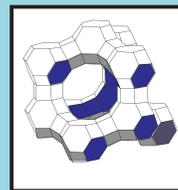


Investigation of the cationic state of extra-framework aluminum in the steamed zeolites H-Y by solid-state NMR spectroscopy



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Abstract

A series of steamed zeolites Y was quantitatively investigated by ^1H , ^{27}Al , and ^{29}Si NMR spectroscopy in the non-hydrated state. Via comparing the data obtained by different methods, the Al distribution and the mean cationic charge of extra-framework Al was studied. After weak steaming, a mean cationic charge of +2 was found.

Introduction

Steaming is an often applied method to modify the acidity and thermal stability of zeolites. In result of steaming, (i) the zeolitic framework is dealuminated, (ii) the coordination of framework Al atoms is changed from fourfold to threefold, and (iii) various extra-framework Al species are formed [1–3]. Extra-framework Al species influence the catalytic activity of zeolites due to their Lewis-acidic properties. In addition, the formation of cationic extra-framework Al species, compensating negative framework charges, influences the concentration and distribution of Brønsted acidic bridging OH groups. In this study, XRD, AES-ICP, ^1H MAS NMR, ^{29}Si MAS NMR, and ^{27}Al spin-echo NMR spectroscopy were applied to investigate the nature of framework and extra-framework Al species in steamed and non-hydrated zeolites Y.

Experimental Section

Zeolite Na-Y ($n_{\text{Si}}/n_{\text{Al}} = 2.7$, Degussa AG, Hanau, Germany) was six-fold ammonium-exchanged leading to an ion-exchange degree of 93.3%. The steaming of zeolites H-Y was carried out under water vapor pressures of 3.4 kPa (sample deH-Y/3.4) to 81.5 kPa (sample deH-Y/81.5) at the temperature of 748 K for 2.5 h. Using an air-lock, the steamed samples were filled into gas-tight glass ampoules without hydration. NMR investigations were performed on a Bruker MSL 400 spectrometer at resonance frequencies of 400.1, 104.2, and 79.46 MHz for ^1H , ^{27}Al , and ^{29}Si nuclei, respectively. Before the ^1H MAS NMR studies, the samples were evacuated under vacuum at 723 K for 12 h.

Results and Discussion

^{29}Si MAS NMR of non-hydrated and hydrated samples

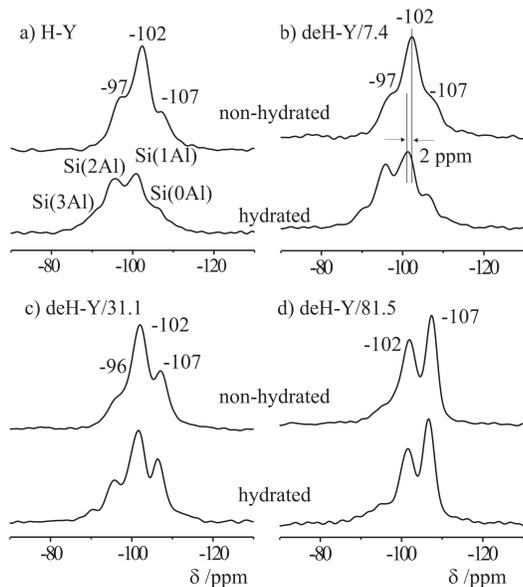


Figure 1 ^{29}Si MAS NMR spectra of non-hydrated (top spectra) and hydrated (bottom spectra) zeolites H-Y (a), deH-Y/7.4 (b), deH-Y/31.1 (c), and deH-Y/81.5 (d).

In Fig. 1, characteristic ^{29}Si MAS NMR spectra of zeolites H-Y and deH-Y in the non-hydrated and hydrated state are shown. For all samples, a high-field shift of ca. 2 ppm was observed for the signals of non-hydrated samples in comparison with those of hydrated samples.

In the case of no or a weak steaming (Figs. 1a and 1b), a significant change of the intensity distribution of the Si(*n*Al) signals occurs, which indicates an additional high-field shift of the signals of silicon atoms with a high number of aluminum atoms in the first coordination sphere of T-atoms. No significant change of the signal distribution was found for strongly dealuminated samples (Figs. 1c and 1d). This finding is explained by a variation of the Si-O-T bond angles of Si(3Al) and Si(2Al) sites in the local structure of non-hydrated framework AlO_4 tetrahedra. The total intensities of non-hydrated and hydrated samples were found to agree for measurements performed in the absolute intensity mode.

