

Mobility of Cations and Guest Compounds in Cesium-Exchanged and Impregnated Zeolites Y and X Investigated by High-Temperature MAS NMR Spectroscopy

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Through the application of high-temperature ^{23}Na and ^{133}Cs magic-angle spinning (MAS) NMR spectroscopy, the mobility of sodium and cesium ions in dehydrated zeolites Y and X in the sodium form, after exchange with cesium cations and after impregnation with cesium hydroxide, has been investigated. At temperatures typical for heterogeneous catalysis on basic zeolites Y and X, sodium and cesium cations exhibit a high mobility and are not rigidly located at their cation positions. Starting at a temperature of 570 K, a chemical exchange of sodium cations in supercages and sodalite cages occurs. At 770 K, sodium cations located at SI positions in the hexagonal prisms are involved in a chemical exchange with sodium cations in sodalite units. ^{133}Cs MAS NMR spectroscopy of zeolites CsNaY and CsNaX indicates that the cesium exchange starts at 380–420 K. Starting at 380 K, a chemical exchange of the cesium atoms contributing to guest compounds with cesium cations located at cation positions in the zeolite cages was observed. For the cesium exchange processes in zeolites CsNaY/CsOH and CsNaX/CsOH occurring at 420–770 K, activation energies of $E_a = 85 \pm 10$ and 115 ± 10 kJ/mol, respectively, were determined.

Introduction

The introduction of cesium ions in zeolites Y and X by cation exchange is an often-used method to prepare solid bases. A subsequent impregnation of zeolites CsNaY and CsNaX by cesium hydroxide or acetate followed by a calcination leads to the formation of strongly basic guest compounds.^{1–4} These materials are interesting as microporous catalysts for a number of industrially important reactions such as dehydrogenation of alcohols, isomerization of olefins, side-chain alkylation of toluene, and the synthesis of 4-methylthiazole.^{5,6} Most of these reactions work at temperatures of more than 623 K. In recently published NMR investigations, it was shown that Brønsted sites in dehydrated zeolites exhibit a high mobility at these temperatures.^{7–9} However, little is known about the dynamic behavior of cations in zeolites. Tokuhito et al. performed variable-temperature (VT) magic-angle spinning (MAS) NMR studies of cesium cations in hydrated CsNaA and CsLiA zeolites and observed a chemical exchange of cesium cations between six-ring and eight-ring sites in the large cages of these materials.¹⁰ By static (without MAS) VT NMR measurements, an activation energy of 44 kJ/mol was determined for this exchange process, being the elementary step of cesium cation diffusion in this zeolite.¹¹ For the self-diffusion of cesium cations in analcite, in which no water was present and the diffusion occurs through six-ring windows, Barrer and Rees obtained an activation energy of 109 kJ/mol.¹² By dielectric spectroscopy of dehydrated zeolites Y, Mortier and Schoonheydt studied the restricted local motion as well as the translational motion of monovalent cations localized on SII and SIII in the supercages of these materials.¹³ Depending on the framework $n_{\text{Si}}/n_{\text{Al}}$ ratio, activation energies of the ionic conduction of 55.5–58.0 kJ/mol for cesium cations and 52.3–79.4 kJ/mol for sodium cations were obtained by these authors.¹³

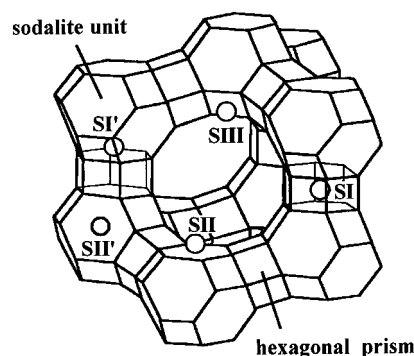


Figure 1. Structure of zeolites Y and X with cation positions SII and SIII in supercages, SI' and SII' in sodalite units, and SI in the centers of hexagonal prisms.

In the present work, the mobility of sodium and cesium cations in dehydrated zeolites Y and X before and after cesium exchange and impregnation with cesium hydroxide was investigated by MAS NMR at temperatures up to 770 K. Because cesium-modified zeolites Y and X are applied as basic catalysts at 570–770 K, high-temperature MAS NMR spectroscopy is a suitable method to investigate the behavior of extraframework cations in these materials under reaction conditions. A prerequisite of the evaluation of the VT MAS NMR spectra of zeolites Y and X is the assignment of signals. Therefore, in a first step, all samples were studied by high-velocity MAS NMR spectroscopy with a sample-spinning rate of ca. 22 kHz, leading to well-resolved spectra without overlapping of spinning sidebands and central lines. The obtained signals were discussed in relation with those described in the literature.

The first solid-state ^{23}Na NMR investigations of dehydrated zeolites Y were performed in 1993 using MAS NMR in different magnetic fields and double rotation (DOR) and two-dimensional nutation techniques.¹⁴ The signals obtained were attributed to cation positions (see Figure 1) according to the quadrupolar

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interactions to which the sodium cations (spin $I = 3/2$) are subjected in the corresponding local structures. Murray et al. published the first ^{133}Cs MAS NMR investigations of cesium cations in dehydrated CsNaY and CsNaX zeolites.¹⁵ By ^{133}Cs NMR spectroscopy of cesium cations (spin $I = 7/2$) in dehydrated zeolites Y in different magnetic fields, Malek et al. determined quadrupole coupling constants (QCCs) of a maximum of 140 kHz.¹⁶ Hence, an influence of quadrupolar interactions on the ^{133}Cs MAS NMR signals of cesium cations in dehydrated faujasites can be neglected. Comparing the cesium cation populations in a dehydrated zeolite CsNaY obtained by X-ray diffraction and Rietveld refinement with the relative signal intensities in the ^{133}Cs MAS NMR spectrum, Koller et al. assigned strong and narrow signals at ca. -62 and -71 ppm to SII and SI' cesium cations, respectively, and weak and broad signals at ca. -79 and -153 ppm to SIII and SI cesium cations, respectively.¹⁷ Applying the same method to a series of cesium-exchanged and dehydrated zeolites Y, Norby et al. attributed strong and narrow signals at ca. -87 and -94 ppm to SII and SIII cesium cations, respectively, and weak and broad signals at ca. -130 and -149 ppm to SII' and SI' cesium cations, respectively.¹⁸ The differences in the absolute chemical shift values are due to the different cation-exchange degrees of the zeolites CsNaY used.^{17,18}

