

OPTIMIZATION OF THERMOCHEMICAL STORAGE BY DEALUMINATION OF ZEOLITIC STORAGE MATERIALS

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1. INTRODUCTION

Thermochemical storage of heat can contribute to environmental benefits by utilization of waste heat as well as solar heat for space heating and cooling applications (Meunier, 1986, Tchernev, 2001). One of the main attractions of this technology is the loss free long term storage of thermal energy for heating, cooling and drying of buildings. Also mobile thermochemical storages for transport of thermal energy came into the focus of research and development. For all of this applications, however, the temperature level of the heat source available for charging of the storage influences the choice of the porous material. Till now ordinary zeolites for higher charging temperatures (>450 K) and silica gel (<370 K) were the most common products for thermochemical storage applications. Recently developed storage materials based on microporous silicoaluminophosphates (Jänchen, 2002, Kakiuchi, 2002) are closing the gap between zeolites and silica gel. The disadvantage of those materials is their synthesis method including an organic template as structure directing agents which has to be removed from the porous structure after the synthesis (by oxidation in most cases).

Therefore, we were in search of another solution of tailoring zeolitic storage materials for low temperature applications. From the catalysis it is well known that a post-synthesis modification of a number of zeolites by a hydrothermal treatment (McDaniel, 1968) reduces the lattice aluminium concentration and improves the thermal/hydrothermal stability and catalytic performance. A partial dealumination of the zeolite Y for instance by a hydrothermal treatment reduces the number of Al atoms and cations in the zeolite without changing the crystal structure. A reduced cation concentration in the zeolite leads to a lower electrostatic field in the micropores, diminishes the adsorption strength of the water and, hence, lower the desorption temperature of the water (corresponds with the charging temperature of the storage). The dealumination process of the zeolite can be controlled easily to adjust any silicon to aluminium ratio between 2 and >100.

2. METHODOLOGY AND EXPERIMENTAL

We used thermogravimetry (TG), differential scanning calorimetry (DSC), the measurements of water isotherms as well as a lab-scaled storage of 1.5 L volume to investigate the adsorption, desorption and storage properties of a set of those NaY zeolites with increasing lattice silicon to aluminium ratio (from 1 to 30). 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. 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 cathetometer 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 for 2-3 h.

The 1.5 L storage (for details see Jänchen, 2004 a) was used for the tests of the storage properties on a larger scale. It consists of an adsorber filled with approximately 1 kg of storage material and is 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. The set-up is equipped with pressure sensors, thermocouples and data acquisition. The maximum charging temperature amounts to 423-473 K. The minimum temperature in the condenser was 283 K. For discharging of the storage the temperature of the evaporator was kept at about 293 K.

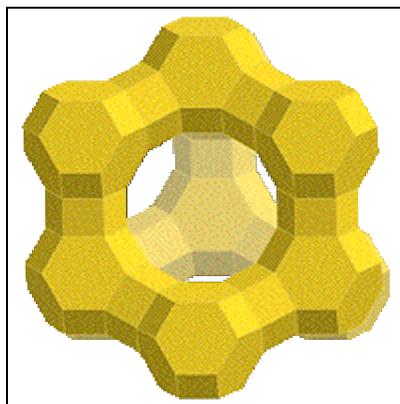


Figure 1: Structure of the faujasite type zeolite (X and Y); it consist of a three-dimensional network of Si^{4+} an Al^{3+} ions (at edges of the cubo-octaeder) connected by oxygen ions (lines between edges). The windows are build by oxygen twelve-membered rings of 0.7 nm in diameter. The compensating Na^+ cations in the pores are not shown.

