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# CHARACTERIZATION OF EXTRA-FRAMEWORK CATIONS IN ZEOLITES

## A temperature-programmed desorption (TPD) study

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## Abstract

We have investigated the interaction of a few 5-ring organic compounds (cyclopentane, cyclopentene, furan, 2-methylfuran, 2,5-dihydrofuran and tetrahydrofuran) with alkali-metal cation-exchanged faujasites (LSX, X and Y types) by means of temperature-programmed desorption (TPD). The desorption behavior at higher temperatures of all probe molecules on the sodium ion containing faujasites with different Si/Al ratios reflects the higher cation content of zeolites with greater aluminum content. Only the desorption profiles of tetrahydrofuran and 2,5-dihydrofuran show, depending on the kind of cation, additional desorption features at higher temperatures. Using a regularization method, desorption energy distribution functions for furan and tetrahydrofuran were calculated. The calculated desorption energy distributions clearly illustrate the very different adsorption behavior of furan and tetrahydrofuran which leads to large differences in the binding energies between the corresponding adsorption complexes.

**Keywords:** adsorption complexes, alkali-metal cation-exchanged faujasites, desorption energy distribution functions, furan, strength of interaction, temperature-programmed desorption (TPD), tetrahydrofuran

## Introduction

The adsorption and catalytic properties of zeolites strongly depend on the nature, number, strength and the environment of their adsorption sites. In this context, the characterization of these sites is of great interest for many practical applications of zeolites as catalysts and adsorbents. The adsorption of probe molecules is one of the most powerful and useful techniques to characterize extra-framework cations in zeolites. In this connection more bulky and complex molecules as probes are of special interest, because they might interact with the Lewis acidic cations and their environment as well. In continuation of our research concerning the interaction of pyrrole

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and its derivatives [1, 2], we report here new results with respect to the interaction of a few other 5-ring organic compounds (cyclopentane, cyclopentene, furan, 2-methylfuran, 2,5-dihydrofuran and tetrahydrofuran) with alkali-metal cation-exchanged faujasites using temperature-programmed desorption (TPD).

## Experimental

### *Zeolites*

A commercial NaX (Si/Al=1.18) and a NaY (Si/Al=2.6) zeolite (Chemie AG Bitterfeld/Wolfen, Germany) were used. A CsNaX zeolite was prepared by ion exchange of the NaX with an aqueous solution of CsCl at 353 K for 8 h. The degree of cation exchange was determined by means of ICP-AES. Furthermore, LSX zeolites with $Li^+$, $Na^+$ and $K^+$ cations produced by Tricat Zeolites GmbH, Bitterfeld, Germany were also studied. The micropore volumes were determined by nitrogen adsorption at 77 K. The characteristics of all zeolites are summarized in Table 1.

**Table 1** Zeolite characteristics

| Zeolite | Si/Al | Chemical composition | Micropore volume/cm$^3$ g$^{-1}$ |
|---|---|---|---|
| NaY | 2.60 | $Na_{53.3}[Al_{53.3}Si_{138.7}O_{384}]$ | 0.296 |
| NaX | 1.18 | $Na_{88.1}[Al_{88.1}Si_{103.9}O_{384}]$ | 0.297 |
| CsNaX | 1.18 | $Cs_{39.6}Na_{48.5}[Al_{88.1}Si_{103.9}O_{384}]$ | 0.194 |
| Li-LSX | 1.01 | $Li_{93.1}Na_{2.4}[Al_{95.5}Si_{96.5}O_{384}]$ | 0.356 |
| Na-LSX | 1.02 | $Na_{95}[Al_{95}Si_{97}O_{384}]$ | 0.299 |
| K-LSX | 1.05 | $K_{86.2}Na_{7.5}[Al_{93.7}Si_{98.3}O_{384}]$ | 0.239 |

