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Adsorption properties of porous materials for solar thermal energy storage and heat pump applications

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Abstract

The water adsorption properties of modified porous sorbents for solar thermal energy storage and heat transformation have been investigated by thermogravimetry (TG) differential thermogravimetry (DTG), microcalorimetry, measurements of water adsorption isotherms, and storage tests. A chabazite type SAPO, a dealuminated faujasite type zeolite, and a mesostructured aluminosilicate, have been synthesized and compared with common zeolites X, Y and silica gel. It has been found that optimized lattice composition and pore architecture contribute to well adapt hydrophilic properties and a beneficial steep isotherm.

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Keywords: water adsorption; thermal adsorption storage; molecular sieves, SAPO-34, MCM-41

1. Introduction

Contributions to significant energy savings and a "greener" energy supply by complex solar energy utilization using compact thermal adsorption storage technologies and advanced heat pump applications ask for the development of optimized hydrophilic materials. So in recent years the need for solid porous sorption materials with tailored adsorption properties became obvious which range in between the very strong hydrophilic character of conventional zeolites on one hand and the weak hydrophilic silica gel on the other hand [1-2]. The chemical composition and the pore structure of the porous materials determine

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the strength of the water interaction as well as the position and the shape of the water adsorption isotherms. These parameters are important to choose for the application of solid sorbents in solar driven heat storage and heat transformation processes based on given temperature levels of the heat sources for charging, vaporisation, and condensation.

Some efforts have been achieved in the last decade by using silicoaluminophosphates (SAPO) having better adapted adsorption properties for heat pump applications [3, 4]. But these materials are still costly to produce and other options may be welcome. So dealumination of conventional zeolites [5] or alternative synthesis of mesostructured molecular sieves [6, 7] can be used to modify the hydrophilic character and the pore architecture.

The aim of this paper is, therefore, to compare the water adsorption behaviour and the shape of the isotherms of a modified faujasite type-, chabazite type-, and mesostructured molecular sieve with common sorbents such as NaX, NaY and silica gel.

2. Materials and methods

The products used for this study have been a SAPO of chabazite type (SAPO-34), to some extent dealuminated faujasite type zeolite NaY 7 and a mesostructured aluminosilicate (MCM-41, cf. [8]). All samples have been selected with the aim to reduce the interaction forces of water and to generate a steep water isotherm by changing the lattice composition and pore architecture. For comparison standard zeolites of type NaX and NaY (CWK Bad Köstritz, Germany) as well as the low silica zeolithe NaLSX have been included in our study.

The adsorption properties of these materials have been studied by TG/DTG as well as by microcalorimetry and gravimetric isotherm measurements. For the isotherm measurements a McBain balance was used measuring isothermsms between T=293-353 K and p=0.001-30 mbar. The SETARAM C 80 microcalorimeter of Calvet-type connected with an adsorption apparatus served for the determination of the differential molar heats of adsorption. Prior to the isotherm and calorimetric measurements the samples (ca. 150 mg for isotherms, ca. 600 mg for calorimetric measurements) were calcined for at least two hours in high vacuum ($p<10^{-5}$ mbar). Our comparative study includes also tests of the storage properties of selected samples in a closed lab-scaled storage of 1.5 L volume. Further experimental details can be found in [3, 9].

3. Results and discussions

The results of the thermogravimetric measurements show in the DTG plot (not displayed) a downshift of the maximum desorption temperature of more than 200 degree from 550-400 K to about 370 K for the change from conventional zeolites NaLSX, NaX and NaY via the dealuminated NaY 7 and SAPO-34 to the mesostructured alumosilicate MCM-41. This result indicates already weakening interaction forces with varying structure type and composition of the materials which were investigated in more detail by microcalorimetry.

Figure 1 illustrates as an example the heat curves of three of the above mentioned molecular sieves. The low silica faujasite NaLSX (uppermost curve) shows the strongest interaction of water with the zeolitic framework. The differential molar heats of adsorption are here the highest due to a Si/Al-ratio close to one causing the highest possible number of charges per unit cell. Thus the number of strong bonded water molecules amounts to about 0.07 g water per g dry zeolite. Because of the high concentration of charges in the pores the general level of the adsorption heat remains higher compared with the dealuminated faujasite. So NaY 7 contains fewer Al and charge compensating cations per unit cell resulting in a lower concentration of charges as well as strong adsorption sites in the cavities.