The samples used in this study were of the same structure type (faujasite type, see Figure 1) and were commercial products as well as new potential storage materials. The zeolites and their Si/Al ratios varying from 1 (NaLSX) to 30 (dealuminated NaY) are listed in Table 1, column 1 and 2. The new low silica zeolite (NaLSX) came from Tricat GmbH Bitterfeld (Germany) and the common zeolites NaX and NaY are products of CWK GmbH (Bad Köstritz, Germany). The remaining three samples are partially dealuminated zeolites prepared by hydrothermal treatment (steaming) of a partially ammonium ion exchanged NaY. For comparison results of a SAPO-34 (microporous silicoaluminophosphate, see Jänchen, 2004 b, 2005) are added. All materials were pelleted into 2-4 mm grains.

3. RESULTS AND DISCUSSIONS

The first part of the results and discussion section focus on the physico-chemical characterization of the storage materials while the second part gives the information about the storage properties in the lab-scaled storage.

Table 1 shows, beside the above discussed chemical composition of the samples, the results of the thermogravimetric and differential scanning calorimetric measurements. As can be seen from the last column of the table the integral heat of desorption decreases with increasing Si/Al ratio. Likewise, the maximum of the desorption temperature decreases with dropping Al content of the materials. The reason for both observations is the reduced electrostatic field in the pores of the zeolites caused by the lower Al content in the zeolite framework and the reduced cation concentration (Na^+) in its pores. The maximum amount of water (adsorbed at a relative pressure of 0.3, desorption temperature 723 K) changes for most of the samples slightly (third column) but drops significantly for NaY(30) indicating that strong dealumination is unsuitable for storage applications. The SAPO molecular sieve ranges between the NaY and the NaY(7.4) with respect to the integral heat of desorption and the DTG maximum.

Thus, it can be expected that the desorption rate at a certain given temperature for this family of zeolites is determined by the aluminium concentration of the framework. Indeed, the measured amount of desorbed water by TG at 373 K for NaY(2.3) amounts to 25% of the total amount only and increases to 50% and 85% with increasing Si/Al ratio from 7.4 to 30, respectively. If the temperature level available for charging of a thermochemical storage is limited (solar heat, or low temperature waste heat) dealumination of the zeolites can contribute to higher storage efficiency by improving the loading interval between charging and discharging.

Table 1: Lattice Si/Al ratio, adsorbed amount of water at relative pressure 0.3, a , temperature of the maximum of the DTG profile and integral heat of desorption (from DSC)

Sample	Lattice Si/Al ratio	a in cm^3/g	T_{max} DTG in K	Q_{int} in kJ/mol
NaLSX(1)	1.0	0.278	430	77.9
NaX(1.2)	1.2	0.283	420	62.7
NaY(2.3)	2.3	0.275	390	61.3
NaY(7.4)	7.4	0.217	370	49.0
NaY(11)	11.4	0.232	350	53.0
NaY(30)	30	0.138	345	-
SAPO-34	-	0.279	390	54.8

Important are informations about the influence of the Si/Al ratio on the water adsorption equilibrium in the same structure type. Figure 2 gives an example of those informations which serve as input data for modelling of the storage process (Stach, 2005, N  nuez, 2001). The figure shows the adsorption isotherms of water at 293 K for a number of faujasite type zeolites with decreasing Al content (from left to right). As can be seen the isotherms are shifted towards higher equilibrium pressure by more than two orders of magnitude. Again, the reduced electrostatic field in the pores of the zeolites makes the materials less hydrophilic. The last isotherm is already similar to isotherms found for silica gel. Finally, a strongly dealuminated Y zeolite (Si/Al ratio of about 100 (not shown) becomes hydrophobic and adsorbs water very close to the condensation pressure only.