^{27}Al spin-echo NMR of non-hydrated samples

Fig. 2 shows characteristic ^{27}Al spin-echo NMR spectra of non-hydrated zeolites H-Y and deH-Y. The simulation of the spectra was performed using quadrupole parameters published by Ernst et al. [4]. The results of the simulation of the ^{27}Al spin-echo NMR spectra are given in Table 1. Quadrupole patterns with quadrupole coupling constants of $C_{\text{QCC}} = 14$ to 15 MHz are characteristic for tetrahedrally coordinated framework Al atoms in local structure of bridging OH groups (signal 1). The narrow signal 2 is due to (i) extra-framework Al species and (ii) tetrahedrally coordinated framework Al atoms, which are compensated by cationic species. The C_{QCC} values of the signal 2 increase with the strength of steaming, which causes a variation of the ratio of species (i) and (ii). Upon strong dealumination, extra-framework Al atoms with C_{QCC} values of ca. 9 MHz are the dominating atoms (species (ii)) responsible for signal 2.

Within an accuracy of $\pm 10\%$, the amount of framework Al atoms in the steamed samples as determined by ^{27}Al spin-echo NMR (signal 1) agrees well with that obtained by ^{29}Si MAS NMR (Tab. 1, column 8, and Tab. 2, column 3). No indication was found for three-coordinated Al species.

Table 1 Quadrupole coupling constants, C_{QCC} , and asymmetry parameters, η_{Q} , and the amounts of framework aluminum determined by simulation of ^{27}Al spin-echo NMR spectra.

Sample	Signal 1			Signal 2			$n_{\text{fr. Al}}/\text{u.c.}$
	$C_{\text{QCC}}/\text{MHz}$	η_{Q}	$n/\text{u.c.}$	$C_{\text{QCC}}/\text{MHz}$	η_{Q}	$n/\text{u.c.}$	
H-Y	14.7	0.37	46.3	6.4	0.77	5.7	49.8
deH-Y/7.4	14.3	0.38	45.6	6.9	0.72	6.4	49.1
deH-Y/31.1	15.0	0.36	30.3	9.1	0.71	21.7	33.8
deH-Y/81.5	14.6	0.36	23.2	9.1	0.77	28.8	26.7

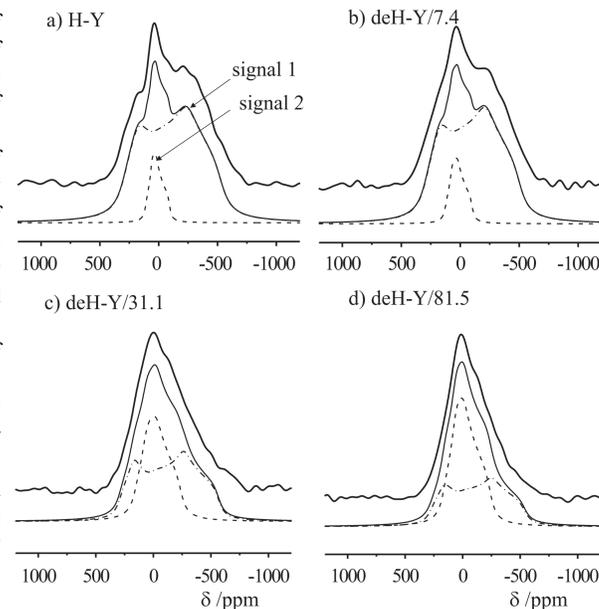


Figure 2

^{27}Al spin-echo NMR spectra of non-hydrated zeolites H-Y (a), deH-Y/7.4 (b), deH-Y/31.1 (c), and deH-Y/81.5 (d). Experimental spectra (top) are compared with simulated spectra (bottom). Two signals (signal 1 and signal 2) were used to simulate the quad-echo NMR spectra. The related parameters are given in Table 1.

^1H MAS NMR of non-hydrated samples

In the ^1H MAS NMR spectra of non-hydrated zeolites H-Y and deH-Y, signals of AlOH (0.6 and 2.6 ppm), SiOH (1.8 ppm), and bridging OH groups in supercages (3.8 ppm) and sodalite cages (4.7 ppm) were observed. In Fig. 3, the amounts of the various hydroxyl groups are plotted as a function of the water vapor pressure during the steaming. After strong dealumination, the amount of bridging OH groups in sodalite cages decreases significantly stronger than the amount of bridging OH groups in supercages. This finding may indicate the presence of more cationic species in sodalite cages than in supercages.

Using the data summarized in Table 2, the mean cationic charge x per extra-framework Al atom was estimated by $x = (n_{\text{Al}}^{\text{IV}} - n_{\text{SiOHAl}}^{\text{after}} - n_{\text{Na}}) / n_{\text{ex. Al}}$. In Fig. 4, this calculated mean cationic charge is plotted as a function of the water vapor pressure. According to the obtained curve, highly charged cationic extra-framework Al species are preferentially formed by a weak steaming, while extra-framework Al clusters with low or without cationic charges are formed by a strong steaming.

