INFLUENCE OF GUEST COMPOUNDS ON THE BASE STRENGTH OF ZEOLITES Y AND X INVESTIGATED BY NMR SPECTROSCOPY

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ABSTRACT

Impregnation of cesium exchanged zeolites Y and X with cesium hydroxide followed by calcination not only creates a basic guest compound, but these treatments also affect the chemical properties of the zeolite framework. By using methoxy groups, formed at framework oxygen atoms, as ^{13}C NMR spectroscopic probes, a decrease in the mean electronegativity of the zeolite framework was observed upon cesium-exchange and impregnation with cesium hydroxide, which corresponds to an increase in the base strength of the zeolite framework. However, the strongest base sites are created by the oxidic guest compound. On zeolite Y, this guest compound is highly dispersed. ^{27}Al DOR NMR spectroscopy of dehydrated zeolites Y and X in different magnetic fields revealed a cation- and impregnation-induced change of the ^{27}Al quadrupolar interaction and, hence, of the local structure of the zeolite framework.

INTRODUCTION

Until recently, only scarce attention has been paid to basic zeolite catalysts, even though such materials show great potential for a number of industrially important reactions - such as dehydrogenation of alcohols, isomerization of olefins, side-chain alkylation of toluene or the synthesis of 4-methylthiazol [1]. The chemical properties of basic zeolites are determined by the alkali metal cations, which act as weak Lewis acid sites, and the basic framework oxygen atoms [2]. Exchanging sodium ions by rubidium or cesium cations leads to a decrease in the mean electronegativity of the framework, and the basicity of the oxygen atoms increases. Strong base sites can be created by incorporating alkali metal oxides into the zeolite pores [3, 4]. Multinuclear NMR spectroscopy, successfully used to characterize basic zeolites [5, 6], was employed to investigate the host-guest interactions of oxidic nanoparticles in zeolites Y and X prepared by exchange with cesium cations followed by impregnation with cesium hydroxide and calcination.

EXPERIMENTAL

Zeolites containing base sites were prepared according to reference [3]. The parent zeolites NaY and NaX (Union Carbide Corp., Tarrytown, N.Y., USA, $n_{Si}/n_{Al} = 2.6$ and 1.3, respectively) were fivefold ion-exchanged at 353 K in a surplus of a 0.4 M aqueous CsCl

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solution, which led to a degree of sodium exchange of 70 % and 55 % (zeolites CsNaY-70 and CsNaX-55), respectively. Subsequently, samples of these materials were suspended in 0.2 M solutions of CsOH. The suspensions were stirred to dryness at 353 K and, subsequently, calcined at 673 K (zeolite Y) or 773 K (zeolite X). For these impregnated materials, the codes CsNaY-70/*n*CsOH and CsNaX-55/*n*CsOH were used, where n ($n = 4, 8, 16$) stands for the number of CsOH per unit cell (u.c.). The chemical compositions of the samples were determined by AAS and ICP-AES. The prepared materials were activated for 12 h at a temperature of 673 K and a pressure below 10^{-2} Pa. The adsorption of probe molecules on the calcined samples was carried out in a vacuum line. The NMR spectra were recorded at resonance frequencies of 400.1 MHz and 100.5 MHz for ^{1}H MAS NMR and ^{13}C CP/MAS NMR (Bruker MSL 400), respectively, and of 104.2 MHz (Bruker MSL 400) and 195.4 MHz (Bruker DMX 750) for ^{27}Al DOR NMR spectroscopy.

RESULTS AND DISCUSSION

Bosacek et al. [7, 8] proposed a new method allowing the characterization of the base strength of the zeolite framework. After formation of methoxy groups bound to the framework of different zeolites by adsorption of methyl iodide, Bosacek found a correlation between the isotropic ^{13}C NMR shifts of these methoxy groups and the mean Sanderson electronegativities, S^m [9], of the zeolite framework. Figure 1 shows the ^{13}C CP/MAS NMR spectra of the dehydrated zeolites NaY (a), CsNaY-70 (b), NaX (c) and CsNaX-55 (d) studied in the present work after adsorption of 16 CH_3I molecules per unit cell. The signals marked by asterisks are

