Journal of Thermal Analysis, Vol. 53 (1998) 449-466

Dedicated to Professor Ferenc Paulik on the occasion of his 75th birthday

DSC AND TG STUDY OF WATER ADSORPTION AND DESORPTION ON ZEOLITE NaA

Powder and attached as layer on metal

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Abstract

Differential scanning calorimetry has been used to study the thermal effects during adsorption and desorption of water on different zeolite NaA samples. An attempt has been made to compare the thermal behaviour of a layer of zeolite attached on metal ('by chemical bond') with zeolite powder pressed on metal. The dependence of the water uptake on temperature has been studied with a powdered sample.

Isothermal measurements of the water uptake of the zeolite after activation, appeared the best way to determine the heat of adsorption. Calibration of the DSC was needed. The adsorbed amounts of water corresponding to the released heats were determined thermogravimetrically. Once the heat of adsorption is known, it is possible to determine the mass of active zeolite of thin synthesized zeolite layers on metal with DSC.

Keywords: DSC calibration, heat of water adsorption, isothermal water adsorption, zeolite NaA (metal-supported)

Introduction

Zeolites are microporous crystalline aluminosilicates with unique uniform pores of molecular dimensions. Because of their large pore volumes between 40 and 50 v% of the crystal volume they are widely used adsorbents. Their high sorption capacity for refrigerants make zeolites of interest for application in heat pump set-ups. With heat pumps low level energy can be upgraded into high level energy. The zeolite heat pump is based on adsorption and desorption cycles during which refrigerant is respectively moving in and out of the zeolite, accompanied with respectively heat release from and heat uptake by the zeolite.

In order to obtain a fast transport of the heat which is involved in the sorption cycles, alternating layers of zeolite and metal are applied. Optimisation of this principle is studied in this project by synthesizing the zeolite directly on the met-

1418–2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

al support. A better contact between the grown zeolite layer and the metal, possibly established by a chemical bond, and a higher density of the grown zeolite layer are assumed to improve the performance of the conventional zeolite heat pump in which zeolite is pressed onto the metal. For the new system a better heat transfer between the zeolite and the metal and a higher thermal conductivity of the zeolite layer are expected. In order to have a fast enough mass transport through the zeolite layer, only thin grown layers are of interest.

With respect to this project the zeolite NaA–water pair was selected. Water has a large heat of evaporation and besides it is environmentally friendly. Zeolite NaA is a very hydrophilic zeolite which can be synthesized easily.

In order to study the water sorption behaviour of "fixed" metal-supported zeolite compared to free crystals, DSC measurements have been carried out. The amounts of adsorbed and desorbed water of the studied samples were determined by thermogravimetry (TG measurements).

Theory

Zeolite NaA

The cubic framework structure of zeolite NaA is shown in Fig. 1 [1]. The pseudo unit cell ($Na_{12}[Al_{12}Si_{12}O_{48}]\cdot27H_2O$, 1/8 of the true unit cell) of zeolite NaA consists of $12SiO_2$- and $12AlO_2$-units, enclosing a large cavity (α-cage, $\varphi=11.4$ Å) and a small cavity (β-cage, $\varphi=6.6$ Å) [2]. The negative charge introduced by each aluminum atom in the framework, is counterbalanced by a sodium ion. Of the 12 sodium ions in the pseudo unit cell, 8 are located near the centre of the 6-rings and the remaining 4 sodium ions are present in the 8-rings. The coordination of water molecules by the sodium ions causes a highly hydrated zeolite NaA. When fully hydrated, there are 27 water molecules in the pseudo unit cell. Most of the water molecules are located in the α-cage in a pentagonal dodecahedral arrangement (cluster of 20 molecules). The β-cage has space for 4 water molecules. The remaining 3 water molecules are adsorbed at the side-faces. The maximal water sorption capacity of dry zeolite NaA is 28 w%, from which 21 w% for α-water, 4 w% for β-water and 3 w% for the side-face water molecules.

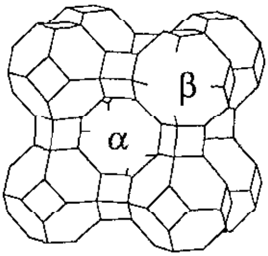

Fig. 1 Framework structure of zeolite NaA [1]. The position of the α- and β-cages is indicated

The water molecules can be removed from the zeolite by heating in a dry purge gas such as nitrogen or during evacuation. At temperatures higher than 0°C nitrogen is not adsorbed by zeolite NaA. Although the nitrogen molecules (σ=3.64 Å) are small enough to enter the α-cage via the 8-rings (φ=4.2 Å), they are not able to displace the sodium ions (σ=0.98 Å) which are located in these rings, like the water molecules (σ=2.65 Å) do by dipole-cation interaction [2].