**Table 2** Desorbed amounts in molecules per unit cell (u.c.) (error: ±2–3 molecules per u.c.)

| Zeolite | Cyclopentane | Tetrahydrofuran | Furan | 2-Methylfuran |
|---|---|---|---|---|
| Li-LSX | 18 | 38 | 44 | 34 |
| Na-LSX | 17 | 37 | 45 | 37 |
| K-LSX | 16 | 22 | 35 | 31 |
| NaX | 17 | 38 | 41 | 41 |
| CsNaX | 14 | 22 | 37 | 27 |
| NaY | No adsorption | 28 | 43 | 29 |

### *Temperature-programmed desorption (TPD)*

The TPD was carried out in a flow apparatus with helium as carrier gas (50 cm$^3$ min$^{-1}$). For evolved gas detection both a thermal conductivity detector (TCD) and a quadrupole mass spectrometer (Leybold, Transpector CIS System) with a capillary-coupling system were used. The zeolites were equilibrated with water vapor over a saturated $Ca(NO_3)_2$-solution in a desiccator. For each experiment 50 mg of the hydrated zeolite were used in a mixture with 1 g quartz of the same grain size (0.2–0.4 mm). At first, the samples were heated at 10 K $min^{-1}$ in the helium flow up to 673 K. The zeolites were thereafter cooled down to 303 K (cyclopentane, cyclopentene) and 340 K (furan, 2-methylfuran, 2,5-dihydrofuran and tetrahydrofuran) and loaded with the organic probe to saturation. The loaded zeolite samples were flushed with helium until no further desorption was observed. The linear temperature program (10 K $min^{-1}$) was then started. For a kinetic evaluation, experiments with different heating rates (2–20 K $min^{-1}$) were carried out.

## Results and discussion

Figure 1 shows the TPD profiles of all probe molecules under study on the NaX zeolite. Decomposition of the probe during non-isothermal desorption was in no case observed. All profiles show a pronounced peak in the temperature region of about 370–450 K, maximum of which shifts to higher temperatures in the sequence cyclopentane<cyclopentene<tetrahydrofuran=2,5-dihydrofuran<furan<2-methylfuran. In this sense the change of the desorbed amounts (Table 2) indicates that the initial uptake corresponds to a higher degree of pore filling in case of probes with stronger interaction (cyclopentane 40%<tetrahydrofuran 77%≈furan 74%<2-methylfuran 92%). The profiles of cyclopentene and furan show a shoulder at higher desorption temperatures indicating a specific interaction with the extra-framework sodium ions as the strongest adsorption sites in the zeolite. In case of 2,5-dihydrofuran and tetrahydrofuran this interaction yields to two additional peaks. Due to their size (about 0.4 nm) the probe molecule cannot penetrate into the sodalite cage (free diameter of the 6-ring window is about 0.26 nm). There-

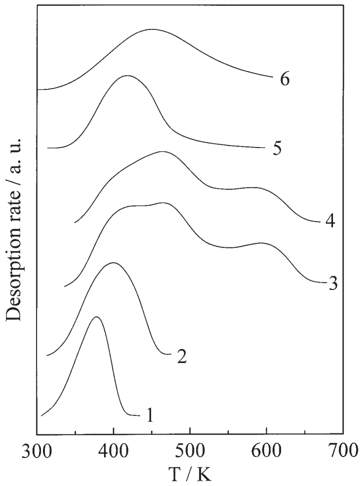

**Fig. 1** TPD profiles of 1 – cyclopentane, 2 – cyclopentene, 3 – tetrahydrofuran, 4 – 2,5-dihydrofuran, 5 – furan and 6 – 2-methylfuran on the NaX zeolite (10 K $min^{-1}$)

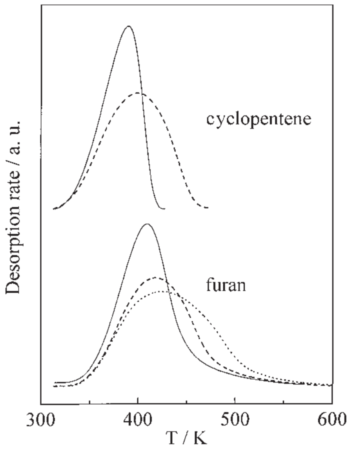

**Fig. 2** TPD profiles of cyclopentene and furan on the Na-LSX (···), NaX (---) and NaY (—) zeolites

fore, the desorption behavior at higher temperatures can in all cases be assigned to an interaction of the probes with sodium ions located in the supercage.

