STEAMING PROCESS FOR SILICON ENRICHMENT IN ZEOLITES FOR HEAT PUMP APPLICATIONS AND SOLAR DRIVEN THERMAL ADSORPTION STORAGE

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Abstract

Silicon enriched zeolites of type DAY (dealuminated Y) have been investigated by BET-Isotherm measurements, infrared spectroscopy, thermogravimetric and water sorption measurements with respect to their characterization of crystal state and water uptake properties. Variation of the adsorption behavior of samples is a result of a steaming process at different temperatures in dependence of time. It was found that different Si/Al ratios affects the typical characteristic of the silicon enriched zeolites, relating to their ad- and desorption temperatures. In comparison with other usual DAY zeolites it was found a different microporous and mesoporous hierarchy of the pore system. As a result of the steaming process, the silicon enriched zeolites enable more possibilities of low temperature application under specific conditions.

Keywords: dealumination; water adsorption; zeolites; adsorption heat pump; thermal adsorption storage

1. Introduction

In recent years more and more new materials have been developed which are specifically adapted for applications in solar driven heat pumps or thermal adsorption storage processes. But actually low-temperature heat pumps gain in importance, due to the increasing necessity to provide cold in industrial processes. It is well known that thermally driven heat pumps are ecological much more efficient in comparison with electrically operated heat pumps. In conjunction with the use of renewable energies it is even possible to develop such a system as carbon-neutral alternative. Quite expensive materials such as silicoaluminophosphates (SAPO) find application in adsorption heat pumps which depend upon low-temperature heat for regeneration aluminiumphosphates (ALPO) have proven their operational capability in low-temperature heat pump applications, too. But silica gel is still most commonly used in those applications due to its low price. On basis of previous results, which have shown that dealuminated Y zeolites [1, 2] are possible substitutes for SAPO's and ALPO's, we redesigned the adsorption affinity of DAY zeolite to a bigger operating range for water vapor pressures level and capacity that it is actually needed in the process. This way offers the possibility to substitute materials of nearby all types.

From catalysis it is well known that a post-synthesis modification of zeolites by hydrothermal treatment [3] reduces the lattice aluminum concentration and improves the thermal stability and catalytic performance. A partial dealumination of the parent zeolite Y by steaming reduces the hydrophilic character of the zeolite as well as leads to a lower energy for water desorption. The observed healing process of the aluminium framework defects by silicon building units reduces the loss of microporous sorption volume.

The aim of this contribution is therefore to describe more in detail the steaming process and its influence on the water adsorption properties of DAY with respect to optimized adsorption/desorption heats and the influence on the secondary pore system hierarchy.

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2. Methods and materials

The adsorption properties of the potential heat pump application materials have been studied by different thermogravimetric methods (TG/DTA), the TG-programs for the H_2O desorption measurements started at 298 K and then followed by a heating range with 3 K/min up to temperature of 723 K, in permanent N_2 current of 1l/h. The samples where preconditioned for 48 h, at temperature of 298 K in a p/p_s=0,33 water atmosphere.

The investigated samples were also studied by gravimetric isotherm measurements using a McBain-Bakr quartz spring balance (tempered at 303 K). The high vacuum glass apparatus works in a pressure range between 10^{-5} up to 1013 mbar and in a temperature range between - 253K up to + 368K (± 0.1K). The apparatus has a measuring sensitivity of 4 mg / mm, with a amplitude of 0.01 mm measured with a Cathetometer. The minimum sample value is between 150 and 100 mg.

The BET nitrogen isotherms of the different DAY and parental NaY samples were measured with a Quantachrome NOVAe 2000e after outgassing the samples at a temperature of 623 K for minimum 2h.

The DAY samples were obtained by a steam treatment at 1 bar water pressure and temperatures of 673 K up to 973 K in dependence on time (1-5 h). The parent NaY zeolite with a framework Si/Al ratio of 2.6 was introduced into the active NH_4Y modification by ion-exchange. The resulting framework Si/Al ratios were characterized by infrared spectroscopic measurements using the specific double-ring vibration band at 278 cm^{-1} for the parent NaY sample for calculation.