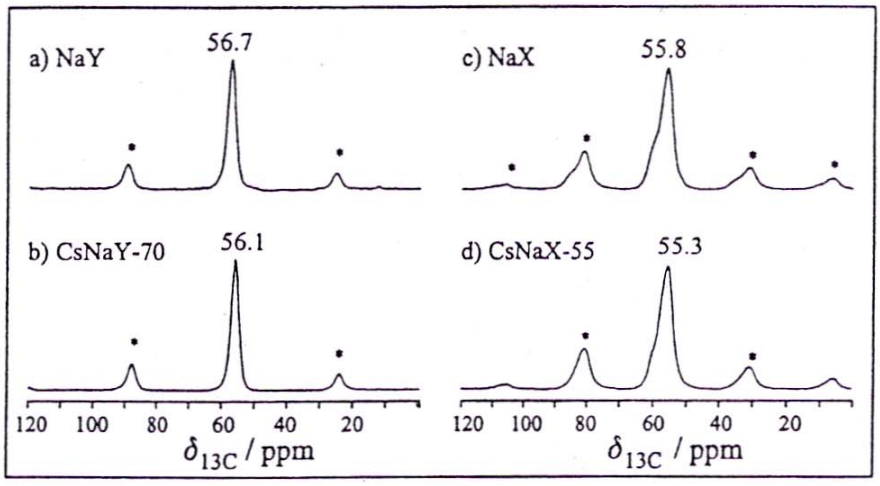

Figure 1. ^{13}C CP/MAS NMR spectra of calcined (673 K) zeolites NaY (a), CsNaY-70 (b), NaX (c) and CsNaX-55 (d), loaded with 16 CH_3I/u.c. and recorded with a sample spinning rate of 2.0 kHz.

due to spinning sidebands and indicate that the species causing the sideband pattern are rigidly bound to the zeolite framework which is typical for methoxy groups. The quantitative analysis of the MAS sideband intensities, applying the method introduced by Herzfeld and Berger [10], allows a determination of the anisotropy, $\Delta\sigma$, of the chemical shift, a characteristic parameter of rigid species. Simulation of the MAS sideband patterns, which are due to the ^{13}C MAS NMR signals at 55 to 57 ppm, leads to a chemical shift anisotropy of $\Delta\sigma = -41 \pm 2$ ppm. This value is in good agreement with the chemical shift anisotropy of methoxy groups in zeolite NaX ($\Delta\sigma = -42.7$ ppm) found by Bosacek et al. [7, 8].

In Figure 2, the isotropic chemical shifts, δ_{13C}, of methoxy groups at zeolite frameworks published by Bosacek [7] (open circles) are depicted as a function of the mean Sanderson electronegativity, S^m. The chemical shifts of the methoxy groups in zeolites NaY (56.7 ppm), CsNaY-70 (56.1 ppm) and NaX (55.8 ppm) found in the present work (closed circles) correlate well with their mean electronegativities. Only the chemical shift observed for methoxy groups in zeolite CsNaX-55 (55.3 ppm) significantly deviates from the dotted line. In the ^{13}C CP/MAS NMR spectra of methoxy groups in zeolite NaX, Bosacek [7] found signals at 53.5 ppm and 58.8 ppm which the author explained by methoxy groups bound to different framework oxygen atoms such as O1 and O4. The above-mentioned signal at ca. 58 ppm can also be observed in Figures 1c and 1d as low-field shoulders. The deviation of the chemical shift of methoxy

