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Adsorption properties of modified zeolites for operating range enhancement of adsorption heat pumps through the use of organic adsorptive agents

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Abstract

Faujasite zeolites with the highest possible Al-content and different cations as well as a dealuminated zeolite Y have been chosen to study the impact on the adsorption behavior in view of differed adsorptive agents for heat pumps or thermochemical storages. Our results show advantages and disadvantages for water, methanol or ethanol adsorption due to the structure of the anion skeleton, kind of cations and size of the adsorbat molecule.

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1. Introduction

In comparison with electrically operated heat pumps, thermally driven heat transformers are ecologically much more efficient. In combination with renewables it is possible to maintain such a system nearby carbon-neutral. Materials such as dealuminated Y-type zeolites [1] have proven their operational capability in low-temperature driven heat pump applications. But they are strictly limited to the operating parameters of water.

It is known that the adsorptive agent has an enormous influence on the boundary conditions of a heat pump application, it's particularly evident on the amount of adsorption heat and the influence on the ad- and desorption properties. The influence is specifically notable on changes of the desorption temperature. Organic adsorptive agents such as methanol (MeOH) and ethanol (EtOH) [2-4] are able to lower the operating temperatures of the vaporizer/condenser system of a heat pump- or heat storage application without losing that much of the adsorption capacity.

The aim of this contribution is therefore to investigate how we can improve the operating range of zeolite driven heat pumps or thermochemical storage systems by substituting the adsorptive agent. Further, how does the functional interaction through the changed Si/Al-ratio and the substituted cations of the zeolite as well as the organic working agents influence the adsorption properties of zeolites? And finally, is there any impact on their crystal lattice structure and long term stability?

2. Methods and materials

The adsorption properties of the zeolitic molecular sieves have been studied with different thermogravimetric methods (TG/DTG) using a Netzsch ST 409 and by adsorption microcalorimetric analyses with a C80 calorimeter from Setaram.

The TG-Program for all three adsorptives started with a 20 min. isothermal dwell, flushing the sample with N₂ at 25°C and then followed by a heating ramp with 3 K/min. up to 450°C. This measure had to be taken to get rid of all weakly bonded methanol or ethanol by condensation. Different to water the conditioning of the samples with MeOH and EtOH had to be carried out at relative pressure close to one (water 0.33).

Gravimetric isotherms have been determined with a McBain-Bakr quartz spring balance. The sensitivity of the spring amounts to 4 mg/mm. The extension of the spring has been determined by a cathetometer with a resolution of 0.01mm. This gives a resolution of the adsorbed amount of 0.0003 g water/g zeolite for about 150 mg samples.

The materials under investigation were the so called low-silica zeolites such as NaLSX and LiLSX with a Si/Al-ratio = 1 on one hand and the dealuminated Y-zeolite like SEY (silicon enriched zeolites) and NaY7K with a Si/Al-ratio = 7 on the other hand. For comparison we included the binderless 4ABF and 13XBF, both products of CWK Bad Köstritz (Germany).

The investigation of long term stability has been tested in liquid phase of all three different adsorption agents which are water (H₂O), ethanol (EtOH) & methanol MeOH.

3. Results and discussions

The results of the TG-measurements are summarized in Table 1 and Fig. 1. Table 1 shows the adsorption capacities of all four zeolites with all three different working agents, after the initial isothermal flush. Water gives the well-known adsorption capacities in g/g for LiLSX, NaLSX and 13XBF and those three are very close to each other. The dealuminated sample NaY7K adsorbs 1/3 less water than the other zeolites because of its structure losses during the process of dealumination. The adsorption capacity in g/g for MeOH and EtOH is smaller because of their lower density in comparison with water but the pore filling degree in ml/g is almost the same. A closer look to NaY7K shows, however, that the capacity for MeOH and EtOH is less reduced most probably because of a compensating process upon adsorption at stronger extra adsorption sites in NaY7K.

Table 1 (column 5 and 6) gives also information about the results of the stability tests in water and EtOH. All samples under investigation were stable under the conditions applied, except 13XBF in water. This molecular sieve showed some degradation in water as already known from experiments in the gas phase.

Fig. 1 gives an information about the thermogravimetric desorption profile for LiLSX as an example. The profiles flatten from water to methanol and ethanol. This is correlated with the increasing heats of adsorption in the same order (not shown) because of the stronger organic character of the alcohol molecules and an increasing dispersion interaction beside the strong polar interaction. The effect in LiLSX is more pronounced than for the dealuminated sample NaY7K (cf. Fig. 2). We interpret this effect in terms of a different adsorption site strength distribution.

The system water/LiLSX seems to be a valuable candidate for heat pump applications because of its high adsorption capacity and also its favorable desorption properties (higher steepness of the TG-curve, cf. Fig.1, as well as for the isotherm, not shown).

