

# IMMOBILIZATION OF ZEOLITES AND THEIR STABILITY ON CERAMIC SUPPORTS WITH HIGH THERMAL CONDUCTIVITY FOR THERMOCHEMICAL STORAGE OF HEAT

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## Abstract

The immobilization of zeolites and their hydrothermal stability on alumina and cordierite of different porosity and heat conductivity was investigated. Alumina with a porosity of 30% can be used for the deposition of the molecular sieves NaX, NaA and CaNaA. The zeolite P (Doucil A24) is unsuitable for those purposes also because of the poor hydrothermal stability.

CaNaA, based on the inexpensive ion exchanger Wessalith P, shows a reasonable long term stability and could be applied for the development of a thermochemical storage with ceramic heat exchanger.

## Introduction

Zeolites and other porous materials are of increasing interest for utilization as storage materials for thermochemical storage of heat such as solar heat, waste heat in industry or surplus of district heat (Mittelbach et al., 2000, Hauer et al., 1999, Levitskij et al., 1996, Jänchen et al., 2000). Open systems with a gas flow (such as air as carrier for the adsorbate and the heat) through the storage, filled with the granulated adsorbens do not have big problems with heat and mass transfer. In a closed system, however, the presence of impurities in the vapor phase of the storage slows down the diffusion of the water vapor in the pores of the storage material. Thus, the mass transfer is the best in a well evacuated storage. Because of the poor heat conductivity of zeolites (0.58 W/m K) or silica gel (0.14-0.2 W/m K) the heat transfer within the granulated storage material is slow. Consequently, measures have to be taken to improve the heat flow by shortening the flow distance and by improving the contact between the active storage material and the surface of the heat exchanger to get a better heat flow from the zeolite to the heat exchanger and vice versa.

Different methods have been applied to immobilize zeolites on different surfaces (Mueller et al. 1993, Tatlier and Erdem-Senatarlar, 1999) by direct synthesis of zeolites on metal surfaces (for heat pump application) or by glue the zeolite crystals to a partially molten glass surface. However, glass is not a very good heat conductor and metal is chemically different from the (inorganic) zeolitic materials which may cause problems with the adhesive strength of the zeolite on the support. Thus, we tried to immobilize zeolites on an inorganic support characterized by a good heat conductivity such as special ceramics.

In the present paper we focus on the immobilization of some modified commercial zeolites on two different ceramic supports with higher thermal conductivity and study the hydrothermal stability of those zeolite on the support. The application of such kind of materials in a thermochemical storage or heat pump will be object of future work.

## Preparation of the ceramic supports

Alumina and cordierite (aluminosilicate containing magnesia, see Winterstein, 1999) were selected as starting materials for the preparation of ceramic supports. To make suitable profiles by extrusion such as tubes for instance it is necessary to convert the ceramic powders into plasticized materials. In the present case the optimum amount of additives was about 13 wt% for alumina and 7 wt% for cordierite. The additives (binder, parting agents and plasticizer) were based on water soluble compounds like cellulose ether and polyethylen glycol. The tubes made as model supports had an outer diameter of 10 mm (inner diameter 7 mm) and a length of 200 mm. After the extrusion the tubes were dried at ambient temperature and sintered at 800 to 1650°C.

Table 1 shows some characteristic data of selected ceramic materials which were tested for application in the immobilization of zeolites. As can be seen the porosity and pore size of the materials were varied. The dense form of alumina shows the highest heat conductivity. But with increasing porosity the heat conductivity drops. In first trials of coating with zeolite X it turned out that the nonporous surface of the dense alumina tubes do not keep the zeolite coat. Obviously, a certain porosity of the surface is necessary to get a strong zeolite coat on the support. Alumina 2 with a porosity of 30% was found to be a favorable material as well as the cordierite materials given in the table.