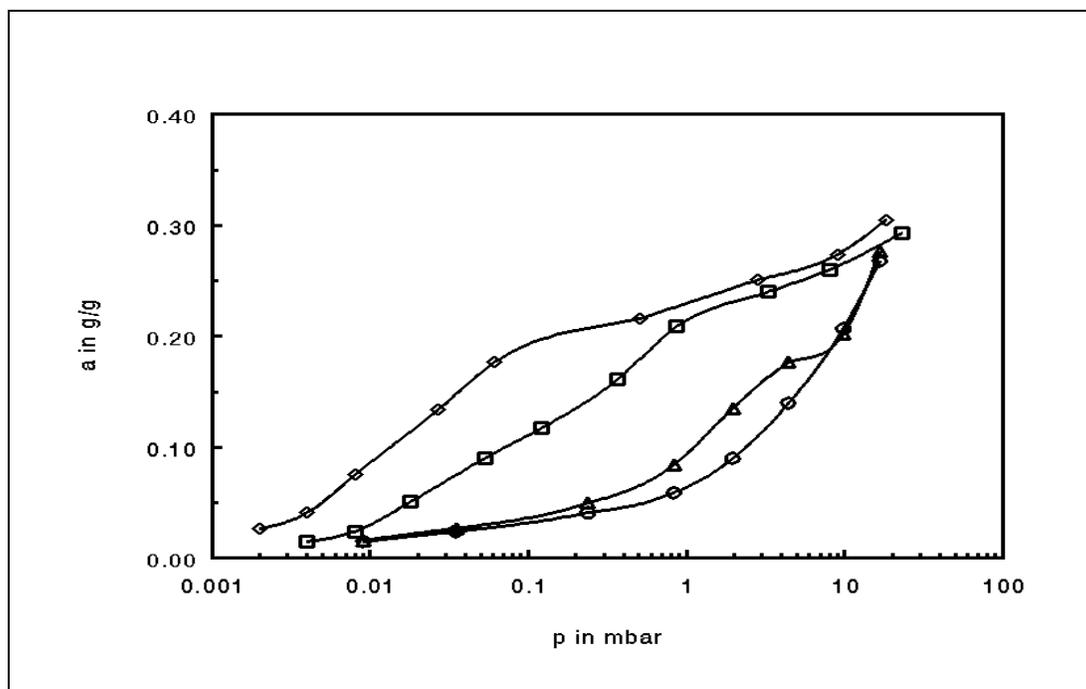


Figure 2: Water adsorption isotherms for (from left to right) NaX(1.2), NaY(2.3), NaY(7.4) and NaY(11) at 293 K, (NaY 298 K)

In conclusion, a step by step diminished Al content of the zeolite lattice changes the ad- and desorption properties of water. So, the zeolites can be tailored in order to optimise storage properties such as the charging temperature of the storage whilst the storage density should still meet a certain level. To proof this, the storage properties of the materials are discussed in the following part.

The results of the investigations in the lab-scaled storage are summarized in the Figures 3-6. As can be seen from the figures the temperature profiles, the maximum temperature in the storage, the adsorbed amount of water, and the storage density changes with the Si/Al ratio of the zeolite systematically. A more or less linear correlation can be found in the Figures 4-6 if the data are plotted against the Si/Al ratio on a logarithmic scale. The corresponding data found for SAPO-34 are: maximum temperature in the storage 345 K, adsorbed amount 0.22 L/kg, specific storage energy 154 Wh/kg.