In our previous investigations of dehydrated zeolites CsNaY impregnated with CsOH ,^{4,19} an additional broad hump with a center of gravity at about -30 ppm was found. This broad signal is due to cesium atoms contributing to alkali-metal-oxide guest compounds.^{4,19} Because the Cs_2O bulk phase causes a signal at 225 ppm,² the above-mentioned resonance position of about -30 ppm indicates that guest compounds, formed on zeolite Y by impregnation with CsOH and subsequent calcination, do not exist as large and isolated Cs_2O clusters.

Experimental Section

Parent zeolites NaY and NaX with $n_{\text{Si}}/n_{\text{Al}}$ ratios of 2.6 and 1.3, respectively, are commercial materials of Union Carbide Corp. (Tarrytown, NY). These materials were five-fold ion-exchanged in a 0.4 M aqueous solution of CsCl (CsCl : Aldrich, 19 831-5) at 353 K, leading to an ion-exchange degree of 70% for zeolite CsNaY and of 55% for zeolite CsNaX which corresponds to 37.3 and 45.9 Cs^+ , respectively, per unit cell (uc). To impregnate the cesium-exchanged zeolites Y and X, these materials were suspended in a 0.2 M aqueous solution of CsOH (CsOH : Aldrich, 19 833-1). The absolute amount of CsOH dissolved was equal to the desired amount in the final materials. The suspension was stirred overnight to dryness at 353 K. The impregnated materials, denoted as CsNaY/CsOH and CsNaX/CsOH , were loaded with 16 CsOH/uc and 24 CsOH/uc , respectively. Finally, the zeolites CsNaY/CsOH and CsNaX/CsOH were calcined in a stream of nitrogen gas at 723 and 773 K, respectively, for 4 h. All materials were characterized by X-ray diffraction, atomic absorption spectroscopy (AAS), and atomic emission spectroscopy with an inductively coupled plasma. By ^{29}Si and ^{27}Al MAS NMR spectroscopy, it was ensured that neither the ion exchange nor the impregnation were accompanied by a dealumination of the zeolite framework. By ^1H MAS NMR spectroscopy of the dehydrated sample, any formation of acidic OH groups during the above-described preparation steps could be excluded.

Prior to the NMR investigations, the powder materials were heated in a vacuum with a rate of 20 K/h up to the final temperature of 673 K. At this temperature, the samples were calcined for 12 h at a pressure below 10^{-2} Pa. A part of the

samples applied for low-temperature MAS NMR investigations was sealed in glass ampules with an outer diameter of 3.0 mm. All of the other samples were filled into the MAS NMR rotors under dry nitrogen using a glovebox and tightly sealed with a rotor cap.

NMR investigations were carried out on a Bruker MSL 400 spectrometer with resonance frequencies of 105.8 MHz for ^{23}Na MAS NMR and 52.5 MHz for ^{133}Cs NMR spectroscopy. All spectra were recorded after single pulse excitation with repetition times of 500 ms for ^{23}Na MAS NMR and 3 s for ^{133}Cs MAS NMR. The chemical shifts were referenced to solid NaCl and a 1.0 M solution of CsCl . MAS NMR experiments were carried out with sample-spinning rates, ν_{rot} , of ca. 22 kHz, using a high-velocity MAS NMR probe, delivered by Ago Samoson (Tallinn, Estonia), of ca. 8 kHz with a 4 mm VT Bruker MAS NMR probe and of ca. 2 kHz applying a 7 mm high-temperature Doty MAS NMR probe. All simulations were performed with the Bruker software WINFIT.

Results and Discussion

Mobility of Sodium Cations in Zeolites NaY, CsNaY , NaX, and CsNaX . In previous investigations, modern techniques of solid-state NMR spectroscopy such as MAS, DOR and two-dimensional nutation,^{20,21} and multiple-quantum NMR spectroscopy^{22,23} were applied to separate signals of sodium cations located at different cation positions in dehydrated zeolites Y and X. The quantitative evaluation of ^{23}Na MAS NMR spectra allows one to determine the populations of different cation sites. However, quadrupolar interactions and spinning sidebands influence the NMR intensities of the central lines and have to be considered. In the present work, first high-velocity ^{23}Na MAS NMR studies ($\nu_{\text{rot}} = 22$ kHz) of sodium cations in dehydrated zeolites were performed, allowing a more accurate evaluation of the central lines. The assignment and simulation of the high-velocity ^{23}Na MAS NMR spectra of zeolites NaY, CsNaY , NaX, and CsNaX shown in Figures 2 and 3 (top) were performed using quadrupole parameters given in the literature.²¹ The sodium cation populations obtained by NMR spectroscopy (see Table 1) agree well with data determined by X-ray diffraction.^{24,25} According to these populations, the exchange of zeolites NaY and NaX with cesium cations leads to a preferential exchange of sodium cations at SII and SIII positions and to a migration of sodium cations to the SI positions in the centers of hexagonal prisms. After impregnation of zeolites CsNaY and CsNaX with cesium hydroxide and calcination, no further sodium exchange could be found by high-velocity ^{23}Na MAS NMR spectroscopy (not shown).