Fig. 3 shows an example for the influence of different kind of cations in a zeolite. The Li-form of LSX release significant more heat of adsorption upon water adsorption than the Na-form (values are related to the amount of water). The molar differential heat of adsorption of LiLSX is slightly higher through the entire course of the heat

curves. However, due to the significant higher adsorption volume of LiLSX the integration of the heat curves gives a higher specific integral heat of adsorption related to the dry zeolite for the Li-form. We measured for LiLSX 329 Wh/kg and for the Na-form only 303 Wh/kg, for our chosen boundary conditions. This increase in interaction strength can be explained by the variation in charge density of the cations ($Li > Na$).

Table 1. Adsorption capacity (a) of different zeolites after conditioning for 48h in water vapor with $p/p_0=0.33$; $p/p_0=0.99$ (MeOH); $p/p_0=0.99$ (EtOH), desorption up to 450°C with 3 K/min. upon initial isothermal flushing at 25°C.

Sample	a in g/g H ₂ O	a in g/g MeOH	a in g/g EtOH	stability in H ₂ O	stability in EtOH
LiLSX	0,31	0,26	0,246	stable	stable
13XBF	0,31	0,26	0,242	less stable	stable
NaYBF	0,31	0,27	0,235	stable	stable
NaY7K	0,20	0,17	0,18	stable	stable

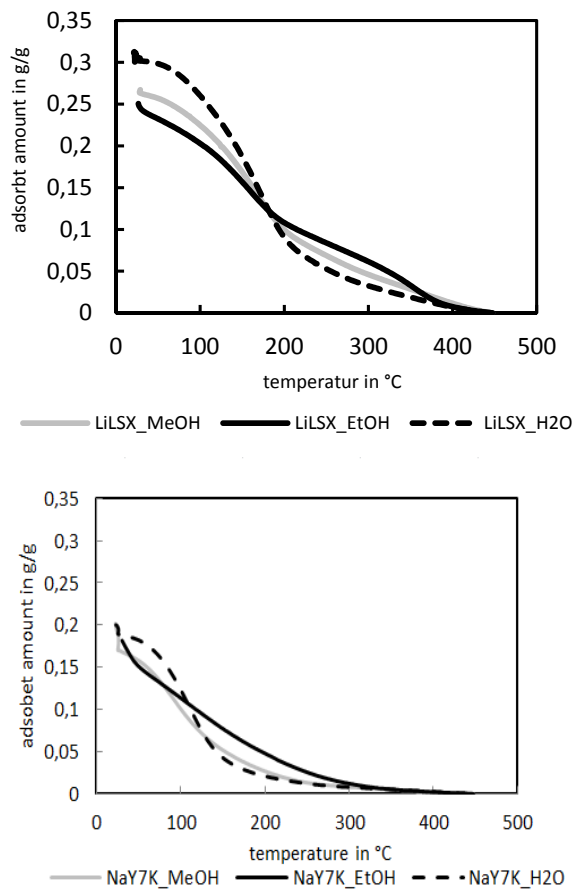


Fig. 1&2: Thermogravimetric profiles of LiLSX (top) and NaY7K, dealuminated Y-Typ zeolite (bottom)

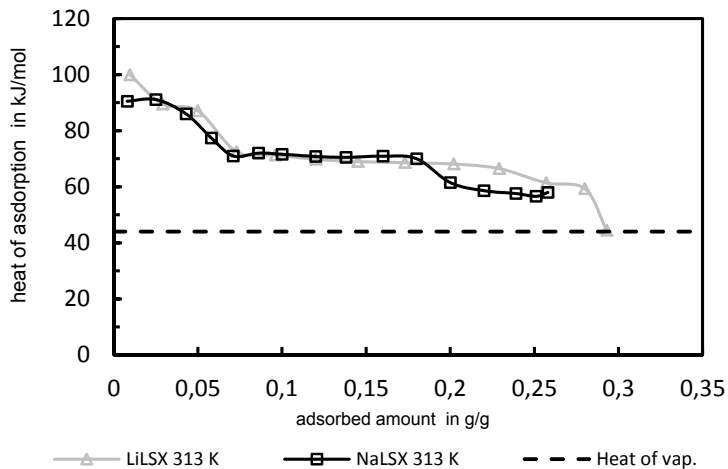


Fig. 3: Comparing calorimetric measurements (differential molar heats of adsorption) of LiLSX/water, and NaLSX/water