To exclude an effect of three-coordinated framework Al species on the above-mentioned estimation of the mean cationic charges, the amount of bridging OH groups was determined after loading zeolites deH-Y with ammonia and calcination [3].

Table 2 Framework $n_{\text{Si}}/n_{\text{Al}}$ ratios (column 2) and amount of framework aluminum atoms per unit cell (column 3) in non-hydrated zeolites H-Y and deH-Y (^{29}Si MAS NMR spectroscopy), amount of extra-framework Al species per unit cell (column 4) calculated from the total amount of Al (AES-ICP) and the values in column 3, total amounts of bridging OH groups before (column 5) and after (column 6) an ammonia adsorption/desorption treatment (^1H MAS NMR spectroscopy), and amounts of tetrahedrally coordinated framework Al atoms (column 7) calculated by the values in column 3 and the difference between the values in columns 5 and 6.

Sample	$n_{\text{Si}}/n_{\text{Al}}$	$n_{\text{fr. Al}}/\text{u.c.}$	$n_{\text{ex. Al}}/\text{u.c.}$	$n_{\text{SiOHAl}}^{\text{before}}/\text{u.c.}$	$n_{\text{SiOHAl}}^{\text{after}}/\text{u.c.}$	$n_{\text{Al}}^{\text{IV}}/\text{u.c.}$
H-Y	2.7	51.7	-	46.5	-	-
deH-Y/7.4	2.9	48.6	3.4	38.9	39.2	48.3
deH-Y/31.1	4.0	38.2	13.8	23.8	25.7	36.3
deH-Y/81.5	6.0	27.6	24.4	10.5	17.3	20.8

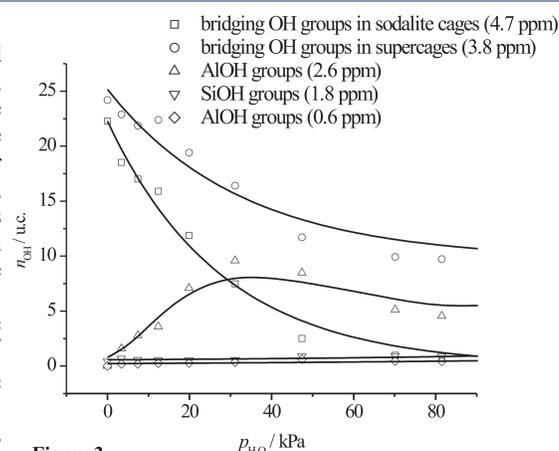


Figure 3

Amounts of hydroxyl groups in non-hydrated zeolites deH-Y determined by ^1H MAS NMR spectroscopy and plotted as a function of the water vapor pressure during the steaming.

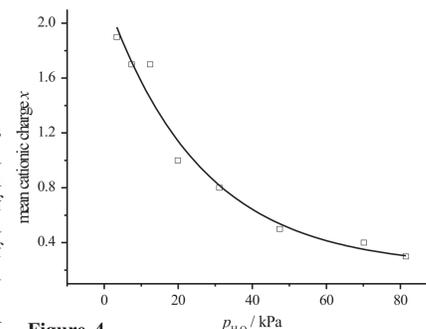


Figure 4

Mean cationic charge x per extra-framework Al atom in non-hydrated zeolites deH-Y calculated by $x = (n_{\text{Al}}^{\text{IV}} - n_{\text{SiOHAl}}^{\text{after}} - n_{\text{Na}}) / n_{\text{ex. Al}}$ and plotted as a function of the water vapor pressure during the steaming ($n_{\text{Na}} = 3.5/\text{u.c.}$).

Conclusions

By a combination of different methods of solid-state NMR spectroscopy, the state of Al atoms in dealuminated and non-hydrated zeolites Y was investigated quantitatively. The results show a discrepancy between the amounts of tetrahedrally coordinated Al atoms, responsible for the negative framework charges and the amounts of charge-compensating compounds, such as residual sodium cations and bridging hydroxyl groups. The NMR data allow an estimation of mean cationic charges of extra-framework Al species. This mean cationic charge per extra-framework Al atom in non-hydrated zeolites Y was found to be high for weakly steamed zeolites and vice versa.

Acknowledgements

Support of this work by Deutsche Forschungsgemeinschaft, Max-Buchner-Forschungsförderung, Fonds der Chemischen Industrie, and Volkswagen-Stiftung Hannover is gratefully acknowledged.

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