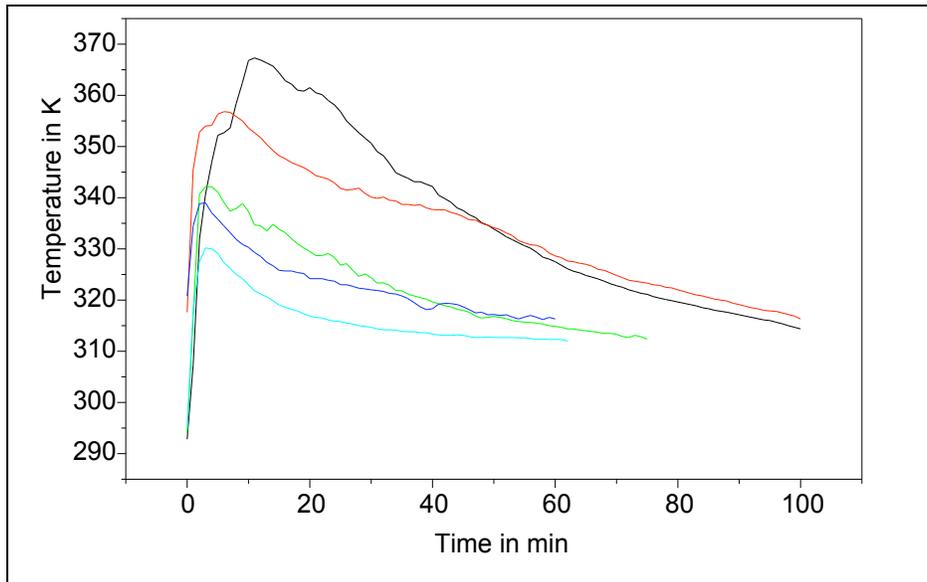


Figure 3: Temperature profiles as function of time during discharging of the storage for different zeolites: NaLSX(1), NaY(2.3), NaY(7.4), NaY(11) and NaY(30), from top to bottom.

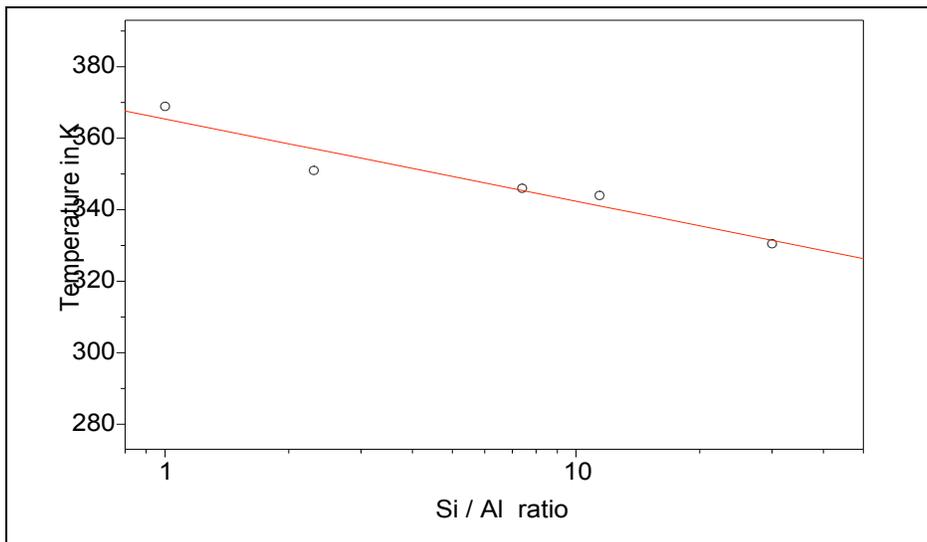


Figure 4: Maximum temperature in the thermochemical storage as function of the chemical composition (framework Si/Al) of the faujasite zeolite: NaLSX(1), NaY(2.3), NaY(7.4), NaY(11) and NaY(30), from left to right.