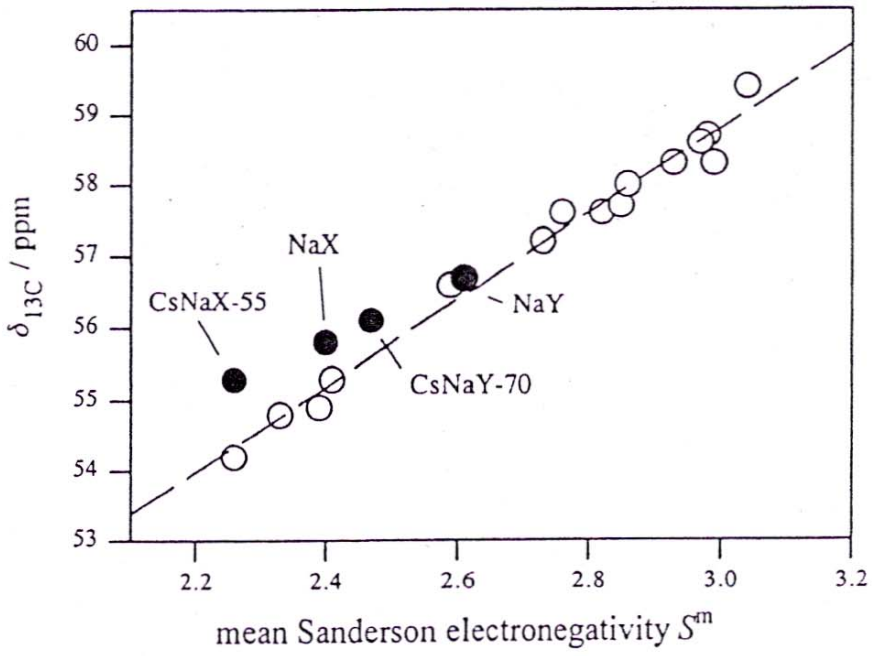

Figure 2. Dependence of the ^{13}C NMR shift of surface bound methoxy groups in zeolites on the mean electronegativity, S^m, of the zeolite framework (○: values taken from Ref. [7], ●: values taken from Figure 1).

groups in zeolite CsNaX-55 from the dotted line in Figure 2 is, therefore, caused by a superposition of the signals due to different types of methoxy groups. In spite of this fact, the ^{13}C NMR high-field shift of methoxy groups in zeolites NaY, CsNaY-70, NaX and CsNaX-55 indicates an increase in the base strength of these materials in the given order. Hence, ^{13}C NMR shifts of methoxy groups are a qualitative measure of the base strength of the cesium-exchanged samples under study. In the following, this method was applied to characterize zeolites Y and X impregnated with cesium hydroxide. To assign the ^{13}C CP/MAS NMR signal of methoxy groups bound to the guest compound, silica gel (Fluka, 500 m^2/g) was impregnated with cesium hydroxide and subsequently calcined at 673 K. The ^{13}C CP/MAS NMR spectrum of this sample loaded with CH_3I (Fig. 3a) consists of a single signal at 50.3 ppm. Obviously, this signal is due to methoxy groups bound to the strongly basic guest compound introduced by impregnation. The spectra of zeolite CsNaY-70 impregnated with 8 and 16 CsOH/u.c. (Figs. 3b and 3c) and loaded with CH_3I consist of signals at 50.3 ppm, 56.0 to 55.4 ppm and 61.0 ppm due to methoxy groups bound to the guest compound and the zeolite framework and due to dimethyl ether as suggested by Bosacek [7], respectively. An additional weak shoulder at 64 ppm is caused by physisorbed dimethylether. Interestingly, an increasing amount of cesium hydroxide, impregnated onto zeolite CsNaY-70, leads to a high-field shift of the ^{13}C NMR signal of methoxy groups. This finding indicates a change in the base strength of the host framework. However, the strongest base sites in this material are caused by the guest compound (*vide supra*). Since the spectrum depicted in Figure 3c does not show a signal at 56.1 ppm (methoxy groups in zeolite CsNaY-70), the whole framework of zeolite CsNaY-70/

