

WATER ADSORPTION BEHAVIOR OF DEALUMINATED ZEOLITE Y

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ABSTRACT

Zeolite Y have been synthesized and modified with three different dealumination techniques: hydrothermal treatment (steaming), dealumination with organic (4H-EDTA) and inorganic (HCl) acids. The modified zeolites were analyzed by X-ray diffraction, SEM-EDX analysis and water adsorption measurements. Results showed similar shapes of adsorption isotherms of original zeolite and modified samples via hydrothermal treatment and treatment with HCl. However, dealumination of original zeolite with 4H-EDTA revealed significant changes in hydrophilic behavior of the modified zeolite, i.e. the main effect was a shift of the adsorption isotherm in the low partial pressure range, which represents an interesting result for adsorption-based applications, including heat storage and reallocation.

Keywords: Water adsorption, adsorption isotherms, dealumination, zeolites.

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^[1]. Zeolites are easily accessible, low cost and largely employed catalytic and adsorbent materials. Thus, to date zeolite/water pair was considered as the most simple and profitable combination of adsorbent material/vapor for heat storage applications^[2]. In recent years the optimization of zeolites for thermochemical heat storage was focused on a maximum storage density and discharging temperature which can be achieved by changing the nature of cations of the zeolites to get high heats of adsorption^{[3],[4]}. However, if the temperature level of the heat available for the desorption (charging) of the zeolitic storage material is too low (<420 K) not all the water adsorbed can be removed. Hence, the potential high storage density of these materials cannot be utilized completely. From the catalysis it is well known that a post-synthesis modification of a number of zeolites by a hydrothermal treatment reduces the lattice aluminium concentration and improves the catalytic performance^[5]. A partial dealumination 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^[6]. Therefore we have studied the influence of different dealumination techniques on the water adsorption of well-known zeolite Y.

EXPERIMENTAL

Sodium form of zeolite Y (FAU) have been synthesized by standard hydrothermal synthesis according to the formula reported in Ref.^[7]. Three different techniques have been used for the preparation of the modified zeolite Y: Hydrothermal treatment (steaming) and dealumination with organic (4H-EDTA) and inorganic (HCl) acids. Prior hydrothermal treatment the initial

zeolite Y was subjected to ammonium ion exchange to replace zeolitic sodium with ammonium ions. The resulting ammonium zeolite was then calcined in the presence of water steam at 500°C for 2 hours. The acid dealumination with HCl and 4H-EDTA was performed in the following manner: 5g sample of initial zeolite Y was reflux for 4 hours with 150 ml of 0.2M acid solutions. After treatment the suspended particles were filtered off and washed with distilled water until neutral pH. The samples were then dried and calcined at 500°C for 2 hours. All obtained materials have been characterized with X-ray diffraction (PANalytical X'Pert PRO, Cu K α). A Zeiss SUPRA 35 VP scanning electron microscope (SEM) was used for microstructural analysis. In addition, energy dispersive X-ray EDX detectors were interfaced to the column to perform semi-quantitative chemical analysis. The water vapor adsorption isotherms were measured on a Hiden Isochema IGA-100 gravimetric analyzer. The samples, before water adsorption, were activated (degassed) at 300°C under high vacuum for 3h. Adsorption isotherms for water vapor were measured at 25°C with an equilibrium time of 80 min for all measurements.

RESULTS AND DISCUSSION

X-ray diffractograms and water adsorption isotherms of the original as-synthesized zeolite Y (Figure 1a,b) confirm the formation of pure, crystalline phase of zeolite Y. In particular, water adsorption isotherm show the typical trend for zeolites (Type I isotherm), where high water uptake values are reached from the very low partial pressures. In case of hydrophilic zeolites X and Y water first fills the smallest b cages of the aluminosilica framework at very low partial pressure. With the increasing partial pressure, water molecules continue to diffuse through the zeolite pores to fill the largest – supercages^[8].

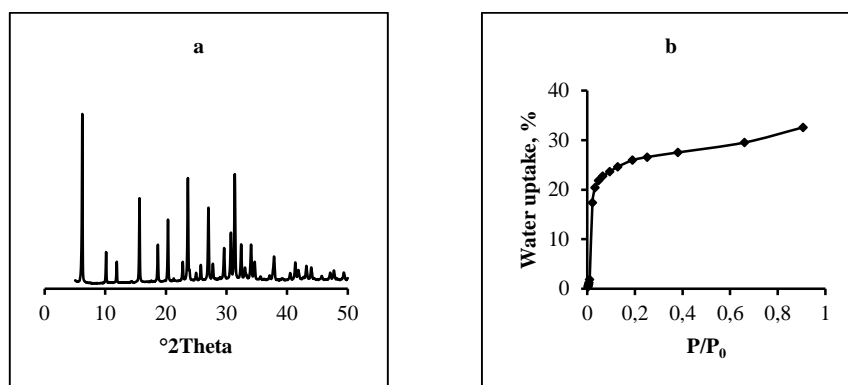


Figure 1. X-Ray diffractogram (a) and water adsorption isotherm (b) of original zeolite Y.

After dealumination procedures X-ray diffractograms (Fig. 2) of all modified zeolites Y show a partial amorphization of the samples. However, there are no significant differences in the patterns if compared to the original zeolite, demonstrating that the zeolite Y framework topology is preserved. The morphology of all samples studied by SEM (here not reported for brevity) reveals that there is no impact of dealumination on the shape and size of the particles. Silicon to aluminum ratios obtained via SEM-EDX analysis revealed comparable values of 5.8, 6.2 and 6.4 for steamed, 4H-EDTA and HCl dealuminated samples respectively.