3. Results and discussions

In Table 1 the chemical composition and adsorption capacity of the DAY samples are presented. For better overview and understanding the results of the parent zeolites NaY (Grace), SAPO-34 and Silica gel are included are presented, too. A moderate dealumination up to Si/Al=3.4 doesn't have a strong influence on the adsorption capacity, which is still comparable the reference materials that are used for heat pump applications actually. At higher Si/Al-ratios the water sorption capacity is reduced, for desorption temperatures up to 523 K. In contrast, the influence on the BET surface is quite strong. It depends on the operating temperature and healing time that is given during the synthesis. For the optimized synthesis condition process it is necessary to find a perfect combination of the three conditions temperature, healing time and Si/Al ratio.

Tab. 1: Si/Al-ratio and adsorption capacity of 48h in RH=33% (p/ps=0.33; 20.45 mbar partial water vapor pressure) conditioned samples, desorbed up to a temperature of 723 K, BET Surface.

Sample	Dealumination conditions	Si/Al	Adsorpt. capacity in g/g	BET Surface in m²/g
DAY1	673K; 1h	2.8	0.32	
DAY2	673K; 3h	3.1	0.31	
DAY3	773K; 1h	3.4	0.30	623
DAY4	773K; 3h	3.8	0.29	578
NaY		2.6	0.32	684
SAPO-34		-	0.30	630 - 650
Silica gel		-	0.20	600 - 700

From Fig.1 (see below) it is easy to find out, that the steaming process has a positive influence on the desorption capability of the modified Y-type zeolites. In spite of the difference of the desorption level that is reachable at 120°C by DAY2 and SAPO-34, the desorption kinetics of DAY2 seems to be better, due to the steeper slope of the TG-curve at the beginning.

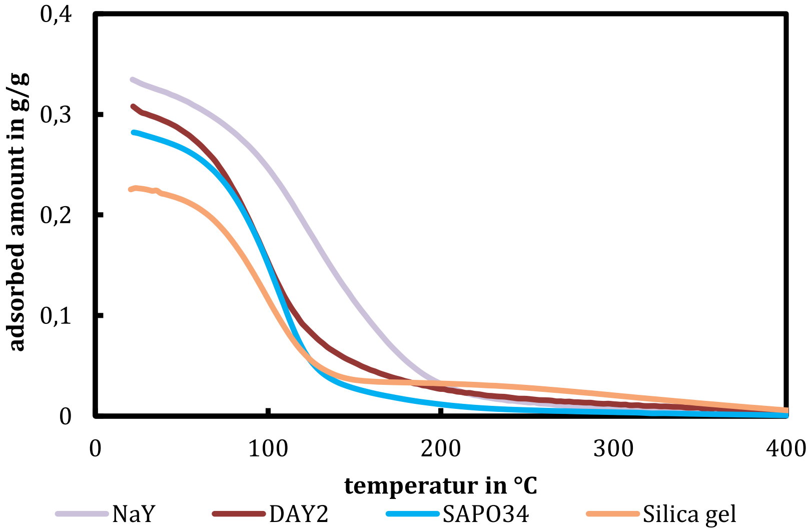

Fig. 1: Thermogravimetric profiles of the parent Y-zeolite, the dealuminated forms of Y-zeolite (DAY2) , SAPO34 and silica gel.

The low angel of the presented thermogravimetric profiles at a temperature above 200 °C is without interest for the relevant regeneration temperatures of those materials. But the clear shift from the light purple parental NaY to the dark red DAY2 curve shows that the dealuminating steaming process gives the opportunity to lower the regeneration temperature level and related to that the desorption time and performance of such a material.