An increase of the temperature to 380 K leads to ^{23}Na MAS NMR spectra which are similar to those obtained at 295 K, excluding the appearance of spinning sidebands due the sample-spinning rate of ca. 8 kHz (Figures 2 and 3, second line). Starting at 570 K, the spectra of zeolites NaY and NaX consist of isotropic signals due to an increased mobility of sodium cations (Figures 2 and 3, third line). The experimentally observed chemical shifts from -36 to -51 ppm correspond to the centers of gravity of the quadrupole patterns Q1 and Q2. This indicates that the sodium mobility occurring at 570 K can be explained by jumps between different cation sites in the supercages and sodalite units. Starting at 770 K, the ^{23}Na MAS NMR spectra of zeolites CsNaY and CsNaX show a high-field shift of the signal of sodium cations located at SI positions. This high-field shift indicates that sodium cations located in the hexagonal prisms are involved in a chemical exchange with residual sodium cations in sodalite units. A similar behavior of sodium cations

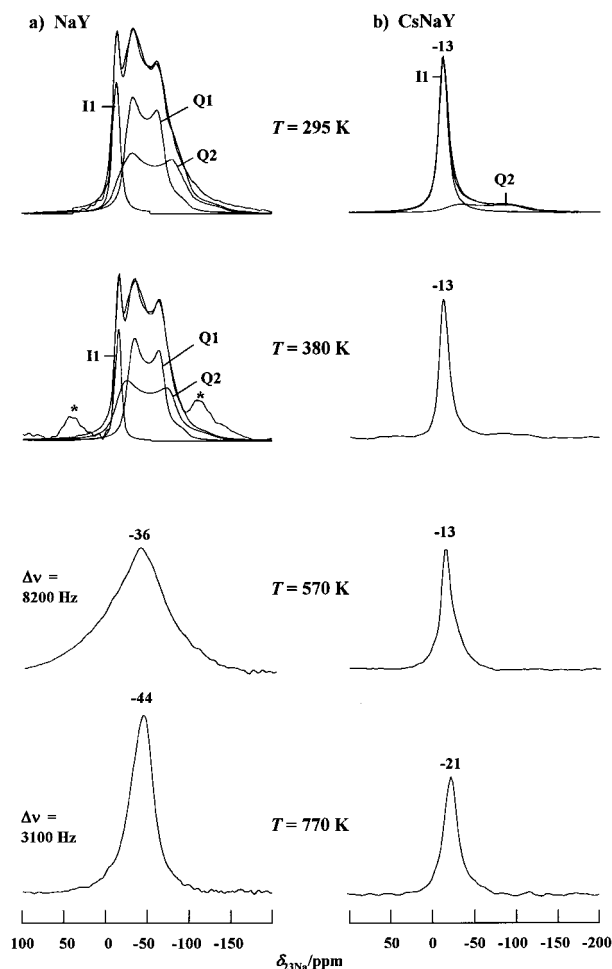


Figure 2. ^{23}Na MAS NMR spectra of dehydrated zeolites NaY (a) and CsNaY (b) recorded at 295 K ($\nu_{\text{rot}} = 22$ kHz), at 380 K ($\nu_{\text{rot}} = 8$ kHz), and at 570 and 770 K ($\nu_{\text{rot}} = 2$ kHz). The assignment of signals, their NMR parameters, and the cation populations determined at 295 K are summarized in Table 1. Asterisks denote spinning sidebands.

was found in the ^{23}Na MAS NMR spectra of zeolites CsNaY/CsOH and CsNaX/CsOH recorded at 295–770 K (not shown). The remaining quadrupolar interactions of sodium cations in dehydrated zeolites Y and X hinder a quantitative evaluation of the line shapes and a determination of the activation energies of thermal mobility.

Assignment of ^{133}Cs MAS NMR Signals and Populations of Cesium Cations in Zeolites Y and X. Because of dipolar interactions and chemical shift anisotropy of cesium cations in dehydrated faujasites, the ^{133}Cs MAS NMR spectra of these materials consist of broad sideband patterns, making a quantitative evaluation difficult. The application of high-velocity MAS NMR probes leads to a significant decrease of these spinning sidebands. However, until now these probes cannot be applied at variable temperatures. In Figures 4 and 5, the ^{133}Cs MAS NMR spectra of dehydrated zeolites CsNaY, CsNaY/CsOH, CsNaX, and CsNaX/CsOH recorded with a sample-spinning rate of ca. 22 kHz are shown. Table 2 gives the populations of cesium cations and concentrations of cesium atoms contributing to the alkali-metal-oxide guest compounds calculated by the relative signal intensities (values in brackets) and the total amounts of cesium atoms obtained by AAS. The relative signal intensities were obtained by a decomposition of the MAS NMR spectra.

The ^{133}Cs MAS NMR signals of cesium cations in zeolites CsNaY and CsNaY/CsOH shown in Figure 4 were assigned