The heat which is released during the adsorption of water on zeolite NaA is much higher than the heat of sublimation of water, being 50 kJ (mol H_2O)$^{-1}$ [3]. Breck *et al.* [2] report isosteric heats of adsorption of 126 and 74 kJ (mol H_2O)$^{-1}$ for respectively 10 and 80% zeolite loadings. Mizota *et al.* [4] found a value of 64 kJ (mol H_2O)$^{-1}$ for the hydration enthalpy of NaA dehydrated 1 h at 100°C in vacuum.

The thermal stability of zeolite NaA is rather good. It can be used up to about 700°C. Above 800°C loss of structure occurs which is accompanied with a reduced water capacity [5].

DSC

DSC can be used to follow the thermal behaviour of sorption processes. The rate in which the heat flow signal changes is related to the heat performance of the sample. DSC should therefore be suitable to see a difference in thermal sorption behaviour, if there is, between the metal-supported 'fixed' zeolite and free pressed zeolite powder on metal.

The peak area under the heat flow versus time curve is related to the sorption heat. During heating runs however, the position of the baseline depends on the heating rate and on the difference in specific heat of the sample and the reference [6]. Since the desorption of water from hydrated zeolite results into a severe decrease of the specific heat, the construction of the baseline cannot be very accurate. Further the loss of water starts immediately in flowing nitrogen at room temperature, so the onset and the initial baseline of the endothermic DSC signal are difficult to determine when starting a linear heating program from room temperature. Measurement at a constant temperature of the water uptake response of the dehydrated zeolite is a better way to determine the heat of adsorption. Then $dT/dt=0$, so the change in specific heat has no influence on the DSC signal. From the peak area under the heat flow versus time curve, the heat of adsorption can be obtained according to:

$$\Delta H_{\mathrm{ads}}=\frac{A_{\mathrm{peak}}CF}{m_{\mathrm{w}}} \qquad (1)$$

For an explanation of the symbols the reader is referred to the end of the article.

Not all the released heat of adsorption is measured by the DSC sensor, also a part will flow directly into the surrounding gas phase, particularly when using an open pan and a not well conducting sample. The fraction of heat which flows to the sensor depends on the thermal properties of the sample and of the gas phase. The calibration factor will compensate for this effect, and is defined as the ratio between the real melting heat and the measured melting heat:

$$CF = \frac{(\Delta H_m)_{real}}{(\Delta H_m)_{meas}} \tag{2}$$

The calibration factor is determined with two experiments: (1) Melting of a pure metal on top of the sample (CF_s); and (2) Melting of a pure metal in an empty pan (CF_b). The value of CF_s corresponds to processes which proceed at the outside of the sample, like catalytic gas reactions [7]. For processes which proceed in the complete sample, as studied in this article, the average value between the values of CF_s and CF_b is a better estimation for the calibration factor and thus:

$$CF = 0.5(CF_s + CF_b) \tag{3}$$

The mass of water which is related to the thermal event can be determined indirectly with a thermobalance:

$$m_w = x_{wet} m_{z,i} \tag{4}$$

The computer connected to the DSC equipment calculates directly the ratio between the peak area under the DSC curve and the initial zeolite mass and will be called the measured heat:

$$q_{meas} = \frac{A_{peak}}{m_{z,i}} \tag{5}$$

The corrected measured heat refers to the heat in which the calibration factor has been taken into account:

$$q_{corr} = q_{meas} CF \tag{6}$$

Experimental

Sample preparation

Four different zeolite NaA samples have been studied (Fig. 2).

(A) Zeolite A powder (φ ~1 μm) delivered by Degussa, slightly compacted by hand pressing with a flat piece of metal in an aluminum DSC pan (φ ~5.5 mm) (Fig. 2a).

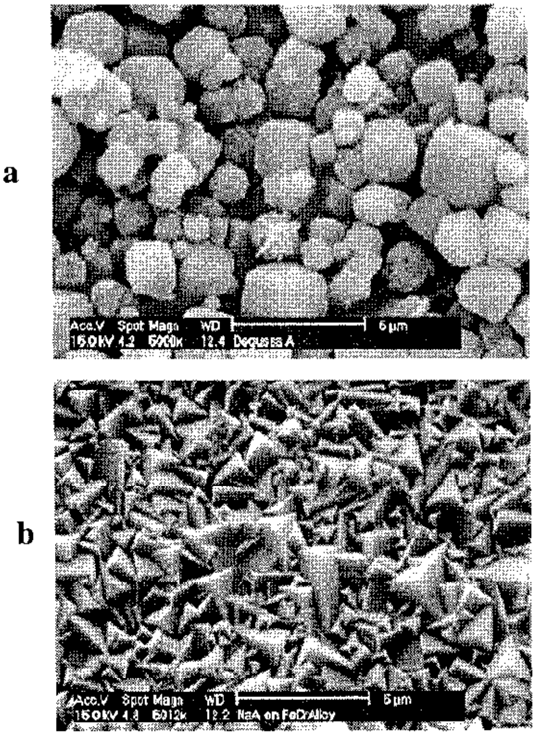

Fig. 2 SEM images of investigated zeolite A samples. (a) Degussa A powder, as received from producer, and (b) self-synthesized zeolite A on FeCrAlloy foil

(B) Some of these powdered samples underwent a hydrothermal treatment in a closed autoclave at 160°C during one week. After this treatment a rather well fixed layer of crystals was present within the aluminum pan. The bulk of the crystals seemed firmly attached to each other. This steaming treatment caused oxidation of the aluminum pan (white discoloration). Also some transformation of zeolite A into another phase seems to happen. The steamed samples will be referred to as 'coarse crystalline samples' in the following.