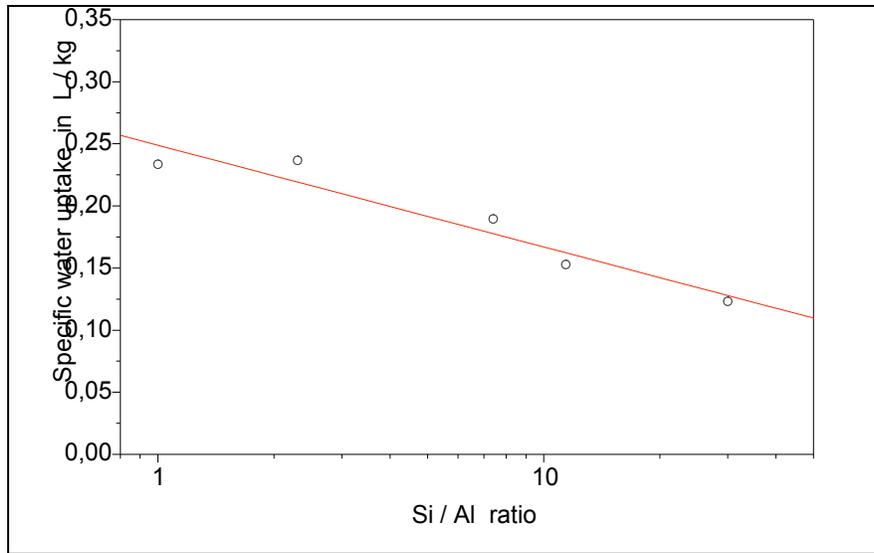


Figure 5: Specific water uptake of the storage materials as function of the chemical composition (framework Si/Al) of the faujasite zeolites: NaLSX(1), NaY(2.3), NaY(7.4), NaY(11) and NaY(30), from left to right.

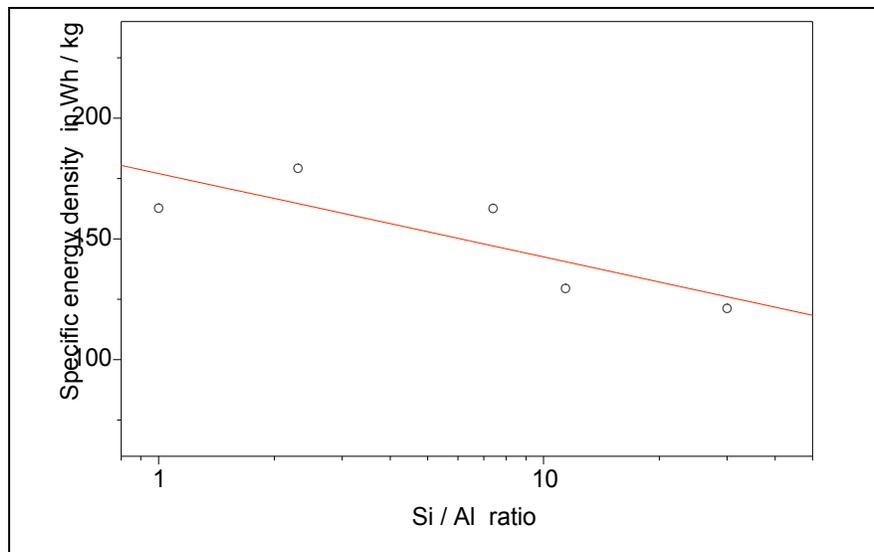


Figure 6: Specific energy density as function of chemical composition (framework Si/Al) of faujasite zeolites: NaLSX(1), NaY(2.3), NaY(7.4), NaY(11) and NaY(30), from left to right.

Thus, the SAPO storage properties are comparable with those of the faujasite type zeolites with a Si/Al ratio between 5 and 10. It is important to mention that the charging temperature for the dealuminated samples and the SAPO-34 could be reduced to 423 K and even lower temperatures. However, the desorption temperature in the case of NaLSX and NaY had to remain at 473 K to reach the storage densities given in Figure 6.

4. CONCLUSIONS

The well known method of zeolite modification by dealumination (steaming) can be successfully applied to direct carefully the water adsorption behaviour in order to optimise the thermochemical storage properties.

A decreasing aluminium to silicon ratio of the faujasite type zeolites from 1 to 30 diminishes the strength of the interaction of water and reduces the desorption temperature for an effective charging of the storage material. Because the specific energy density is influenced as well an optimum ratio can be found between 5 and 10 to keep the storage density >150 Wh/kg whilst the charging temperature can be reduced from 470 to <420 K.

Finally, partial dealumination of zeolites is a suitable method to optimise the properties of a thermochemical storage with regard to the charging temperature level available from low temperature waste heat or from solar thermal energy. Dealuminated faujasites could be an alternative or completion to the recently introduced microporous silicoaluminophosphates and AlPO molecular sieves.

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