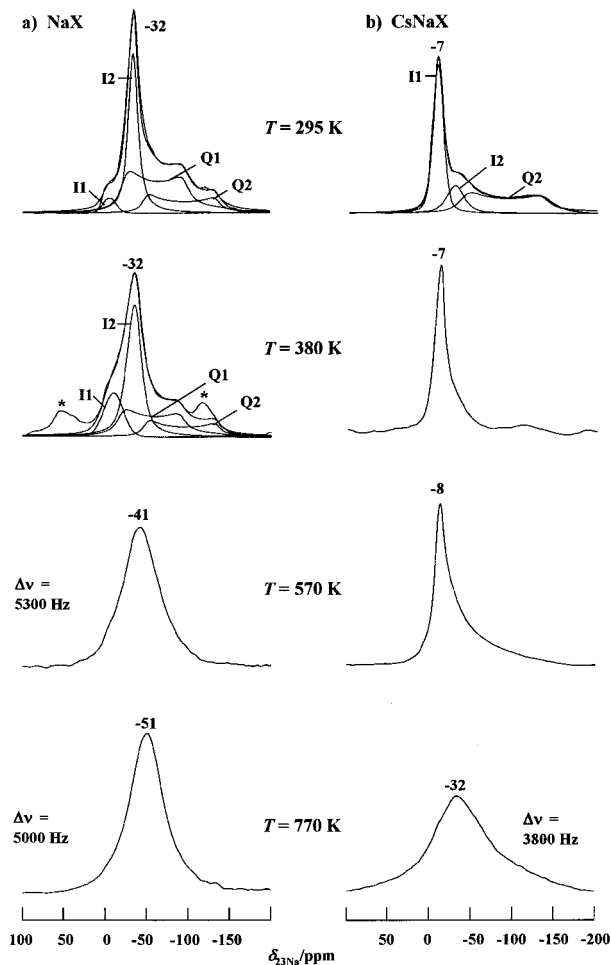


Figure 3. ^{23}Na MAS NMR spectra of dehydrated zeolites NaX (a) and CsNaX (b) recorded at 295 K ($\nu_{\text{rot}} = 22$ kHz), at 380 K ($\nu_{\text{rot}} = 8$ kHz), and at 570 and 770 K ($\nu_{\text{rot}} = 2$ kHz). The assignment of signals, their NMR parameters, and the cation populations determined at 295 K are summarized in Table 1. Asterisks denote spinning sidebands.

TABLE 1: Assignments and Parameters of ^{23}Na MAS NMR Signals and Populations of Sodium Cations in Dehydrated Zeolites NaY, CsNaY, NaX, and CsNaX Obtained by a Simulation of the High-Velocity Spectra ($\nu_{\text{rot}} = 22$ kHz) Shown in Figures 2 and 3 (Top)^a

	signal (cation site)			
	I1 (SI)	I2 (SIII)	Q1 (SII)	Q2 (SI')
$\delta_{\text{iso}}/\text{ppm}^b$	−4 to −13	−16 to −27	−12 to −16	−3 to −19
QCC/MHz	ca. 1.0	1.5–2.6	3.9–5.0	4.8–6.0
η^c	0	0	0.1–0.3	0.1–0.3
NaY				
population/uc ^{−1}	4 (0.08)		31 (0.59)	18 (0.23)
CsNaY				
population/uc ^{−1}	12 (0.76)			4 (0.24)
NaX				
population/uc ^{−1}	3 (0.04)	36 (0.43)	30 (0.36)	14 (0.17)
CsNaX				
population/uc ^{−1}	15 (0.40)	7 (0.19)		15 (0.41)

^a The experimental accuracy of the populations is $\pm 5\%$. ^b δ_{iso} : isotropic chemical shift after correction of the second-order quadrupolar shift. ^c η : asymmetry parameter of the quadrupolar interaction.

according to Norby et al.¹⁸ The broad low-field signals at ca. −15 ppm appearing after impregnation with CsOH correspond to previously observed cesium atoms of alkali-metal-oxide guest compounds.^{4,19} Decomposition of the ^{133}Cs MAS NMR spectra of zeolites CsNaX and CsNaX/CsOH yields signals at resonance

TABLE 2: Populations of Cesium Cations and Concentrations of Cesium Atoms Contributing to Alkali-Metal-Oxide Guest Compounds (per uc) in Cesium-Exchanged and Impregnated Zeolites Y and X, Calculated by the Relative Signal Intensities (Given in Brackets) Obtained by a Decomposition of the ^{133}Cs MAS NMR Spectra in Figures 4 and 5 and the Total Amounts of Cesium Atoms Obtained by AAS^a

	cation site				guest compounds
	SII	SIII	SII'	SI'	
$\delta_{^{133}\text{Cs}}/\text{ppm}$	-73	-92	-107 to -115	-152 to -155	ca. -15
CsNaY					
population/uc ⁻¹	14 (0.39)	9 (0.25)	10 (0.28)	3 (0.08)	0
CsNaY/CsOH					
population/uc ⁻¹	19 (0.36)	5 (0.09)	7 (0.13)	6 (0.12)	16 (0.30)
$\delta_{^{133}\text{Cs}}/\text{ppm}$	-45 to -62	-84 to -90	-103	-128 to -130	ca. +28 and -12
CsNaX					
population/uc ⁻¹	3 (0.06)	26 (0.57)	15 (0.33)	2 (0.04)	0
CsNaX/CsOH					
population/uc ⁻¹	7 (0.10)	28 (0.40)		10 (0.15)	16 (0.23) and 8 (0.12)

^a The experimental accuracy of the populations is $\pm 5\%$.

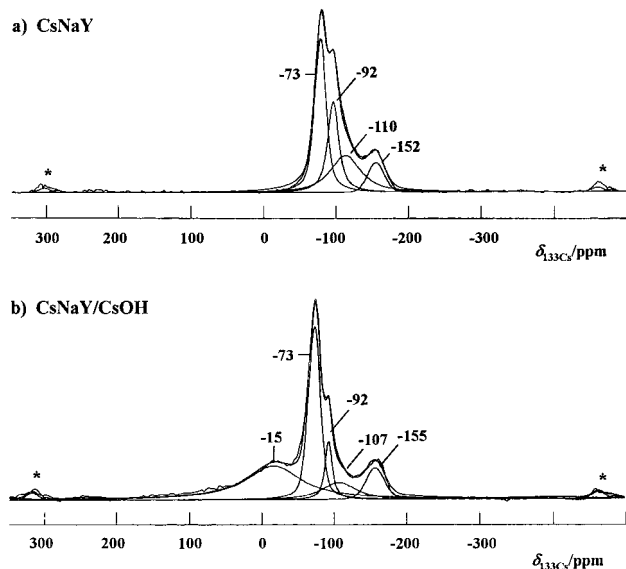


Figure 4. ^{133}Cs MAS NMR spectra of dehydrated zeolites CsNaY (a) and CsNaY/CsOH (b) recorded at 295 K with a sample-spinning rate of ca. 22 kHz. The assignment of the signals and the NMR parameters are given in Table 2. Asterisks denote spinning sidebands.