(C) Attempts were made to grow a zeolite layer directly inside a DSC pan. The common aluminum pan could not be used, because it dissolves in the strongly alkaline zeolite synthesis mixture with a molar composition of $5SiO_2$:Al_2O_3:$50Na_2O$:$1000H_2O$ [8]. Better results were obtained with copper pans. The reaction mixture inside the copper pan formed after 3–5 h at 80°C, a thin (few µm's) porous layer of zeolite NaA on the inner wall of the pan. The outside of the copper pan was blackened, probably by the formation of surface oxides.

(D) The best results were obtained by crystallization of zeolite NaA on temperature treated FeCrAlloy foil. Flat circular discs of this material (φ~5.6 mm and d~90 µm) with on both sides a compact layer of zeolite NaA, obtained by repeated syntheses with the disc in vertical position, have been tested also (Fig. 2b).

In all cases the samples were kept in a desiccator with a supersaturated solution of ammonium chloride, which established a relative humidity of about 80% (p_W~14 mm Hg at 20°C). The samples were weighed on a Sartorius analytic balance A200S with a sensitivity of 0.1 mg. The mass of the calibration metals was determined on a Sartorius microbalance with a sensitivity of 1 µg.

DSC measurements

DSC measurements were performed with a DSC Gold cell from Rheometric Scientific. The investigated samples were placed on the sample side of the DSC cell, while the reference side contained an identical open DSC pan filled with Al_2O_3 powder (often twice the mass of the hydrated zeolite). Because interaction with the gas phase should be investigated, no lids were used. In the case of the thin zeolite samples, grown in a copper pan, an empty copper pan was used on the reference side, while during the DSC experiments with zeolite synthesized on FeCrAlloy foil discs, a blank disc of this type of foil was used on the reference side.

The gas flow through the DSC cell consisted of pure nitrogen (2 l h^{-1}) or a nitrogen/water mixture, saturated in an evaporator filled with ice (p_W~4.6 mm Hg), also at a flow rate of about 2 l h^{-1} (measured at room temperature). Sometimes higher water vapour pressures were used by evaporation at room temperature (p_W~17.5 mm Hg).

In the first experiments the zeolite was activated to 450°C with a heating rate of 3°C min^{-1} in order to determine the desorption heat, but as discussed before, quantification of the results was not possible. Later on, the activation temperature was lowered to 300°C in most experiments.

In general the experiments consisted of several steps: (a) Equilibration in dry nitrogen during 10 min at 0°C; (b) Linear heating to 300°C with a rate of 10°C min^{-1}; (c) An isothermal step at 300°C, for the removal of all the water from the sample and from the DSC cell, during 30 min; (d) Cooling down to a constant temperature between 40 and 300°C with a rate of 20°C min^{-1}; (e) An isothermal step at this temperature, during which the dry nitrogen was changed into a wet nitrogen flow; (f) When the signal was back to the baseline, sometimes the wet nitrogen flow was changed into a dry nitrogen flow again, while the temperature remained constant; (g) Sometimes the water adsorption peak was measured for a second time. The experiments (step (a)–(g)) were sometimes repeated, in order to test the cyclic behaviour of the zeolite sample (Fig. 4).

With each sample calibration measurements were carried out by melting small flat pieces of gallium, indium or tin on top of the zeolite. The melting heats of the metals in empty pans were also measured. The literature melting heats of gallium, indium and tin are respectively 79.87, 28.62 and 60.40 mJ mg^{-1} and their melting temperatures are respectively 29.765, 156.60 and 231.93°C [9].

TG measurements

The amounts of water involved in the sorption process of the different samples were determined with a self-developed thermobalance, provided with a C.I. electronics balance [10]. The sample department consisted of a quartz tube. The gas flew over the sample, but below the sample a dead volume existed. For this reason the response of the balance upon changes of the gas flow is rather slow. The samples were contained in a flat quartz crucible with a large diameter (φ~14.5 mm), in order to establish a good contact between the zeolite sample and the surrounding gas.

The water loss was determined at different temperatures up to 600°C. For the measurement of the adsorption of water the zeolite was first activated at 300°C in a dry nitrogen flow of about 4 l h^{-1} until constant mass. Then the sample was cooled down to an isothermal temperature between 40 and 300°C, after which the dry nitrogen flow was changed into a nitrogen flow saturated with water vapour at 0°C (p_w~4.6 mm Hg). The increase in mass up to a constant maximum value was recorded. The water uptake was calculated by taking the mass difference between this maximum value and the isothermal (dry) mass at 300°C.