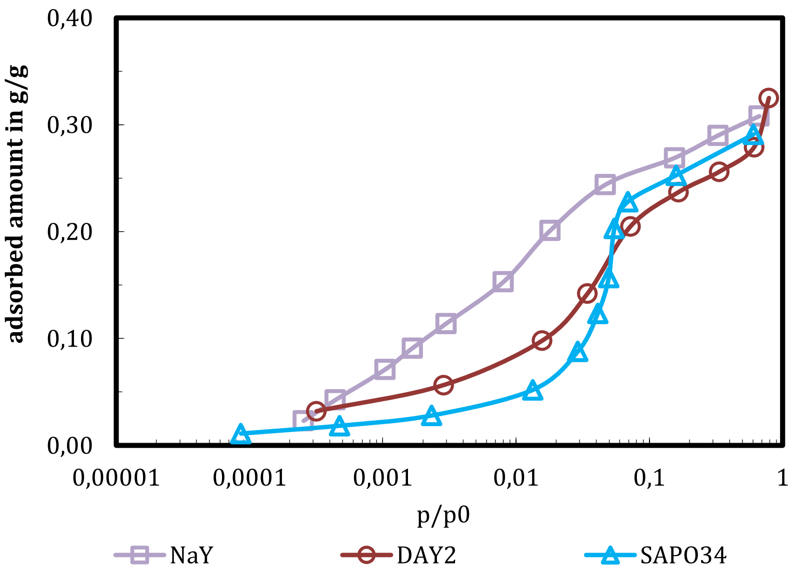

Fig. 2: Water isotherms of zeolite NaY, the dealuminated form of a Y-type zeolite and the zeotype SAPO-34 at 298 K.

The adsorption isotherms shown in Figure 2 of DAY2 and SAPO-34 show a similar beneficial steep rise in the usual working range for low temperature heat pimp applications. This results through the dealumination of the parental Y type zeolite (NaY). The Figure 2 gives also information about the position of the water isotherms of the dealuminated zeolite and the SAPO-34 compared with the parent NaY. As it can be seen, the DAY2 isotherm is shifted towards the SAPO-34 isotherm into the pressure interval between 0.01-0.3 mbar as the heat pump needs for low temperature applications.

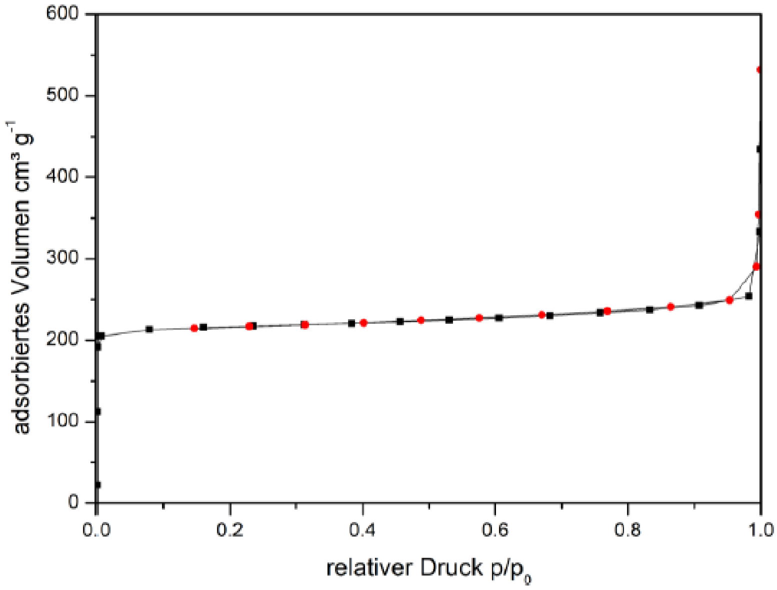

Fig. 3: Nitrogen isotherm of the parental NaY zeolite measured with a Quantachrome NOVAe 2000e after outgassing the samples at a temperature of 623 K for minimum 2h.

The influence of the dealuminting steaming process on the inner pore system of the Y-type zeolite is proven with the measurements given in Fig. 3 and 4 and the results illustrated in Table 2.The microporous inner pore structure is dissolving partly, through the influence of free H_3O^+ molecules, provided by the steaming process. Those molecules are able to remove the alumina part of the faujasite structure, in result the adsorption capacity is degrades slightly (see Tab. 1), the transformation of secondary pore system at the surface to a larger average diameter, has a positive influence on the mass transfer in and out of the material itself. Which explains the observed shift of the desorption temperature to the lower temperatures in Fig. 1. and a previous observation that the dealumination process improves the adsorption kinetic (not shown).