positions similar to those of zeolites CsNaY and CsNaY/CsOH. The assignment given in Table 2 was supported by the low-temperature experiments described below. In contrast to the ^{133}Cs MAS NMR spectra of zeolite CsNaY/CsOH, the spectra of zeolite CsNaX/CsOH indicate the formation of different alkali-metal-oxide guest compounds with resonance positions of -12 to +28 ppm. The concentrations of cesium atoms calculated by the relative intensities of the signals at -12 to +28 ppm agree well with the amounts of CsOH used to impregnate zeolites CsNaY and CsNaX. The impregnation of zeolites CsNaY and CsNaX leads to a variation of the cesium cation distribution (see Table 2). After the impregnation of zeolite CsNaX, no ^{133}Cs MAS NMR signal of cesium cations at the SII' position could be observed.

Low-Temperature ^{133}Cs MAS NMR Spectroscopy of Cesium Cations in Zeolites Y and X. The interaction of nitrogen molecules with cesium cations occurring at low temperatures causes a low-field shift of the corresponding ^{133}Cs MAS NMR signals and is, therefore, a suitable method to investigate the accessibility and location of these cations in the zeolite cages.¹⁸ To record the ^{133}Cs MAS NMR spectra of dehydrated zeolites CsNaY and CsNaX shown in Figures 6a and 7a, samples calcined in a vacuum and fused in glass ampules

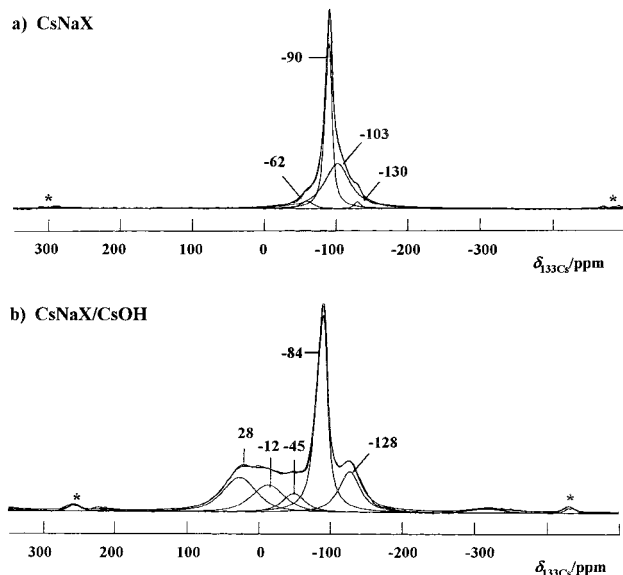


Figure 5. ^{133}Cs MAS NMR spectra of dehydrated zeolites CsNaX (a) and CsNaX/CsOH (b) recorded at 295 K with a sample-spinning rate of ca. 22 kHz. The assignment of the signals and the NMR parameters are given in Table 2. Asterisks denote spinning sidebands.

were used. The spectra in Figures 6b and 7b were obtained using samples calcined in a vacuum and filled into the MAS NMR rotors under dry nitrogen. For zeolite CsNaY fused in a glass ampule, no influence of the temperature decrease to 150 K could be observed. The increase of the sideband intensities in the spectra of zeolite CsNaX fused in a glass ampule by decreasing the temperature indicates that cesium cations in this zeolite exhibit a significant mobility at 295 K, which is frozen at 150 K. However, no variation of the resonance positions of the central lines occurs. In the low-temperature ^{133}Cs MAS NMR spectroscopy of zeolites CsNaY and CsNaX filled under dry nitrogen (Figures 6b and 7b), the decrease of the temperature to 150 K causes a systematic low-field shift of the dominating ^{133}Cs MAS NMR signals of cesium cations, supporting their assignments to cesium cations located at SII and SIII positions. It is also interesting to note that, at 200 and 150 K, cesium cations assigned to cations at SII' positions in zeolite CsNaY are low-field-shifted (Figure 6c). Only the signal of cesium cations located at SI' positions remains unaffected by nitrogen molecules at a chemical shift of -152 ppm. In the low-temperature spectra of zeolite CsNaX filled under dry nitrogen into the MAS NMR rotor (Figure 7c), the weak signals at -103