Results and discussion

TG measurements

Hydrated Degussa A powder lost 20.1 w% of the initial mass of the zeolite sample (~80 mg) upon heating from 20 to 450°C in a dry nitrogen flow, see Fig. 3. Heating to 200°C showed an initial mass loss of 16.5 w%, increasing to a nearly constant value of 17.2 w% during 2 h of isothermal treatment at 200°C. Heating to 300°C resulted into a mass loss of 17.7 w%, respectively 18.1 w% of the initial zeolite mass. The mass loss after heating to 600°C was 20.5 w%. At this temperature the zeolite is assumed to be dry. The water content of the (fully) hydrated Degussa A is thus 25.7 w% based on the mass of the dehydrated zeolite. This figure is somewhat lower than the theoretically expected sorption capacity, being 28 w%, indicating that the starting zeolite sample is not completely filled with adsorbed water. This is probably caused by the preliminary storage at 80% humidity, resulting into the preliminary loss of water which is located in the sidefaces.

Most of the mass loss occurs in the range up to 200°C, while the last 4–5 w% water is removed at higher temperatures. This behaviour agrees quite well with what is expected: first desorption of water from the α-cages and then from the β-cages.

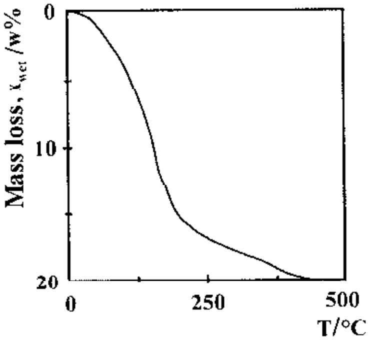

Fig. 3 TG curve of the dehydration in dry nitrogen (~4 l h^{-1}) of a 83 mg Degussa A powder sample in the range between 20 and 450°C with a heating rate of 3°C min^{-1}

Adsorption measurements at 40 and 60°C with Degussa A powder samples activated at 300°C showed water uptakes of respectively 15.7 and 13.6 w% of the initial zeolite mass, see Table 3. One measurement with a coarse crystalline Degussa A sample at 40°C showed a water uptake of 11.0 w% of the initial zeolite mass (the amount which was put in the pan before the steaming treatment). The water sorption capacity of the hydrothermally treated Degussa A powder seems thus somewhat lower than for the untreated powder. The forming of an other phase can be an explanation herefore. The sensitivity of the thermobalance was too small to measure the water loss of the zeolite grown in the copper pan and the zeolite crystallized on the FeCrAlloy foil disc.

DSC measurements

DSC response of zeolite A

In Fig. 4 the response of a DSC measurement with the zeolite A–water system is given. Four different peaks have been measured and will be discussed now.

(I) Linear heating of the sample from 0 to 300°C (step (b)) showed a large endothermic peak, corresponding with the desorption of water from the zeolite. The top of the peak varied between 100 and 150°C, depending on the size and configuration of the zeolite sample in the pan. Higher masses of zeolite or higher heating rates did shift the peak to somewhat higher temperatures. The same trend was observed when the desorption was performed in a wet nitrogen flow instead of a dry nitrogen flow.

The desorption started immediately after the programmed heating started. As discussed before, the determination of the desorption heat from the heating curve is difficult, since the baseline changes a lot during the desorption process, caused by the very high decrease of the specific heat of the sample. Also the corresponding mass loss (measured by TG) is not very accurate, since the sample already

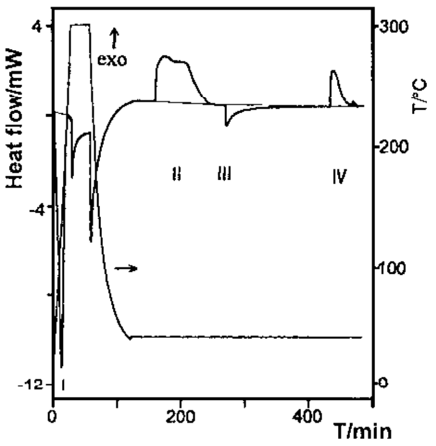

Fig. 4 DSC measurement of a 12.9 mg Degussa A powder sample. Responses of the heat flow and temperature *vs.* time.
(I) Desorption of water in nitrogen; $A_{peak} = +494$ J (g initial sample)$^{-1}$;
(II) Adsorption of water (p_w~4.6 mm Hg) at 40°C; $A_{peak} = -555$ J (g initial sample)$^{-1}$;
(III) Desorption of water in nitrogen; $A_{peak} = +101$ J (g initial sample)$^{-1}$;
(IV) Adsorption of water; $A_{peak} = -128$ J (g initial sample)$^{-1}$.
The other peaks are due to changes in the temperature/time program

loses water at room temperature in dry nitrogen, before the measurement is started. For these reasons this desorption peak has not been used for further evaluation.