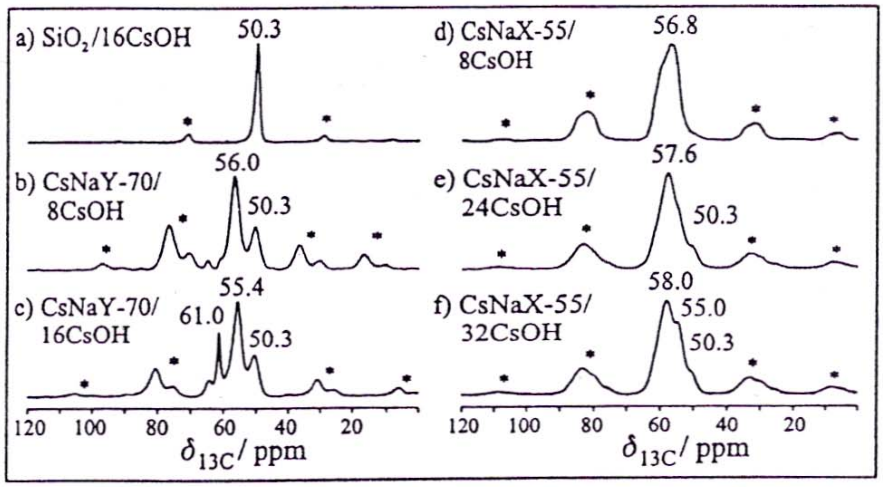

Figure 3. ^{13}C CP/MAS NMR spectra of calcined (673 K) silica gel impregnated with 16 wt.-% CsOH (a), of zeolite CsNaY-70 impregnated with 8 (b) and 16 CsOH/u.c (c) and of zeolite CsNaX-55 impregnated with 8 (d), 24 (e) and 32 (f) CsOH/u.c. All samples were loaded with 16 CH_3I/u.c.

16CsOH is affected uniformly by the impregnation with cesium hydroxide. The simulation of the MAS sideband pattern of the signal at 50.3 ppm, observed with increasing intensities in the ^{13}C MAS NMR spectra of zeolites Y after impregnation, yields a chemical shift anisotropy of -42 ± 2 ppm. The high intensity of this signal, observed for zeolite CsNaY-70/16CsOH (32 ± 2 % of the total intensity), points to a large surface and, therefore, a high dispersion of the guest compound on this sample.

The ^{13}C CP/MAS NMR spectra of zeolite CsNaX-55 impregnated with cesium hydroxide (Figs. 3d, 3e and 3f) consist of broad signals with a line width of up to 10 ppm. With increasing amount of cesium hydroxide introduced by impregnation, the peaks of the broad signal shift from 56.8 ppm (CsNaX-55/8CsOH) to 58.0 ppm (CsNaX-55/32CsOH) while high-field shoulders appear at 55.0 and 50.3 ppm. The chemical shifts of the latter two signals correspond to the resonance positions expected for methoxy groups bound to basic framework sites of zeolite X (see Figs. 1c and 1d) and to the basic guest compound (see Fig. 3a). However, the low intensities of these signals of 25 ± 2 % and 10 ± 2 %, respectively, for zeolite CsNaX-55/32CsOH indicate that the guest compound is not highly dispersed in the zeolite particles. This may be due to sterical reasons originating from the large number of cesium cations located in the supercages. On the other hand, a significant portion of methoxy groups is bound to framework oxygen atoms with a lower base strength responsible for the low-field shift of the peak from 56.8 to 58.0 ppm. These methoxy groups are identical with those causing the shoulder at 58.8 ppm observed in the ^{13}C CP/MAS NMR spectra of zeolites NaX and CsNaX-55 in Figures 1c and 1d. Hence, impregnated zeolites CsNaX-55 possess a variety of base sites with different base strength.

To clarify whether hydroxyl groups are formed on zeolites Y and X as a result of cation exchange and impregnation with cesium hydroxide, the calcined samples were characterized by ^{1}H MAS NMR spectroscopy. The spectra shown in Figure 4 can be decomposed into signals at ca. 0 ppm due to unperturbed metal OH groups, at 1.3 to 2.0 ppm caused by silanol groups and at 2.3 to 3.0 ppm originating from metal OH groups located in small cavities [11]. A weak signal of acidic bridging OH groups can be observed only in the spectrum of zeolite CsNaX-55 at ca. 4 ppm (Fig. 4e). As a result of cesium exchange the amount of silanol groups at framework defects increases from 1.4 ± 0.2 SiOH/u.c. for zeolite NaY to 1.8 ±0 .2 SiOH/u.c for zeolite CsNaY-70 and from 0.8 ± 0.2 SiOH/u.c. for zeolite NaX to 3.6 ± 0.2 SiOH/u.c. for zeolite CsNaX-55. Surprisingly, impregnation with CsOH leads to a decrease of the amount of