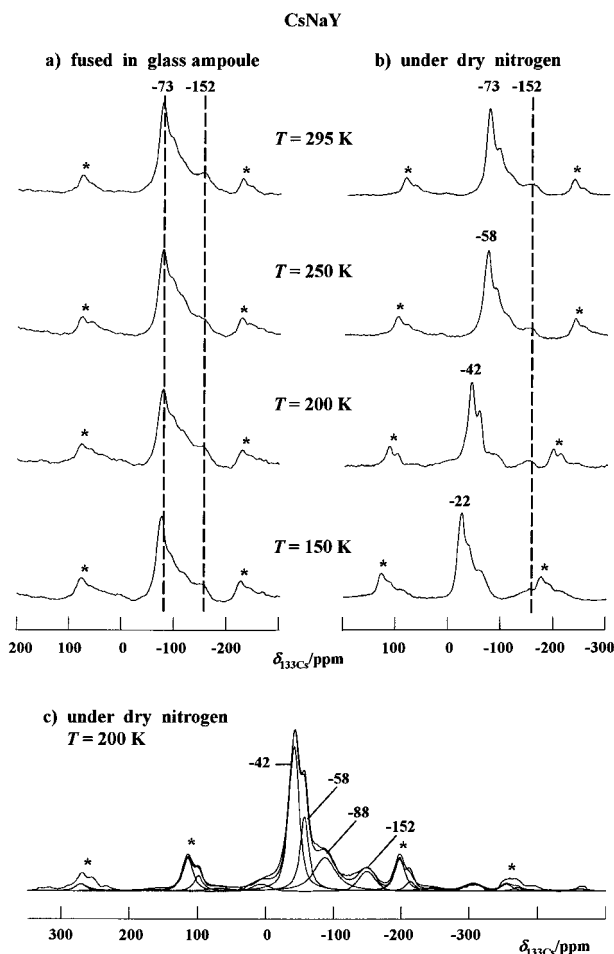


Figure 6. Low-temperature ^{133}Cs MAS NMR spectra of dehydrated zeolite CsNaY fused in a glass ampoule (a) and filled into the MAS NMR rotor under dry nitrogen using a glovebox (b). In c, the decomposition of the spectrum of series b recorded at 200 K is shown. Asterisks denote spinning sidebands.

and -130 ppm, assigned to cesium cations located at SiI' and SiI' positions, respectively, are unaffected by nitrogen molecules, whereas the dominating signal assigned to cesium cations at SiII positions is shifted to -37 ppm. Hence, the above-mentioned low-field shifts of ^{133}Cs MAS NMR signals observed at low temperatures support the assignments of cesium cations in zeolites CsNaY and CsNaX given in Table 2.

Mobility of Cesium Cations at Temperatures between 295 and 770 K. High-temperature ^{133}Cs MAS NMR investigations of zeolites CsNaY, CsNaY/CsOH, CsNaX, and CsNaX/CsOH were performed with samples filled under dry nitrogen into the MAS NMR rotors. According to the spectra shown in Figure 8a, cesium cations in zeolite CsNaY are rigidly located at their cation positions up to 340 K. A further increase of the temperature causes a decrease of the spinning sidebands and a narrowing of the central lines. At 770 K, the spectrum consists of a narrow line at -92 ppm, indicating a rapid chemical exchange of cesium cations. The weak signal at -145 ppm is due to cesium cations located at SiI' positions. Considering the relative weights, p_i , of the ^{133}Cs MAS NMR signals and the chemical shifts, δ_i , of cesium cations of type i in zeolite CsNaY given in Table 2, a rapid chemical exchange of all cesium cations including about 50% of the cations located at SiI' positions leads to the experimentally observed signal with a center of gravity, $\delta_{\text{cg}} = \sum p_i \delta_i$, at -92 ppm.

In contrast to the high-temperature ^{133}Cs MAS NMR spectra of zeolite CsNaY, the spectra of zeolite CsNaX (Figure 9a) show

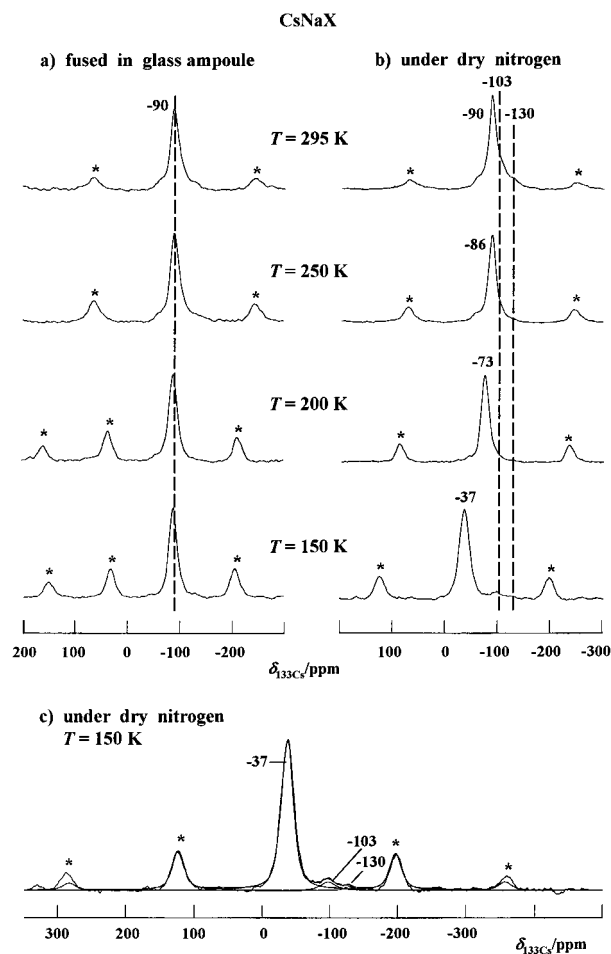


Figure 7. Low-temperature ^{133}Cs MAS NMR spectra of dehydrated zeolite CsNaX fused in a glass ampoule (a) and filled into the MAS NMR rotor under dry nitrogen using a glovebox (b). In c, the decomposition of the spectrum of series b recorded at 150 K is shown. Asterisks denote spinning sidebands.

only a weak variation of the line positions and line shapes. As mentioned above, already at room temperature, cesium cations in zeolite CsNaX exhibit a significant mobility, which is further increased by raising the temperature. At 770 K, the center of gravity of the dominating signal occurring at -92 ppm can be explained by a chemical exchange of cesium cations according to their relative weights and resonance positions observed at room temperature (see Table 2), including about 50% of cesium cations at SiI' positions. The remaining signal of cesium cations located at SiI' positions becomes narrow and is low-field-shifted to -122 ppm.