(II) After dehydration of the zeolite sample at 300°C and cooling down to a constant temperature, the change from a dry into a wet nitrogen flow (step (e)) resulted in a fast exothermic signal, caused by the uptake of water by the zeolite. When the adsorption was completed the DSC signal came back to the baseline. The area of this exothermic peak could be measured quite well, since the baseline before and after this effect is about the same.

(III) After completion of the adsorption in a wet nitrogen flow at isothermal temperature, the change into a dry nitrogen flow showed again an endothermic peak. The peak area of this desorption peak was much smaller than of the exothermic water uptake peak before, indicating that only a part of the water could be removed from the zeolite at this low temperature.

(IV) After completion of the desorption at isothermal temperature, a switch from a dry to a wet nitrogen flow again showed an adsorption peak with also a small peak area, with a heat effect corresponding to the desorption of the foregoing step.

Calibration

In Table 1 a summary of the calibration experiments is given. As can be seen the value of *CF* depends on the nature of the calibration metal (and thus on the temperature of the measurement) and on the nature and size of the sample. The contact between the sample and the sensor has also influence on the *CF* value.

Table 1 Calibration factors determined with pieces of gallium, indium or tin on top of different zeolite A samples. $CF=0.5(CF_s+CF_b)$ for the Degussa A samples (A and B)

Sample no.	m_{sam}/ mg	m_{ref}/ mg	CF_s values for			CF values for		
			Ga	In	Sn	Ga	In	Sn
A1	12.9	25.8	0.97	0.97	1.11	0.88	0.93	1.10
A2	21.7	41.5	1.16	1.21	1.25	0.97	1.05	1.17
B1	21.3	41.1	1.10	x	x	0.94	x	x
C1	(0)	0	0.91	x	x	0.91	x	x
D1	(0)	0	0.77	x	x	0.77	x	x
				CF_b values*				
Blank	0	0	0.78	0.88	1.09			

* The CF_b values are the same for untreated sample pans (samples A) and for oxidized pans (samples B)

The thermal conductivity of the zeolite will decrease at higher temperatures due to the dehydration of the zeolite. During the melting of gallium, zeolite A is nearly completely filled with water, while at the melting temperature of indium and tin, zeolite A is rather empty. It can therefore be expected that with gallium the lowest calibration factor will be obtained. Indeed, the *CF* values of the three calibration metals did increase, going from Ga → In → Sn. Further, tin appeared difficult to measure, due to some reaction and the tendency to change from a flat piece into a ball.

A better contact between the crystals is reflected in a lower value of CF_s. The powdered sample (A), with the lowest thermal conductivity, give the largest value of CF_s. A better packing of the crystals reduces the CF_s value. The thermal conductivity of the coarse crystalline sample (B) is better than for the powdered sample, reflected in a lower value of CF_s. The thermal conductivity of both other samples (C and D) is nearly the same as for the blank metal, because of the very thin zeolite layers and the good thermal contact between the zeolite and the metal support, and resulted into the lowest values of CF_s. For the samples C and D no difference was found between the corresponding values of CF_s and CF_b.

The size of the sample plays an important role for less conducting samples. For a smaller amount of Degussa A powder a lower CF_s value is obtained, which can be expected from the reduced layer thickness.

It was found that the CF_b values for oxidized pans (samples B) are about the same as for untreated sample pans (samples A).

Water adsorption

Some DSC curves of the water adsorption at 40°C are shown in Fig. 5 and the relevant figures are tabulated in Table 2. It can be seen that:

- The maximum adsorption rate depends on the water supply rate and is nearly independent of the sample size and structure. In the measurements with the coarse crystalline Degussa A sample (B1) the heat flow rises almost 4 times higher when a water vapour pressure of 17.5 instead of 4.6 mm Hg was applied in the adsorption step.
- All samples show a fast initial heat flow increase until a maximum value. This maximum value is remained during a great part of the adsorption process, indicating that the rate determining step is formed by the transport of water vapour through the gas phase to the surface area of the sample. A difference in response between the fine and coarse crystalline Degussa A powder could therefore not be observed. To observe any difference, smaller samples or higher water supply rates should be used.
- Activation of the zeolite at 300°C for 30 min gives comparable heats of adsorption in repeated measurements. Longer activation times however, will result into a somewhat higher water loss which will be accompanied by a higher observed heat effect in the subsequent isothermal adsorption step. For that reason a higher heat was measured for the 21.7 mg Degussa A sample (A1) after overnight heating at 300°C, namely 554 J (g initial sample)$^{-1}$ (run 2) compared to 488 J (g initial sample)$^{-1}$ (run 1). Measurements with a coarse crystalline Degussa A sample (B1) showed also that after twice subsequently heating to 300°C for 30 min a higher adsorption heat effect is measured, being 532 J (g initial sample)$^{-1}$ (run 2) instead of 463 J (g initial sample)$^{-1}$ (run 4).
- The measured value for the heat of adsorption seems dependent on the sample size. The value for the 12.9 mg Degussa A sample (A1) is somewhat lower than for the 21.7 mg sample (A2), respectively 535 and 489 J (g initial sample)$^{-1}$ (run 1). It indicates that during the cooling down from 300 to 40°C in dry nitrogen already some water on the zeolite was adsorbed. This undesired uptake of water which remains anywhere in the equipment, will have a relatively greater effect for a smaller sample than for a larger sample.