The desorption curves of cyclopentene and furan and those of tetrahydrofuran on the Na-LSX, NaX and NaY zeolites are presented in Figs 2 and 3, respectively. The TPD profiles show a strong influence of the Si/Al ratio upon the strength of interaction with the probe molecules. There is a significant increase of the intensity of the high temperature part of the TPD curves in case of cyclopentene and furan with decreasing Si/Al ratio of the zeolite, whereas for tetrahydrofuran an additional high temperature peak appears. These effects are mostly to be explained with a larger number of sodium ions on the zeolites with low Si/Al ratios. The higher aluminum content also increases the partial negative charge of the framework oxygen atoms [3, 4] which, due to an interaction with the hydrogen atoms of the probe molecules, also leads to a stronger effective interaction.

As it can be clearly seen in Fig. 4 there are relatively small differences between the TPD profiles of cyclopentane on the Li-LSX and the CsNaX zeolite. It is obvious that cyclopentane cannot interact specifically with the cations. In case of furan only the desorption curve of the Li-LSX zeolite shows a noticeable additional desorption feature at higher temperatures (Fig. 5) indicating a specific interaction with the $Li^+$ ions, while the course of desorption on the other zeolites suggests no significant dependence on the kind of cation. In contrast to this, as shown in Fig. 6, the desorption behavior of tetrahydrofuran is strongly dependent on the kind of cation.

The observed desorption profiles $r_d(T)$ were analyzed by considering a first order desorption process with a distribution function $f(E)$ of the effective desorption energy $E$ [5, 6]:

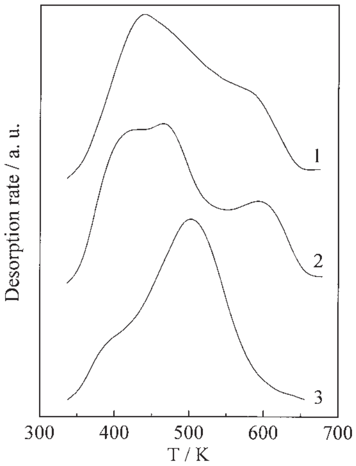

**Fig. 3** TPD profiles of tetrahydrofuran on the 1 – Na-LSX, 2 – NaX and 3 – NaY zeolites

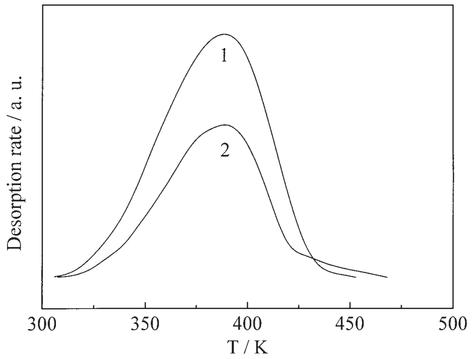

**Fig. 4** TPD profiles of cyclopentane on the 1 – Li-LSX and 2 – CsNaX zeolites

$$r_{\mathrm{d}}(T) = -\frac{\mathrm{d}\theta}{\mathrm{d}t} = A\int_{\mathrm{E_{min}}}^{\mathrm{E_{max}}}\theta_{\mathrm{loc}}(E,T)\exp(-E/RT)f(E)\mathrm{d}E \qquad (1)$$