According to the high-temperature ^{133}Cs MAS NMR spectra of zeolites CsNaY/CsOH and CsNaX/CsOH shown in Figures 8b and 9b, cesium atoms contributing to alkali-metal-oxide guest compounds are involved in a chemical exchange with cesium cations located at positions SiII and SiII at ca. 380 K. After a further increase of the temperature, the signals of cesium cations and of cesium atoms contributing to guest compounds become broader and fuse to a single signal. At the point of coalescence, the correlation time, τ_c , of the chemical exchange reaches a value which fulfils the equation $\tau_c \Delta\omega \approx 1$.²⁶ $\Delta\omega$ is the frequency difference between the resonance positions of the components involved in the chemical exchange. For zeolites CsNaY/CsOH and CsNaX/CsOH, the coalescence is reached between 380 and 420 K. With consideration of the shift differences of cesium cations and cesium atoms contributing to guest compounds given in Table 2, the correlation times of the rapid cesium exchange

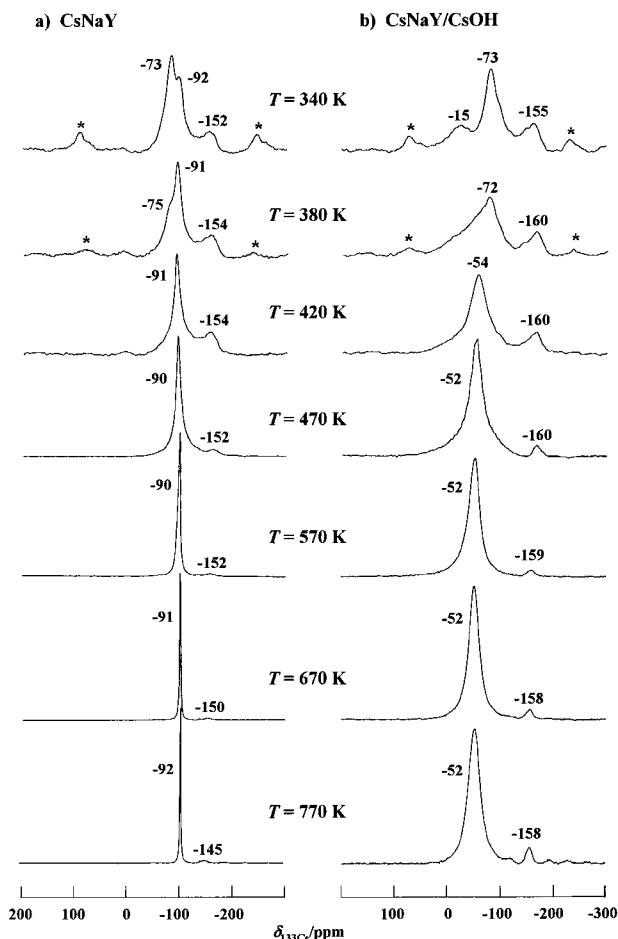


Figure 8. High-temperature ^{133}Cs MAS NMR spectra of dehydrated zeolites CsNaY (a) and CsNaY/CsOH (b) filled into the MAS NMR rotor under dry nitrogen using a glovebox. Measurements were performed at 340 and 380 K with a VT 4 mm Bruker MAS NMR probe and at 420–770 K with a high-temperature 7 mm Doty MAS NMR probe. Asterisks denote spinning sidebands.

in zeolites CsNaY/CsOH and CsNaX/CsOH of $\tau_c \approx 50$ and $30 \mu\text{s}$, respectively, can be estimated. At 770 K, the spectra of zeolites CsNaY/CsOH and CsNaX/CsOH consist of narrow signals at -52 and -33 ppm and weak signals of cesium cations at SI' positions at -158 to -124 ppm, respectively. The signals at -52 and -33 ppm agree well with the centers of gravity estimated for a chemical exchange of the cesium atoms contributing to the guest compounds and all cesium cations according to their relative weights and chemical shifts (Table 2), excluding cesium cations located at SI' positions.

The temperature dependence of the rate constant, k , of the chemical exchange processes occurring in zeolites CsNaY/CsOH and CsNaX/CsOH allows one to estimate the activation energy, E_a . The rate constants, k , at different temperatures are given by $k = \tau_c^{-1} = \pi\Delta\delta^2/\Delta\nu$, where $\Delta\delta$ is the difference of the resonance positions of the components involved in the chemical exchange given in hertz and $\Delta\nu$ is the line width of the mean signal at elevated temperatures.²⁶ The activation energy, E_a , of a chemical exchange can be determined via the Arrhenius equation, $k = A \exp(-E_a/RT)$, by plotting $\ln k$ over $1/T$. To calculate the rate constants, k , the ^{133}Cs MAS NMR spectra of zeolites CsNaY/CsOH and CsNaX/CsOH recorded at 420–770 K were simulated, yielding the line widths $\Delta\nu$. The chemical shift differences ($\Delta\delta = \delta_2 - \delta_1$) were calculated assuming a chemical exchange of cesium ions at resonance positions which correspond to the centers of gravity of cesium cations at