Although the reproducibility of the DSC measurements is rather good, the translation of the measured peak areas into values for the heat of adsorption is difficult. The involved amount of adsorbed water is difficult to measure and introduces the greatest error in the calculated values of the heat of adsorption, especially in the case of low water fractions. With the TG experiments an estimation can be obtained. However, because the sorption properties of zeolites are somewhat time dependent, the conditions in both set-ups will not exactly be the same. There is a great difference in adsorption efficiency between both types of measurements (DSC and TG), as will be discussed in the next paragraph. A set-up in which the adsorbed amount of water is simultaneously measured with the corresponding heat of adsorption, like Gatta [11] reported, is preferred. Besides, adsorption and subsequent desorption of water in cold parts of the instrument is a serious problem, since zeolite A is already hydrated to some extent at very low water vapour pressure.

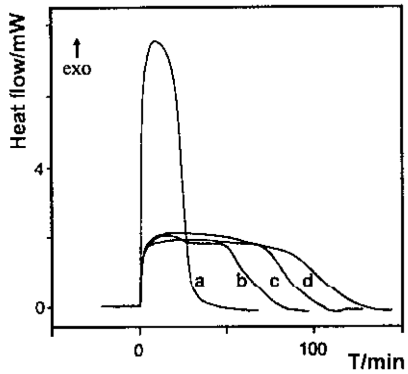

Fig. 5 DSC heat flow responses of different Degussa A powder samples during water adsorption at 40°C. Coarse crystalline Degussa A: 21.3 mg, p_w= (a) 17.5 mm Hg and (c) 4.6 mm Hg; Degussa A powder: (b) 12.9 mg and (d) 21.7 mg, p_w = 4.6 mm Hg

Table 2 Heats of adsorption calculated from the measured peak areas under the water uptake responses of Degussa A samples at 40°C, using the *CF*-Ga values of Table 1. In general p_w~4.6 mm Hg, but for two experiments (B1, run 2 and run 4) p_w~17.5 mm Hg. The activation of the zeolite differed from the standard program in two measurements, resp. overnight at 300°C (A1, run 2) and heating twice to 300°C for 30 min (B1, run 2)

Sample no.	Meas. no.	m_{sam}/ mg	*CF*	q_{meas}/ J (g sam)$^{-1}$	q_{corr}/ J (g sam)$^{-1}$	x_{wet}/ w%	ΔH_{ads}/ kJ (mol H_2O)$^{-1}$
A1	1	12.9	0.88	555	488	15.7	56
"	2	"	"	629	554	(17.2)*	(58)
A2	1	21.7	0.97	551	534	15.7	61
"	15	21.0	"	546	530	15.7	61
B1	1	21.3	0.94	463	435	11.0	71
"	2	"	"	566	532	x	x
"	3	"	"	454	427	11.0	70
"	4	"	"	493	463	x	x

* This figure is the water uptake after drying for a long time at 300°C

For the experiment with about 21 mg of Degussa A powder (A2) the measured heat of adsorption is 532 J (g initial sample)$^{-1}$. Combined with the TG experiment (15.7 w% uptake) this corresponds with a heat effect of (0.532×18/0.157=) 61 kJ (mol H_2O)$^{-1}$. For the coarse crystalline sample (B1) the average measured heat of adsorption is 431 J (g initial sample)$^{-1}$ (under standard conditions). Combined with the 11.0 w% mass increase found by TG, this results into a heat effect, being (0.431×18/0.110)=71 kJ (mol H_2O)$^{-1}$. The difference in heat of adsorption between both types of samples lies within the range of error.

Calculation of the adsorption efficiency from the gas phase for TG and DSC

The time needed for the isothermal water uptake lasted with DSC much shorter (10–100 min) than with TG (20–40 h). An explanation for the great difference in duration of time of both measurement techniques can be found in the different size and geometry of the sample. In the DSC experiments the sample size was about four times smaller than in the TG experiments (20 mg *vs.* 80 mg). Besides the contact between the flowing gas and the sample was in the DSC experiments better than in the TG experiments. In the DSC cell the gas flows directly over the sample, while in the thermobalance there is some distance between sample and flowing gas.

The maximum mass increase rate, measured during the isothermal TG experiment at 40°C with 82.7 mg Degussa A powder, was 0.94 mg H_2O h^{-1}. The wet nitrogen flow (~4 l h^{-1}; p_w~4.6 mm Hg) transports 17.3 mg H_2O h^{-1}, so the efficiency of the adsorption process is only 5.4%.