**Table 1** Characteristic data of ceramic supports used for the immobilization of zeolites

Material	Porosity in %	Pore diameter in $\mu\text{m}$	Heat conductivity in $\text{W m}^{-1}\text{K}^{-1}$
alumina 1	0	-	24.3-29
alumina 2	30	3	14.6
cordierite 1	36	4.8	1.8
cordierite 2	52-55	6.8-7.8	<1.4
cordierite 3	73	38	<1.4

## Deposition of the zeolites and hydrothermal stability experiments

Table 2 gives some characteristic data of the zeolites used. Zeolite NaX (Chemiewerk Köstritz, CKW) was taken as reference for the A-type zeolite and Gismondine (zeolite P). Wessalith P (Degussa) and the Gismondine Doucil A 24 (Crosfield B.V.) are inexpensive commercial products for household and industrial detergents. They were used in the Na-form and after ion exchange in the CaNa-form.

The zeolites were immobilized on the ceramic tubes by the slurry dip method. The optimum composition of the slurry and the dipping time of the tubes into the slurry which consists of the zeolite powder and Köstrosol 0830 (silica sol) as binder was determined in many trials before. A dipping time of 1 or 2 minutes was applied. After coating with the zeolite slurry the tubes were dried at ambient temperature followed by calcination at 500°C for 1 h. The amount of the immobilized zeolite was determined gravimetrically and varied between 1 and 3.5 g dry material.

**Table 2** Characteristic data of zeolites deposited on the ceramic supports

Sample	Si/Al ratio	ion exchange degree
NaX (CWK)	1.2	0
NaA (Wessalith P)	1	0
CaNaA	1	44
NaP (Doucil A24)	1	0
CaNaP	1	42

The so coated tubes were used for the investigation of the hydrothermal stability of the immobilized molecular sieves by being subject to many cycles of adsorption and desorption. The saturation of the zeolite layer with water vapor was carried out over night in a desiccator at room temperature at a relative pressure of 0.3. The desorption of the water followed in an oven by heating the coated tubes for 2 h at 250°C. The ad- and desorbed amounts of water were determined gravimetrically. From time to time in between of the measuring procedure the tubes were stored in the desiccator for some weeks, covering a period of time of about two years for the entire investigation. Decreasing amounts of adsorbed water with increasing number of cycles adsorption/desorption were taken as a measure of the hydrothermal damage of the zeolites.

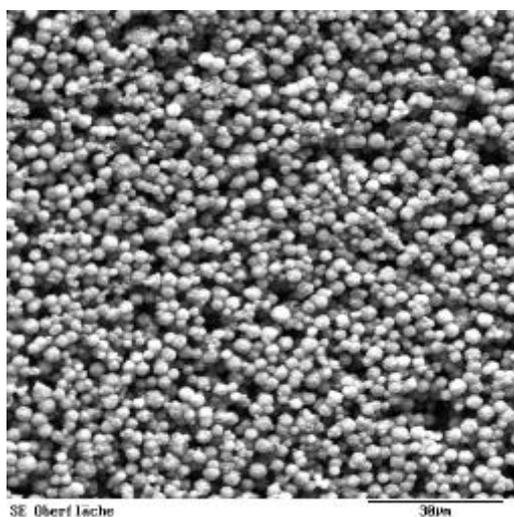
## Results and Discussion

### Immobilization of the zeolites

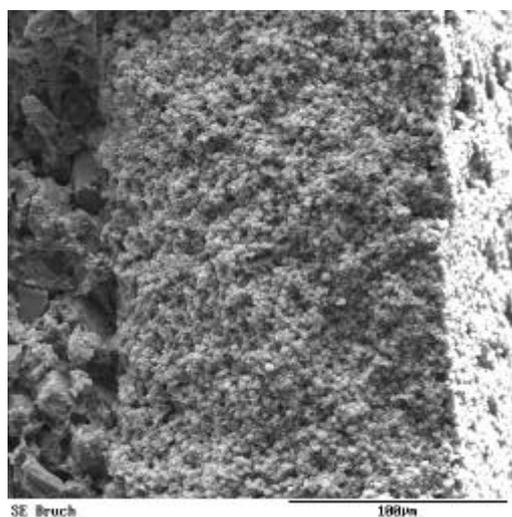
According to the optimized method given above the tubes of cordierite 1 to 3 and alumina 2 were coated with different zeolites. Figures 1 (view of the layer) and 2 (fracture view) show, as an example, the electronmicroscopic images of zeolite X deposited on alumina with the porosity of 30%. As can be seen from Figure 2 a zeolite layer of about 200 µm is formed on the surface of the alumina surface (left hand side). Whereas NaX, NaA, CaNaA and the sodium form of Doucil A 24, NaP, gives a zeolite layer on alumina 2 it was impossible to immobilize the CaNaP. It cannot be explained yet.