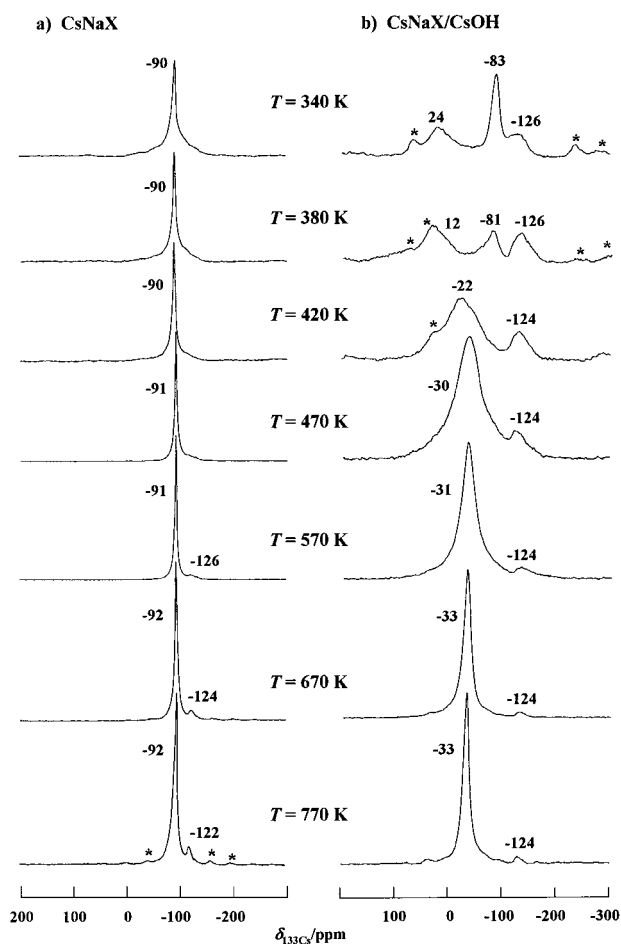


Figure 9. High-temperature ^{133}Cs MAS NMR spectra of dehydrated zeolites CsNaX (a) and CsNaX/CsOH (b) filled into the MAS NMR rotor under dry nitrogen using a glovebox. Measurements were performed at 340 and 380 K with a VT 4 mm Bruker MAS NMR probe and at 420–770 K with a high-temperature 7 mm Doty MAS NMR probe. Asterisks denote spinning sidebands.

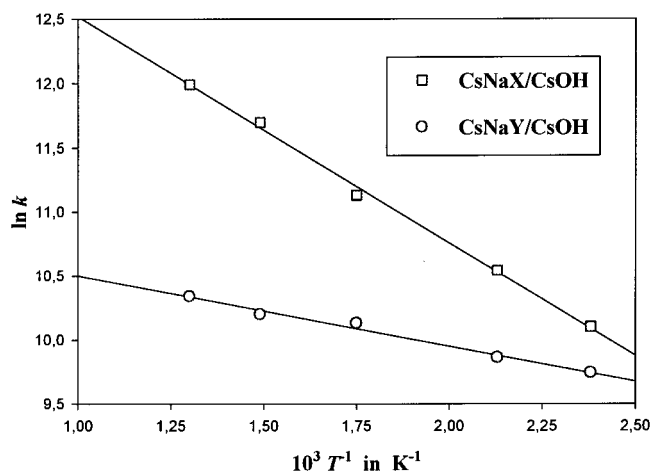


Figure 10. Arrhenius plot of the rate constants k of the rapid cesium exchange over $1/T$ using the data obtained by ^{133}Cs MAS NMR spectroscopy of dehydrated zeolites CsNaY/CsOH and CsNaX/CsOH at 420–770 K.

positions SII and SIII (δ_1) and of cesium atoms in the guest compounds (δ_2). The slopes of the straight lines shown in Figure 10 yield activation energies of the cesium exchange processes in dehydrated zeolites CsNaY/CsOH and CsNaX/CsOH of $E_a = 85 \pm 10$ and 115 ± 10 kJ/mol, respectively. It is interesting to note that the cesium exchange processes in zeolites CsNaY/

CsOH and CsNaX/CsOH, which involve cesium atoms of alkali-metal-oxide guest compounds formed by impregnation with cesium hydroxide, are characterized by activation energies similar to those of cesium cation migration and translation in dehydrated zeolites.^{12,13}

Conclusions

Modern high-temperature MAS NMR probes make it possible to investigate the mobility of extraframework cations and guest atoms in basic zeolites at temperatures which are typical for an application of these materials as catalysts in the chemical industry. With a raise in the temperature up to 770 K, a rapid chemical exchange of sodium and cesium cations and of cesium atoms contributing to alkali-metal-oxide guest compounds in dehydrated zeolites Y and X occurs. Sodium cations in supercages and sodalite units of dehydrated zeolites NaY, CsNaY, NaX, and CsNaX start to exchange at a temperature of 570 K. However, the remaining influence of quadrupolar interactions on the ²³Na MAS NMR line shapes makes a quantitative evaluation difficult. At 770 K, sodium cations located at SI positions in hexagonal prisms are involved in a chemical exchange with cations in sodalite units. Cesium cations in dehydrated zeolites CsNaY and CsNaX start to exchange at a temperature of 380 K. A similar behavior was found for cesium atoms contributing to alkali-metal-oxide guest compounds formed by impregnation with cesium hydroxide and subsequent calcination. At 380–420 K, a coalescence of all signals excluding the signal of cesium cations at SI' positions occurs in the ¹³³Cs MAS NMR spectra of zeolites CsNaY/CsOH and CsNaX/CsOH. The centers of gravity of the dominating ¹³³Cs MAS NMR signals observed at 770 K can be explained by a rapid chemical exchange of all cesium cations and cesium atoms of alkali-metal-oxide guest compounds excluding cesium cations located at SI' positions. An Arrhenius plot of the rate constants obtained at 420–770 K yields activation energies of the cesium exchange processes in dehydrated zeolites CsNaY/CsOH and CsNaX/CsOH of 85 ± 10 and 115 ± 10 kJ/mol, respectively. These values are on the order of activation energies of cesium cation migration and translation in dehydrated zeolites and indicate that the alkali-metal-oxide guest compounds are atomic-dispersed on the zeolitic host and do not exist as isolated Cs₂O clusters.

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