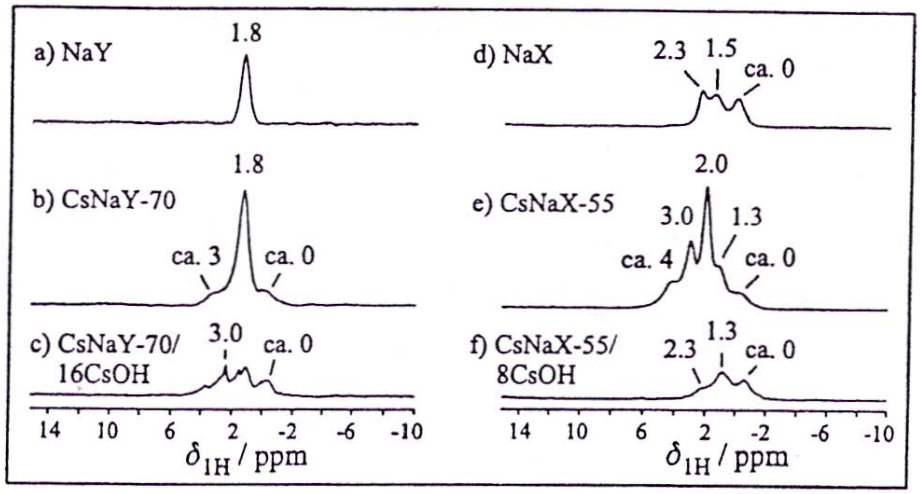

Figure 4. ^{1}H MAS NMR spectra of calcined (673 K) zeolites NaY (a), CsNaY-70 (b), CsNaY-70/16CsOH (c), NaX (d), CsNaX-55 (e) and CsNaX-55/8CsOH (f), recorded with a sample spinning rate of 10 kHz.

silanol groups to 0.4 ± 0.2 SiOH/u.c. in zeolite Y and 0.8 ± 0.2 SiOH/u.c. in zeolite X. No change in the OH concentrations was found after increasing the impregnation of zeolite CsNaX-55 from 8 CsOH/u.c. to 32 CsOH/u.c. (not shown). Generally, after impregnation of cesium-exchanged zeolites Y and X a significant decrease of defect OH groups was found. Probably, this effect is caused by a bonding of the guest compound to initial framework defects.

In a recently published work [5], static ^{27}Al spin-echo NMR spectroscopy was applied to investigate dehydrated basic zeolites Y. In this study, a variation of the local geometry of framework aluminum atoms after cation exchange and impregnation was found. In the present work, ^{27}Al DOR NMR spectroscopy of dehydrated zeolites Y and X was performed in two different magnetic fields. The ^{27}Al DOR NMR spectra of zeolites NaY, CsNaY-70 and CsNaY-70/16CsOH shown in Figure 5 and of zeolites NaX, CsNaX-55 and CsNaX-55/8CsOH shown in Figure 6 were recorded with a spinning rate of the outer DOR rotor of 1400 Hz and at resonance frequencies of 104.2 MHz (left) and 195.4 MHz (right). The dominating solid state interaction of aluminum atoms (spin I = 5/2) in dehydrated zeolites is the quadrupolar interaction between the electric quadrupole moment and the electric field gradient at the sites of the resonating nuclei [12]. The strength of the quadrupolar interaction is described by the *SOQE* parameter (*SOQE*: second-order quadrupolar effect). The *SOQE* parameter can be obtained by a evaluation of the field-dependent second-order quadrupolar shift [13]. Applying this method, the following parameters were calculated for zeolites Y: *SOQE* = 5.8 MHz for