Cordierite was only used for the immobilization of NaX to study the influence of the porosity on the amount of zeolite deposited on the support. Because of the higher porosity reached for cordierite, indeed, it was possible to increase the immobilized amount of zeolite from 1 to 3.5 g.

The adhesive strength of the NaX, NaA and CaNaA crystals on the porous alumina surface was satisfactory where as CaNaP did not stay on this surface at all. As this ion exchanged form of the Doucil A 24, the parent material (NaP) is not suitable for immobilization on our ceramic supports as well because after deposition of NaP the zeolite skin peels off easily.



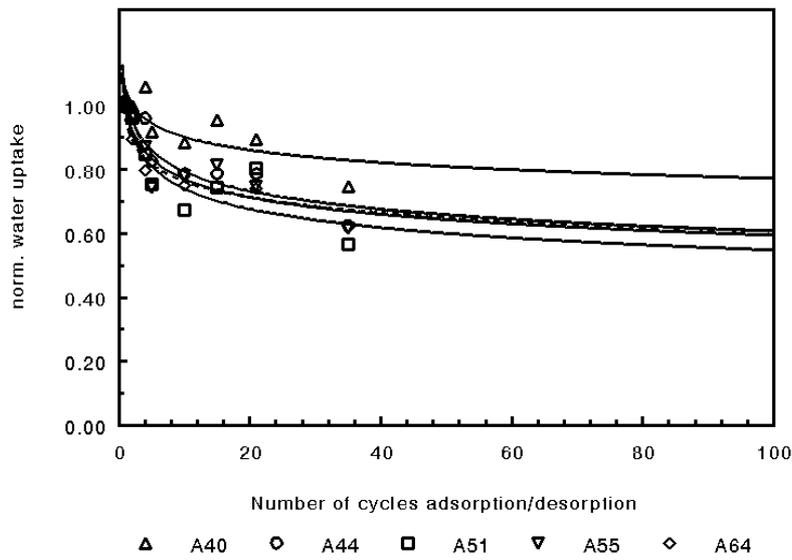
**Figure 1** Electronmicroscopic image of NaX deposited on alumina, surface of the layer



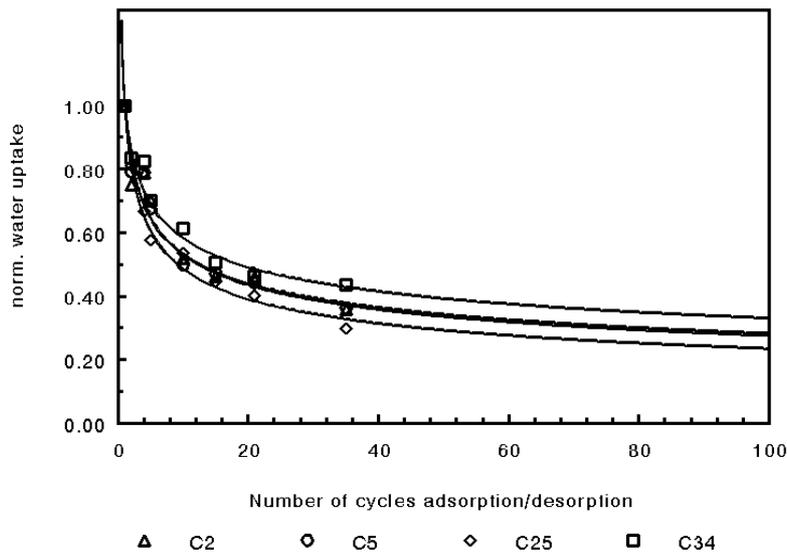
**Figure 2** Electronmicroscopic image of NaX deposited on alumina, fracture view

