equilibrium pressure of about 20 mbar at the end of the heat curves. The strong decrease of the differential molar heats of adsorption of LiLSX (100–70 kJ/mol water) can be correlated (see [15]) to strong interaction of the first water molecules on Li cations accessible on positions in the large cavities. The weaker bonded water (at about 70 kJ/mol) may interact with lattice oxygens and could form OH-bridges with the oxygen atoms of the inner surface of the LSX as was shown by DRIFTS experiments [16].

The strong decrease at the beginning of the curve of SAPO-34 (90–60 kJ/mol) may be correlated to the amount of acidic OH groups compensating the surplus charges of lattice oxygens as result of a possible monomeric substitution of phosphorous atoms by silicon. According to a chemical analysis of the SAPO-34, three Si/UC are incorporated into the lattice. If water forms first a monomeric complex with the Brønsted sites which would correspond to a adsorbed amount of water of about 0.03 g/g (with the higher heat), this would not be in contradiction with the course of the heat curve shown in Fig. 3. The following almost straight part of the curve at 60–65 kJ/mol would be due to the formation of a hydrate following the discussion of the isotherms above.

Finally, the first part of the $CaCl_2$/attapulgite heat curve (up to a loading of about 0.1 g/g in the range 75 kJ/mol down to 50 kJ/mol) should be characteristic for the formation of the dihydrate of the $CaCl_2$ followed by the formation of the other hydrates with significant less heat gain upon water uptake. The value found amounts to 50 kJ/mol and is only slightly higher as the heat of condensation of the water (dashed line in Fig. 3). Consequently, removing of the water from those samples will be easy and the temperature dependence of the water uptake, however, will be strong different to the other two materials [9].

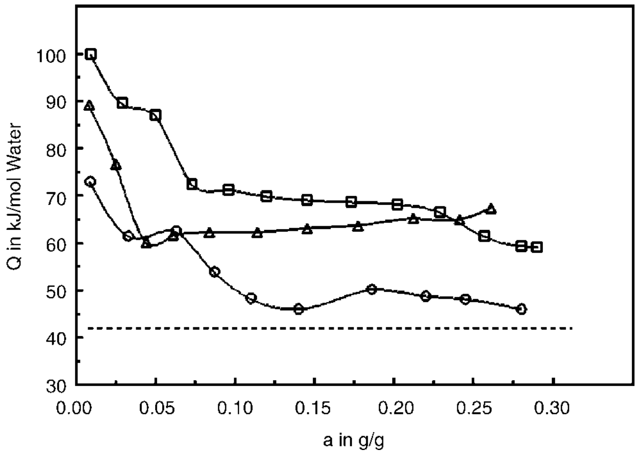

Fig. 3. Differential molar heats of sorption of water at 313 K for LiLSX, SAPO-34 and $CaCl_2$/attapulgite (from top to bottom), dashed line indicates heat of condensation.

Table 2
Energy densities (ρ_Q; integral heats of adsorption related to the amount of adsorbens) calculated from the differential heats of adsorption of water, at different temperatures

Sample	ρ_Q (kJ/kg adsorbens at 313 K)	ρ_Q (kJ/kg adsorbens at 333 K)
LiLSX	1184	1091
NaLSX	1033	950
SAPO-34	997	547
Attapulgite/$CaCl_2$	871	330

Table 2 summarizes the results of the calorimetric investigations from the point of view of the thermochemical storage. By integration of the differential heats of (ad)sorption in Fig. 3 the energy density (storage density) of the materials is calculated. The so evaluated integral heats of (ad)sorption are related to the amount of adsorbens not to the adsorptive. As can be seen from Table 2 the energy density of the LiLSX and NaLSX are the highest at 313 K as well as 333 K (temperature for hot water supply) followed by the SAPO-34. The hydratation of the $CaCl_2$ confined in the attapulgite delivers the lowest specific amount of heat at 313 K and a much lower value at 333 K (about 330 kJ/kg). However, if the sorption temperature of the composite is 293 K the energy density amounts to about 1500 kJ/kg mainly because of a much higher uptake of water.

Those changes of storage densities with the temperature are observed for all four materials in Table 2. The main reason is, as already said for the salt hydrate, the decreasing sorption capacity with rising temperature. The differential molar heats (as function of the loading) of the different materials decrease very little only with rising temperatures. The sorption capacity, however, changes with the temperature to a very large extent. The zeolites with relatively high adsorption heats are “insensitive” to this effect and the salt hydrates (also silica gel) on the other hand are sensitive because of their low heats of adsorption. The aluminophosphates and SAPO’s are in between due to their “medium” heats of adsorption. The desorption temperatures, however, are comparable low as is found for the mesoporous/impregnated samples.

4. Conclusions

The $AlPO_4$ molecular sieves as well as SAPO-34 give compared with zeolites similar values of adsorbed amounts of water and the energy densities, however, their desorption temperatures for water are significant lower as for the ordinary zeolites.

The high energy density of the impregnated materials is the result of the large amount of sorbed water, but the strength of the water interaction is low and close to the heat of condensation of the water.

The microporous aluminophosphates and SAPO-34 show significant higher heats of adsorption which range between the zeolites and the impregnated mesoporous material. Thus, the lattice modification of zeolite like materials reveal a high potential for optimization of the adsorption properties regarding improved thermochemical storage of low temperature heat. Following those new guide lines, the $AlPO_4$ and SAPO molecular sieves may have the potential as storage materials between the zeolites and the impregnated mesoporous materials and can fill the gap between the storage properties of the ordinary zeolites and common silica gel.

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