Here θ is the average coverage or loading, and $A$ an effective pre-exponential factor. $\theta_{\mathrm{loc}}$ is the coverage of adsorption sites with desorption energy $E$. $E_{\mathrm{min}}$ and $E_{\mathrm{max}}$ are the limits of the energy range of desorption energy. The energy distributions $f(E)$ were determined from the experimental desorption curves $r_{\mathrm{d}}(T)$ by means of the program INTEG [6], which involves a regularization method to solve the integral Eq. (1) [6, 7]. The pre-exponential factor $A$ required to solve the integral Eq. (1) was estimated by means of an extended integral equation using TPD profiles with different heating rates [7].

The calculated desorption energy distributions are shown in Figs 7 and 8. The energy range of the distribution functions corresponds with micro-calorimetrically determined differential heats of adsorption for different adsorbed amounts of furan

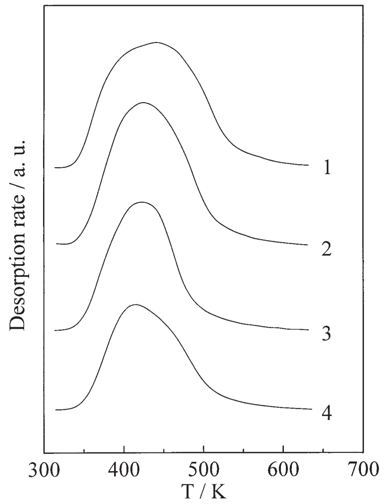

**Fig. 5** TPD profiles of furan on X type zeolites containing different cations: 1 – Li-LSX, 2 – Na-LSX, 3 – K-LSX, 4 – CsNaX

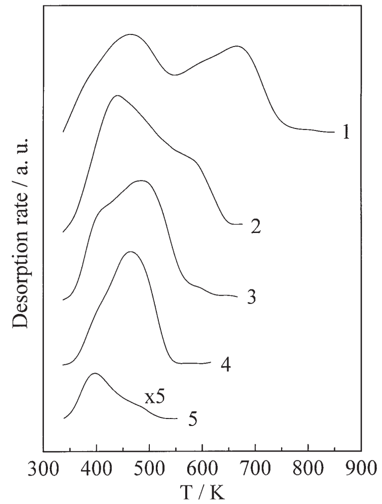

**Fig. 6** TPD profiles of tetrahydrofuran on X type zeolites containing different cations: 1 – Li-LSX, 2 – Na-LSX, 3 – K-LSX, 4 – CsNaX, 5 – FAU (Si/Al=100)

and tetrahydrofuran on a comparable LiNaHX zeolite [8]. The peak or shoulder at lower energy values of the desorption energy distribution can be assigned mostly to weakly bonded molecules interacting non-specifically with zeolite framework. This assignment is also supported by the observed desorption profile of tetrahydrofuran on a siliceous faujasite with a very small cation content (Si/Al=100) which shows only one desorption peak of low intensity at about 400 K (Fig. 6). The other peaks of the desorption energy distributions at higher energy values can be attributed to a stron-

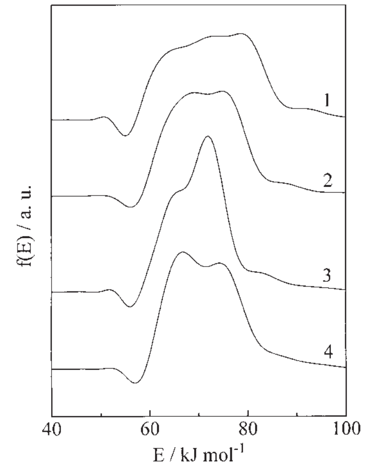

**Fig. 7** Desorption energy distributions of furan on X type zeolites containing different cations ($A$=2·10$^{8}$ min$^{-1}$): 1 – Li-LSX, 2 – Na-LSX, 3 – K-LSX, 4 – CsNaX