### Hydrothermal stability of the zeolites

The Figures 3-6 show the results of the long term investigations of the hydrothermal stability of NaX and the A type zeolites. In all cases the normalized adsorption capacity of water is plotted as function of the number of cycles adsorption/desorption. As could be expected (see Hauer, 1999) the maximum

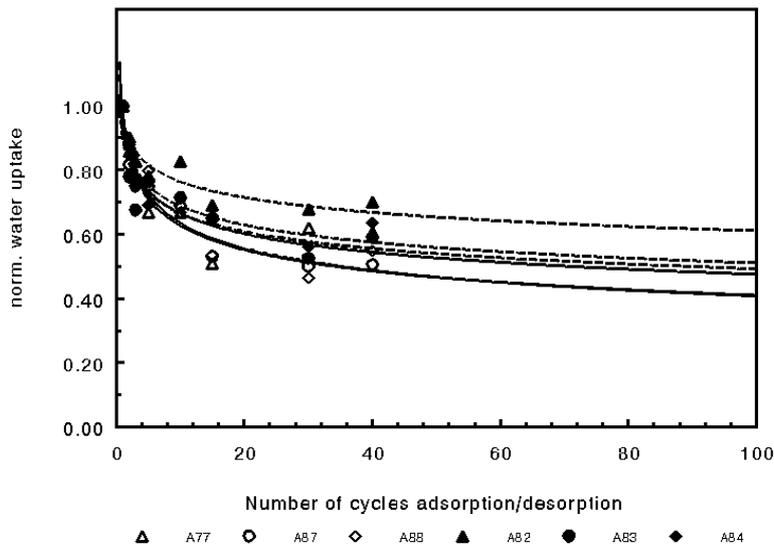


**Figure 3** Normalized water uptake vs. the number of ad/desorption cycles for NaX deposited on alumina 2.

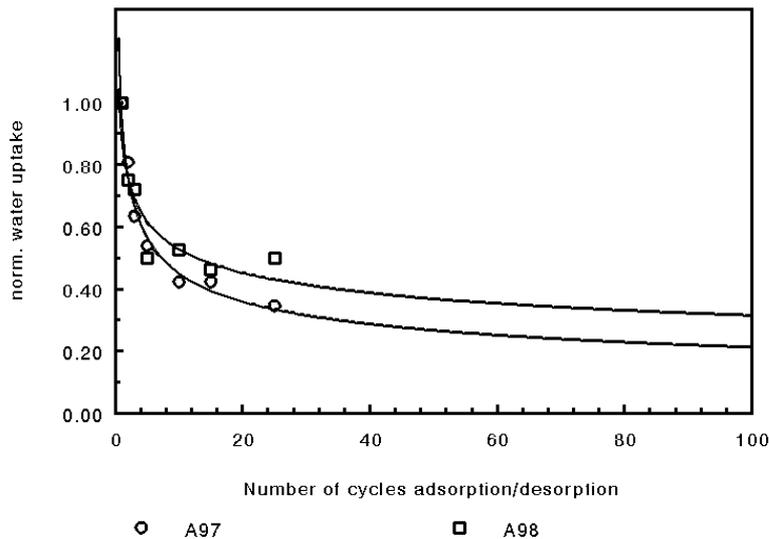


**Figure 4** Normalized water uptake vs. the number of ad/desorption cycles for NaX deposited on cordierite 2 and 3.

adsorbed amount (0.18 g/g zeolite layer) decreases with the increasing number of cycles. But there are differences between the type of zeolites and the kind of support.