In case of the isothermal DSC experiments at 40°C with 20.7 mg Degussa A powder, the maximal DSC signal is 2.3 mW, using a wet nitrogen flow (2 l h^{-1}; p_w~4.6 mm Hg). When for <*CF*> a value of 0.97 and for the heat of adsorption a value of 3.4 J mg^{-1} is taken, a water uptake rate can be calculated, being (0.0023×0.97×3600 [J h^{-1}])/(3.4 [J mg^{-1}])=2.4 mg H_2O h^{-1}. The inlet rate is 8.7 mg H_2O h^{-1}, thus the adsorption efficiency is (2.4/8.7)=27% for the DSC experiment.

Adsorption at different temperatures

The temperature dependence of the water uptake response has been studied with a Degussa A powder sample (A2) in the range from 40 to 300°C. Some of the adsorption DSC curves are shown in Fig. 6 and the relevant data are given in Table 3. As can be seen the measured heat effect reduces strongly at higher temperatures. A rise in temperature does not have effect on the step height of the water uptake response, but two transport regions become visible.

In Fig. 7 the corrected measured heat is plotted as a function of the temperature. It shows two kinds of water are adsorbed: low temperature water (*L*) and high temperature water (*H*). At the lower temperatures the measured heat effect decreases continuously. At higher temperatures, above 150°C, the heat effect remains nearly constant, corresponding to a water adsorption of about 1.5 w%. With the thermobalance a mass loss of 2.4 w% was measured between 300 and

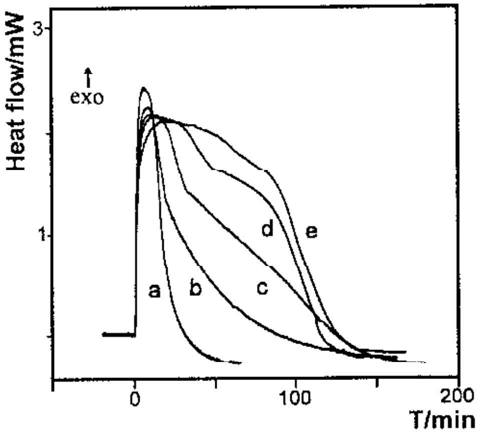

Fig. 6 DSC heat flow responses of a 21.7 mg Degussa A powder sample during water adsorption ($p_w \sim 4.6$ mm Hg) at different temperatures: (a) 140, (b) 100, (c) 80, (d) 60 and (e) 40°C

Table 3 Isothermal water adsorption on a 21 mg Degussa A powder sample (A2) in an aluminum pan at different temperatures. Most of the *CF* values were estimated by extrapolation, using the *CF*-Ga, *CF*-In and *CF*-Sn values of Table 1 for resp. 40, 160 and 240°C

Meas. no.	T/ °C	CF	q_{meas}/ J (g sam)$^{-1}$	q_{corr}/ J (g sam)$^{-1}$	x_{wet}/ w%	ΔH_{ads}/ kJ (mol H_2O)$^{-1}$
1	40	0.97	551	534	15.7	61
2	60	0.98	498	488	13.6	65
3	80	1.00	394	394	(11.3)*	(63)
4	100	1.01	210	212	(6.1)*	(63)
5	120	1.02	122	124	(3.5)*	(63)
6	140	1.04	114	119	(3.4)*	(63)
7	160	1.05	75	79	(2.3)*	(63)
8	180	1.08	70	76	(2.2)*	(63)
9	200	1.11	61	68	(1.9)*	(63)
10	220	1.14	65	74	(2.1)*	(63)
11	240	1.17	52	61	(1.7)*	(63)
12	260	1.20	42	50	(1.4)*	(63)
13	280	1.23	48	59	(1.7)*	(63)
14	300	1.26	51	64	(1.8)*	(63)
15	40	0.97	546	530	15.7	61

*Calculated figures, assuming that ΔH_{ads}=63 kJ (mol H_2O)$^{-1}$

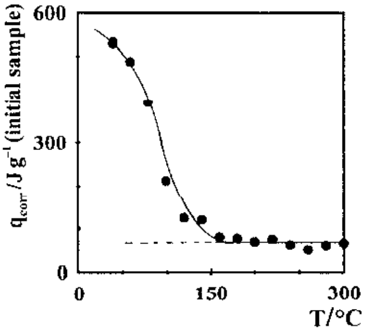

Fig. 7 Heat of adsorption (J (g initial sample)$^{-1}$) for a Degussa A–water system as a function of the temperature

600°C. Together with the 1.5 w% this is 4 w%, which corresponds with the theoretical amount of water in the β-cages. So, above 150°C only adsorption of water in the β-cages occurs.

Investigation of self-synthesized thin zeolite layers on metal

The water uptake responses of the thin synthesized zeolite layers (C and D) at 40°C could be measured quite well with DSC. However it was not possible to obtain values for the heats of adsorption from the peak areas of these samples, because their masses were not well known and their water losses could not be measured thermogravimetrically.