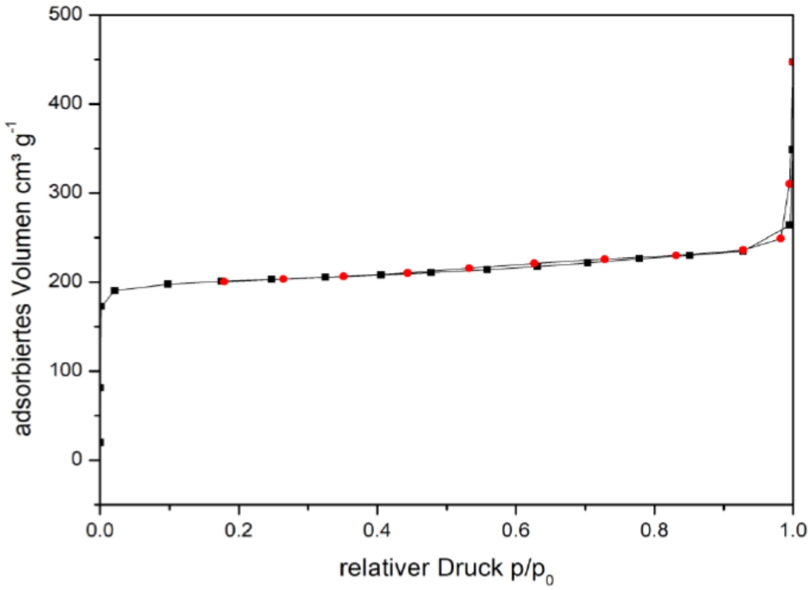

Fig. 4: Nitrogen isotherms of DAY3 zeolite measured with a Quantachrome NOVAe 2000e after outgassing the samples at a temperature of 623 K for minimum 2h.

Tab. 2: BET surface, pore diameter (BJH), pore volume (BJH), pore volume (p/p_0 = 0.97), micropore volume (t-Plot) micropore surface (t-Plot)

parameter	NAY	DAY3	DAY4	unit
BET surface	684 ± 20	623 ± 20	578 ± 20	$m^2\ g^{-1}$
pore diameter (BJH)	3,6	4,0	3,8	nm
pore volume (BJH)	0,49	0,40	0,48	$cm^3\ g^{-1}$
pore volume (p/p_0 0,97)	0,39	0,41	0,38	$cm^3\ g^{-1}$
micropore volume (t-Plot)	0,31	0,28	0,23	$cm^3\ g^{-1}$
micropore surface (t-Plot)	629	539	463	$m^2\ g^{-1}$

As it is shown in Table 2 the influence of the streaming process on the BET surface is quite strong. It depends on the operating temperature and the so called healing time (time for regenerating the disturbed inner lattice structure) that is given during the dealumination. For the optimized synthesis condition process it is necessary to find a perfect combination of the three conditions temperature, healing, time and Si/Al ratio (see Table 1).

4. Conclusions

The optimized post synthesis steaming process seems to be a powerful tool to tailor the hydrophilic character and the inner structure of Y-type zeolites and to reach the special needs of nearby all kind of heat pumps and storages.

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References

[1] Kakiuchi H., Takewaki T. et al. (2002). Adsorption heat pump, and use of adsorption material as adsorption material for adsorption heat pump. 2002. European Patent Application, EP 1 363 085 A1.

[2] Jänchen J, Ackermann D, Stach H.. Adsorption properties of aluminophosphate molecular sieves – potential applications for low temperature heat utilization. In: Wang, R.Z., Editor, SHPC 2002, Int. Sorp. Heat Pump Con., Shanghai, 2002; 635-638.

[3] McDaniel, C.W., Maher, P.K. New ultrastable form of faujasite. In: Molecular Sieves, Soc. Chem. Ind., London, 1968; 186-194.

[4] Thomas H. Herzog, Jochen Jänchen, Eythymius M. Kontogeorgopoulos, Wolfgang Lutz. Steamed Zeolites for Heat Pump Applications and Solar Driven Thermal Adsorption Storage., Energy Procedia, Volume 48, 2014, Pages 380–383, SHC 2013