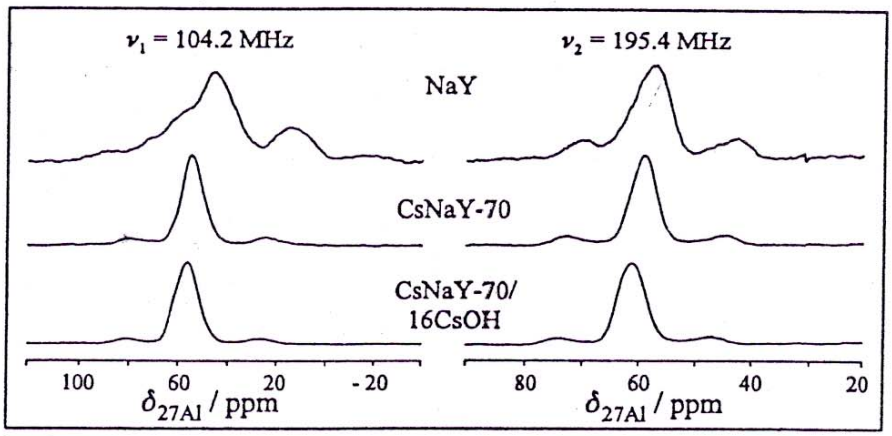

Figure 5. ^{27}Al DOR NMR spectra of calcined (673 K) zeolites NaY (top), CsNaY-70 (middle) and CsNaY-70/16CsOH (bottom), recorded at resonance frequencies of 104.23 MHz (left) and 195.43 MHz (right).

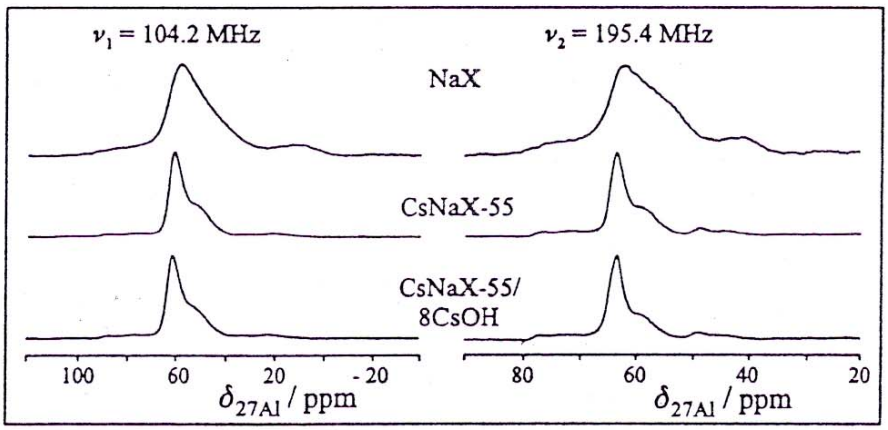

Figure 6. ^{27}Al DOR NMR spectra of calcined (673 K) zeolites NaX (top), CsNaX-55 (middle) and CsNaX-55/8CsOH (bottom), recorded at resonance frequencies of 104.23 MHz (left) and 195.43 MHz (right).

NaY, *SOQE* = 3.7 MHz for CsNaY-70 and *SOQE* = 3.4 MHz for CsNaY-70/16CsOH. Interestingly, the ^{27}Al DOR NMR spectra of zeolite X consist of at least two signals, a strong low-field line and a weak high-field shoulder with an experimental intensity ratio of 60 ± 5 % : 30 ± 5 % (Fig. 6). The parameters determined for the low-field line of zeolite X are: *SOQE* = 3.7 MHz for NaX, *SOQE* = 2.8 MHz for CsNaX-55 and *SOQE* = 2.8 MHz for CsNaX-55/8CsOH. The parameters obtained for the high-field shoulder are: *SOQE* = 5.2 MHz for NaX, *SOQE* = 4.0 MHz for CsNaX-55 and *SOQE* = 3.7 MHz for CsNaX-55/8CsOH. In all cases, the exchange of the sodium form zeolites Y and X with cesium cations and subsequent impregnation with cesium hydroxide leads to a decrease of the quadrupolar interaction of the framework aluminum atoms. According to Ghose and Tsang [14], the above-mentioned decrease of the *SOQE* parameters can be explained by a cation exchange- and guest-induced variation of the local geometry of the framework aluminum atoms.

CONCLUSIONS

By application of multinuclear solid state NMR spectroscopy it is shown that both cesium exchange and impregnation of zeolites Y and X with cesium hydroxide increase the base strength of the host framework and affect the local geometry of the framework aluminum atoms. While impregnation of zeolite CsNaY with cesium hydroxide leads to the formation of a well dispersed and strongly basic guest compound, only a small amount of strong base sites is formed on impregnated zeolite CsNaX.

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