When the heat of adsorption is known, the peak area can be used to estimate the mass of the zeolite sample. By assuming that the adsorption data measured with Degussa A samples (A) are valid, a zeolite mass of about 0.2 mg could be found for both self-synthesized samples (C1 and D1). In Table 4 relevant figures are tabulated. With a balance for both samples a mass of about 0.6 mg was found, assuming that the mass of the sample holder (copper pan or FeCrAlloy disc) remained unchanged during the preparation of the zeolite layer. This mass differ-

Table 4 Water adsorption on very small zeolite samples grown on metal at 40°C, using the *CF*-Ga values of Table 1, and assuming q_{corr} = 532 mJ (mg initial sample)$^{-1}$ (see the result of sample (A2) in Table 2)

Sample no.	$m_{z,i}$/ mg	Meas. no.	*CF*	q_{meas}/ mJ	q_{corr}/ mJ	$(m_{z,i})_{calc}$/ mg
C1	~0.6	1	0.91	153	139	0.26
"	"	2	0.91	112	102	0.19
"	"	3	0.91	114	104	0.19
"	"	4	0.91	108	98	0.18
D1	~0.6	1	0.77	135	104	0.19

ence between DSC and balance measurements can be explained by three factors: (1) The real mass of the zeolite is lower than 0.6 mg, caused by mass increase of the sample holders (oxidation) during the preparation procedure; (2) It is possible that not all the zeolite is active; and (3) During the cooling of the zeolite after activation at 300°C some water adsorption has already taken place. For very small samples this water uptake can be very important, and could explain the difference between the first and subsequent experiments with sample (C1).

Conclusions

- The adsorption of water on large zeolite A samples (10–30 mg) can be measured quite well with DSC.
- DSC experiments are more sensitive and faster than TG experiments, also because the needed sample mass is smaller in the case of DSC (10–30 mg *vs.* 80 mg).
- The gas efficiency for water adsorption from the gas flow is for the applied DSC about 27% and for the thermobalance about 5%.
- TG experiments are needed for measurement of the exact mass changes during the desorption and adsorption processes.
- The initial mass loss of the wet zeolite Degussa A powder is 17.2 w% after heating to 300°C and 18.1 w% to 450°C. The final mass loss, after heating to 600°C, is 20.5 w% of the initial (wet) zeolite mass.
- The adsorption of water at 40°C in a nitrogen flow mixed with water vapour (p_w~4.6 mm Hg) shows a mass increase of 15.7 w% and at 60°C 13.6 w% for Degussa A powder activated at 300°C. For the coarse crystalline Degussa A, obtained by hydrothermal treatment for 1 week at 160°C, the mass increase is 11.0 w% at 40°C. At higher water vapour pressures these figures will be somewhat higher.
- For exact DSC measurements calibration factors have to be measured by melting pure pieces of metal (gallium, indium, tin) on top of the sample and in an empty pan.
- The calibration factors of the coarse crystalline Degussa A samples are somewhat smaller than of the untreated Degussa A powders, indicating that the thermal contact between the crystals is improved by hydrothermal treatment.
- The measured heat effect upon water adsorption at 40°C is 535 J (g initial sample)$^{-1}$ for Degussa A powder activated at 300°C and 435 J g^{-1} for the coarse crystalline Degussa A sample.
- From the TG experiments heats of adsorption of respectively 61 and 71 kJ (mol H_2O)$^{-1}$ are obtained. The difference between both values lies within the error range.
- In the temperature range from 40 to 150°C a continuous decrease in heat effect is observed. At higher temperatures the measured heat remains constant, and corresponds to occupancy of only the ß-cages of the zeolite.

- For very small samples (0.1–1 mg), like thin zeolite layers on metal, it is possible to measure the water uptake response. The quantification of the measured heat effect is difficult because the mass of the adsorbed water or of the zeolite can not be measured well for these samples.
- Once the heat of adsorption is known, DSC can be used to determine the mass of the zeolite.
- For exact measurements condensation of water in the cold parts of the equipment has to be avoided, especially when very small samples are measured. In the applied DSC equipment this problem was encountered, causing the greatest error in the determined values for the heat of adsorption.

List of symbols

Symbol	Description	Unit
A_{peak}	peak area under DSC curve	mJ
CF	calibration factor (average of CF_b and CF_s)	–
CF_b	calibration factor of blank experiment	–
CF_s	calibration factor of sample experiment	–
d	thickness	μm
ΔH_{ads}	heat of water adsorption	$J\ (mol\ H_2O)^{-1}$
ΔH_m	melting heat of a pure metal	$J\ g^{-1}$
m_w	mass of adsorbed or desorbed water	mg
$m_{z,i}$	initial zeolite mass	mg
p_w	water vapour pressure	mm Hg
q_{corr}	corrected (for CF) measured heat effect	$J\ (g\ sample)^{-1}$
q_{meas}	measured heat effect	$J\ (g\ sample)^{-1}$
t	time	s, min
T	temperature	°C
x_{wet}	mass fraction of water molecules which are adsorbed or desorbed, based on the initial (hydrated) zeolite mass	g/g, w%
σ	Kinetic diameter	Å
φ	Diameter	Å, μm, mm

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