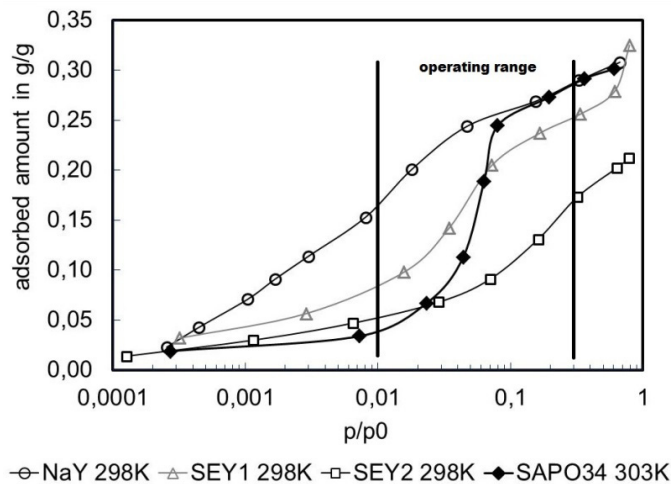


Fig. 4: Water (H₂O) isotherms of different samples taken at 289K for NaY, SEY1& SEY2, SAPO34 at 303 K

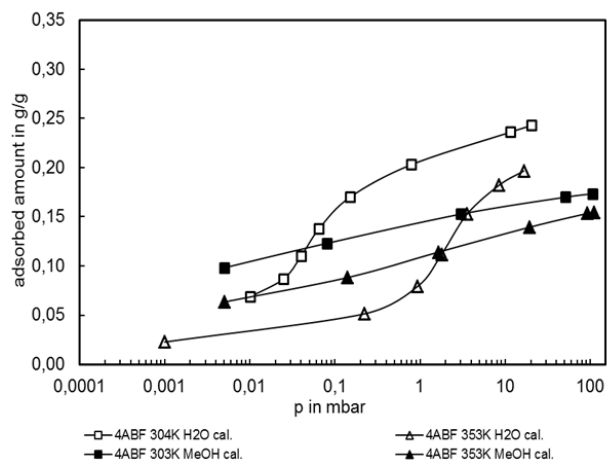


Fig. 5: Isotherms at 303/304 K and 353 K for 4ABF with different organic and anorganic adsorptive agents Methanol (MeOH) and Water (H₂O)

At the first glance, dealumination seems like a negative modification comparing just the total adsorbed amount (cf Fig. 5). However, if the deltas of the adsorbed amount in the relevant pressure range of the heat pump is compared the capacity of SAPO-34 is much better as for NaY. The same effect can be achieved by dealumination. So the shift of the isotherm curves brings an enormous effect on the water uptake. The adsorption capacity in the operating range of a low temperature driven heat pump is up to 60% higher after the dealumination of the Y-type zeolite. The impact of dealumination on the hydrophilic character of Y-Type zeolites is impressively demonstrated by the change of the water isotherms in Fig. 4- As can be seen the modified silicon enriched zeolites (SEY) are able to cover the full operating range for low temperature heat pump applications if SAPO-34 serves as a benchmark.

Finally, we compare the adsorption behavior of water and MeOH by isotherm measurements. The results of the TG experiments (Fig. 1&2) showed already a flatter course of the TG-profiles as indication of a stronger interaction of the alcohols in LiLSX and in the SEY-zeolites. Fig. 5 gives another example for 4ABF/water and 4ABF/MeOH. The isotherms of MeOH are rather flat because of a stronger interaction of MeOH in the pores of 4ABF and an apparent different adsorption site distribution for MeOH.

Against the expectation which gives the motivation to investigate the influence of organic adsorptive agents it is relatively clear that under the chosen conditions MeOH is not able to improve the adsorption properties in respect of adsorption capacity and adsorption stroke (Fig. 5). Still the advantages of a low freezing point and a higher vapor pressure at the same temperature (compared with water) remain as favorable physical properties of MeOH if the vaporizer/condenser experience low environmental temperatures.

4. Conclusions

The ion exchange of zeolites may improve the adsorption properties in regard to the energy density without a bigger impact on the steepness of the TG or the isotherm curve. This is important for storage and heat transformation. Dealumination changes more likely the adsorption site strength distribution especially for the alcohols.

The steaming process is a powerful tool to tailor the hydrophilic character of Y-type zeolites/water for almost any requirement documented by the shift of the adsorption isotherms towards higher equilibrium pressure. Therefore, special specifications of materials for low temperature driven heat pump and storage systems can be met.

The use of organic molecules instead of water does not enhance the discussed effect of improving adsorption properties in respect of adsorption capacity and adsorption stroke. On the contrary the exchange of the adsorption agent brings other disadvantages, like lower cumulative adsorption capacity and higher desorption temperatures

which have a negative influence on the performance parameters of adsorption heat pumps. The physical properties of the alcohols such as low freezing point and higher vapor pressure remain as beneficial if the environmental condition for the vaporizer/condenser can reach temperatures $< 0^{\circ}\text{C}$.

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