**Figure 5** Normalized water uptake vs. the number of ad/desorption cycles for NaA (solid lines) and CaNaA (dashed lines) deposited on alumina 2.

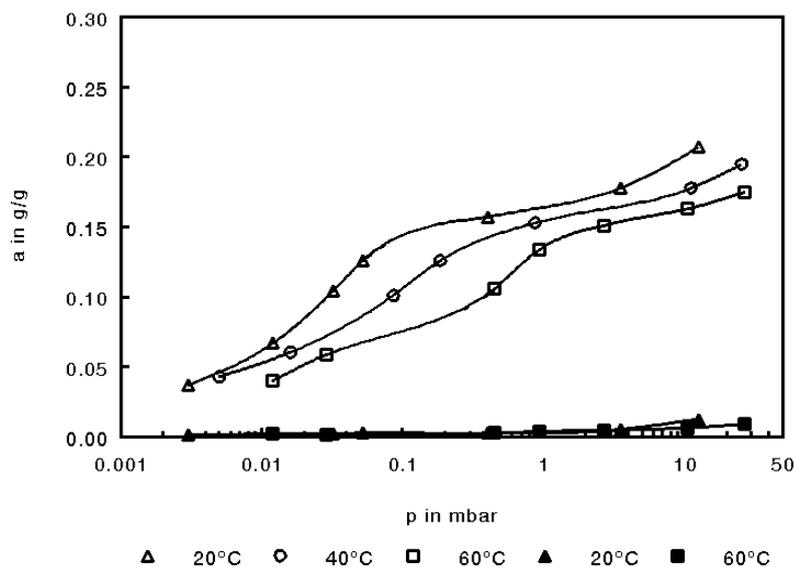


**Figure 6** Normalized water uptake vs. the number of ad/desorption cycles for Doucil A 24 deposited on alumina 2.

Figures 3 and 4 compare the influence of the support on the stability of the zeolite. The decrease of the adsorption capacity is extrapolated up to a number of 100 cycles. It turned out clearly that NaX seems to be hydrothermal much more stable on alumina than on cordierite. The reason for this behavior may be the fact that the zeolite crystals form a layer on top of the alumina surface (Figure 2) and water vapor diffuses freely. On the other hand cordierite shows a much higher porosity and larger pores which allow

the zeolite crystals to penetrate into the bulk phase of the tubes during the dipping into the slurry. Because of the embedding the desorption of the water may be hindered and the hydrothermal treatment is more effective.

Figures 5 and 6 give the results of the long term investigations for the A-type zeolites deposited on alumina 2. CaNaA shows a comparable stability with NaX and, as could be expected, is slightly more stable than the pure sodium form of this zeolite. The curves in Figure 6, however, indicate high instability of Doucil A 24 in a hydrothermal process. This can also be seen from the following Figure 7.



**Figure 7** Adsorption isotherms of water on CaNaA and CaNaP (filled symbols) zeolites at 20, 40 and 60°C

Figure 7 gives the adsorption isotherms of water in CaNaA at different temperatures in comparison to the CaNa-form of Doucil. Both samples were pelleted and thereafter calcined at 650°C. Obviously, the latter sample did not survive the pelleting procedure because the adsorption capacity is close to zero. The adsorption capacity of CaNaA amounts to 0.19 g/g at 10 mbar which is usual for (with binder) pelleted A-type zeolites.

## Conclusions

It was shown that zeolites of different types can be immobilized on ceramic supports. Most suitable for this purpose is alumina with a porosity of 30% and pores of about 3 μm. Cordierite of higher porosity allows the deposition of larger amounts of zeolite. However, the hydrothermal stability of the zeolite on cordierite and the heat conductivity of that support are insufficient.

Concerning a good heat conductivity a compromise between a minimum porosity (high heat conductivity) and the adhesive forces of the zeolite layer on the support has to be found.

The hydrothermal stability of the inexpensive CaNaA on alumina is comparable with that of NaX and therefore suitable for application as storage material in thermochemical storage of heat.

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