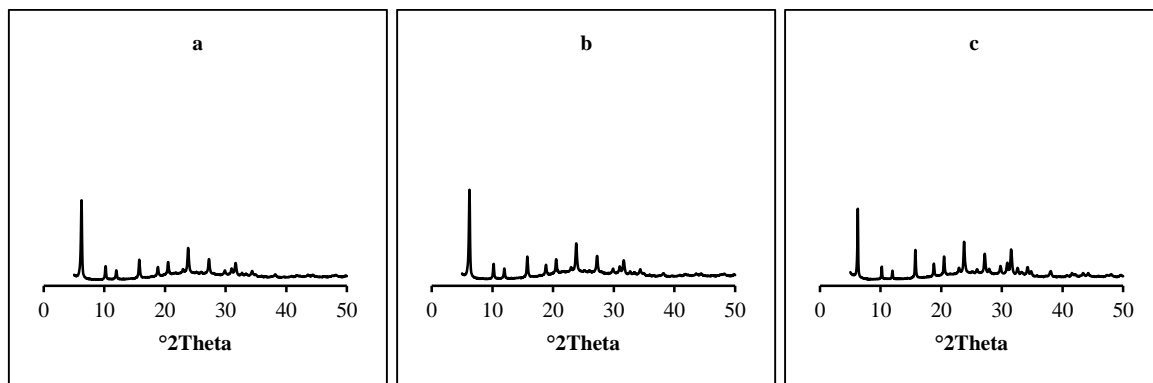


Figure 2. X-Ray diffractograms of Steamed (a) HCl (b) and 4H-EDTA (c) dealuminated zeolite Y.

Fig.3(a,b) shows water adsorption isotherms at 25°C for steamed and HCl modified zeolites. The shape of the adsorption isotherms of the modified samples and original zeolite was similar in the low partial pressures range while a slight decrease of the water capacity at increasing P/P_0 was observed for the modified zeolites due to the partial amorphization. The most interesting result has been obtained measuring water adsorption isotherms of zeolite Y modified with 4H-EDTA (Fig.3c).

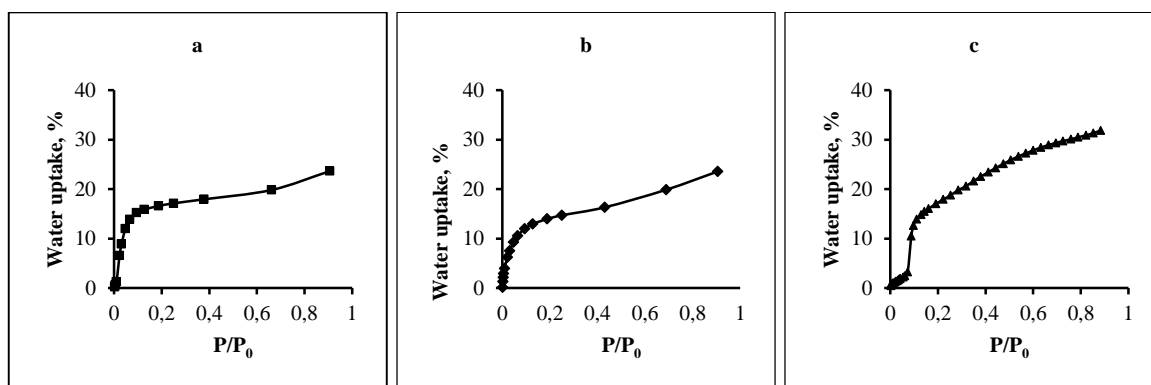


Figure 3. Water adsorption isotherms of Steamed (a) HCl (b) and 4H-EDTA (c) dealuminated zeolite Y.

The final water uptake did not show any variation in comparison with the original zeolite. In the low pressure range, however, the 4H-EDTA dealumination modified the typical shape of the adsorption isotherm of the pure zeolite Y, shifting the starting point of the water adsorption toward higher partial pressure values.

Possible explanation for the observed result is that the molecule of 4H-EDTA has a diameter (estimated on the basis of Connolly molecular surface) $\approx 8 \text{ \AA}$, while at the same time the largest 12-T ring windows of the FAU structure have size $\approx 7.35 \text{ \AA}$. Thus the possibility for the 4H-EDTA molecule to diffuse into cages of zeolite Y is very limited or even excluded for steric reasons and the dealumination process can only occur on the particle surface. From this point of view, the observed induction period of water adsorption on 4H-EDTA dealuminated sample can be explained through formation of hydrophobic, silica rich area on the surface of zeolite particles (shell), which resists the adsorption of water to the certain point of relative pressure. The such "S-shape" of the adsorption isotherms is known the ideal behavior of an adsorbent material for energy recovery applications^[9].

CONCLUSIONS

The effects of the different dealumination techniques of the zeolite Y have been investigated. Adsorption isotherms of modified zeolite Y demonstrated that dealumination with bulk organic acid 4H-EDTA is able to reduce the original intense water affinity. This effect was attributed to the inability of 4H-EDTA molecule to enter into the zeolite pores due to its size and polarity. Thus, dealumination occurs only on the surface of zeolite particles creating the hydrophobic, silica rich area.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support by the Slovenian Research Agency for the project L1-7665 „Advanced heat storage materials for integrated storage solutions“. We thank Mrs. Mojca Opresnik for SEM/EDX measurements and Mr. Edi Kranjc for XRD measurements.

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