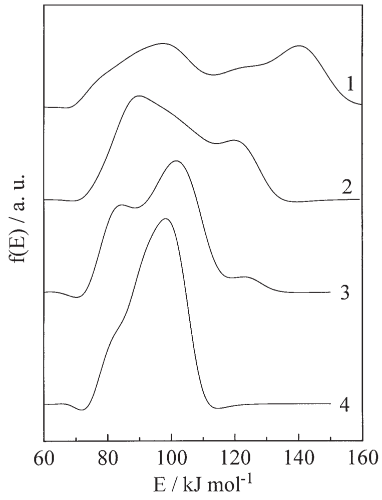

**Fig. 8** Desorption energy distributions of tetrahydrofuran on X type zeolites containing different cations ($A$=2·10$^{10}$ min$^{-1}$): 1 – Li-LSX, 2 – Na-LSX, 3 – K-LSX, 4 – CsNaX

ger, direct interaction with the cations located in the supercage of the zeolites. To determine the number of molecules which correspond to the different energy ranges the desorption energy distributions were fitted with two or three Gaussian functions. As a result of this procedure about 18–34 furan or tetrahydrofuran molecules per unit cell (u.c.) (Li-LSX: 34±2 molecules per u.c., Na-LSX: 23±2 molecules per u.c., K-LSX: 18±2 molecules per u.c. and CsNaX: 20±2 molecules per u.c) could be assigned to adsorbed species which interact specifically with the cations.

Both the large differences between the desorption energies of furan and tetrahydrofuran (Li-LSX: 61, Na-LSX: 46, K-LSX: 31 and CsNaX: 28 kJ mol$^{-1}$) and the different number of peaks and shoulders of the desorption energy distributions of both probe molecules provide hints for the existence of different adsorption complexes for furan and tetrahydrofuran. Tetrahydrofuran is a highly polar molecule with a large negative charge on its oxygen atom. The latter should therefore represent the docking center which interacts specifically with the cations without significant steric hindrances. As a result higher binding energies which strongly depend on the kind cation should be expected. The rapid decrease of the energy value of the peak at higher energies with decreasing Lewis acidity of the cations (Li-LSX: 141>Na-LSX: 122> K-LSX: 103≈CsNaX: 102 kJ mol$^{-1}$) supports this interpretation. The relatively high value in case of the CsNaX zeolite may be caused by the higher sodium ion content of this zeolite. The two peaks of the desorption energy distribution function for TPD of tetrahydrofuran on the Na-LSX zeolite (Fig. 8, curve 2; 102 and 122 kJ mol$^{-1}$) can be related to a by pairs arrangement of two tetrahydrofuran molecules on a sodium ion at a SII* position as it could be found for pyrrole on a NaX by a combined TPD and X-ray diffraction study [1].

The energy values for furan seem, however, to be almost independent of the kind of cation (Li-LSX: 80, Na-LSX: 76, K-LSX: 72, CsNaX: 74 kJ mol$^{-1}$). This finding can be explained as follows. Furan can interact specifically with the cations through its π-electron system. In addition, the hydrogen atoms of the slightly acid CH bonds of furan can interact with the basic lattice oxygen atoms of the zeolite as could be observed by means of a combined inelastic neutron scattering (INS) and infrared spectroscopic study [9]. Because the negative partial charge of the oxygen atoms and their proton affinity increase with increasing size of the alkali-metal cation [3, 4, 10], this interaction should be stronger in case of the $Cs^+$ ion-exchanged zeolite. Thus the decreasing strength of interaction between the π-electron system and the Lewis acid cations in the sequence $Li^+>Na^+>K^+>Cs^+$ would be compensated and the overall interaction energy would just slightly decrease. On the other hand, steric effects could also cause a weakening of the interaction of the π-electron system with the cations of different sizes. However, a definite clarification of this problem requires further investigations including X-ray diffraction studies to localize the probe molecules in different host/guest arrangements.

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