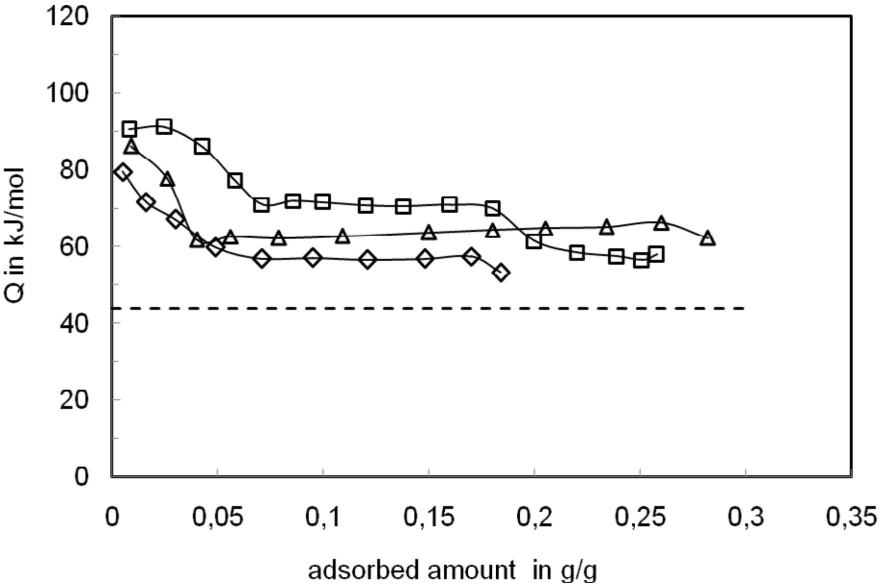

Fig. 1. Differential molar heats of adsorption of water, Q, for (from top to bottom): NaLSX (at 313 K), chabazite type silocoaluminophosphate SAPO-34 and NaY 7 (at 303 K). The dashed line denotes the heat of condensation of the water.

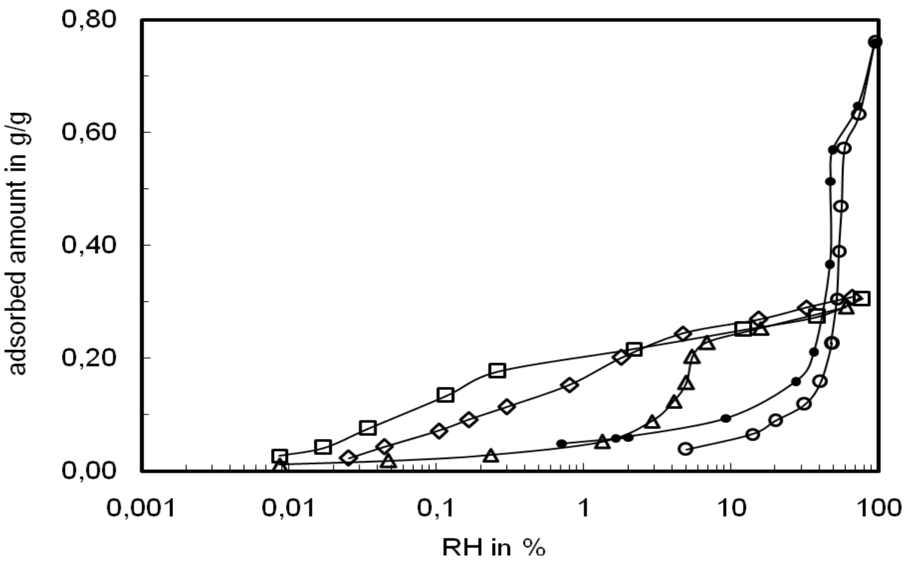

Fig. 2. Water adsorption isotherms as function of the relative humidity, RH, for (from left to right): NaX, NaY, SAPO-34 and the silocoaluminophosphate MCM-41, filled symbols denote desorption.

Consequently, less water is less strong bonded (about 0.05 g/g) and the entire heat curve is downshifted by approximately 20 kJ/mol. The SAPO-34 is in between pointing to a similar low concentration of charges in its cavities as NaY 7 shows. However, in this case the number of Al isomorphously substituted into the aluminophosphate lattice determines the number of charges which seems to be comparable with this in NaY 7.

Figure 2 shows the adsorption isotherms of another selection of samples (NaX, NaY, SAPO-34 and MCM-41) to illustrate the possible shift of the isotherms towards higher relative pressure (here plotted as relative humidity) as a result of the decreasing strength of the water-surface-interaction as described above. Important to note is, beside the considerable shift of three orders of magnitude, the steep shape of the isotherms for SAPO-34 and MCM-41 compared to the common zeolites X and Y. A similar shape as for the SAPO-34 has been found for the dealuminated faujasite (not shown).

Table 1 gives a comparison of the value of the relative pressure at what the isotherms show upraise for the samples investigated. Obvious is the broad p/p_s-range of the conventional sorbents (NaX, silica gel) and the big difference in the absolute values between them. The modified sorbents, however, show relative pressure values ranging in between the two others, offering beneficial adsorption properties for solar applications because of the individual tight p/p_s- ranges. Another advantage is the tailored adsorption range possible by comparably simple material modifications.

The storage densities (cf. Table 1, column 4) are similar but it has to be taken into account that with raising relative pressure (column 3) the temperature lift diminishes. Consequently, a compromise has to be found between charging temperature, storage density, temperature lift, and performance of the system.

Table 1. Comparison of the adsorbed amount of water, a, in g/g taken from isotherms at p/p_s=0.3, the relative pressure interval of the isotherm upraise, and the storage density

Molecular sieve	a in g/g (from isotherms at 293K,)	p/p_s at upraise of isotherms	storage density in Wh/kg
NaX	0.28	0.0004-0.004	156
SAPO 34,	0,29	0.043	130
NaY 7	0.20	0,04-0.13	155
MCM-41	0.7	0.48	-
Silica gel	0.23	0.004-0.4	123

4. Conclusions

A new approach of solid sorbent modification offers an extended range of tailored porous materials with medium hydrophilic character for solar thermal adsorption storage and solar driven heat transformation. The chemical composition of the framework and with this the concentration of charges in the pore structure as well as the pore architecture of the materials determine the adsorption equilibrium of water having a strong dipole. Controlling these parameters offers the possibility to modify materials for solar driven thermal adsorption storage applications.

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