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High-temperature MAS NMR investigation of the mobility of cations and guest compounds in zeolites X and Y

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The mobility of sodium and cesium cations in dehydrated zeolites X and Y in the sodium form, after exchange with cesium cations and after impregnation with cesium hydroxide has been investigated by high-temperature ^{23}Na and ^{133}Cs MAS NMR spectroscopy. At temperatures typical for heterogeneous catalysis on zeolites, alkali metal cations exhibit a high mobility and are not rigidly located at their cation positions. As found by ^{23}Na MAS NMR spectroscopy, the rapid exchange of sodium cations in dehydrated zeolite Na-Y starts at ca. 573 K and is characterized by an activation energy of E_A = 20±2 kJ/mol. The rapid exchange of cesium cations in dehydrated zeolite CsNa-Y starts at ca. 423 K. By ^{133}Cs MAS NMR spectroscopy, an activation energy for the cesium exchange in zeolite Y equal to that for the sodium exchange was determined. These activation energies are significantly lower than those estimated for cesium exchange processes observed at temperatures of 423 to 773 K for dehydrated zeolites CsNa-Y and CsNa-X impregnated with cesium hydroxide as guest compound (E_A ca. 85 to 115 kJ/mol).

1. INTRODUCTION

Cations in zeolites act as adsorption sites for adsorbate molecule and reactants and influence the mean electronegativity of the zeolite framework. In addition, the shape selectivity of zeolites, i.e. the free diameters of their pores and cages, strongly depend on the distribution of cations in the zeolite lattice. Basic zeolites X and Y, exchanged with electropositive alkali metal cations, are interesting 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-methylthiazol [1,2]. Most of these reactions work at temperatures of more than 623 K. Little is known about the dynamic behavior of cations in dehydrated zeolites at these temperatures. For the self-diffusion of cesium cations in analcite, in which the diffusion occurs through six-ring windows, Barrer and Rees determined an activation energy of 109 kJ/mol [3]. By dielectric spectroscopy of dehydrated zeolites Y, Mortier and Schoonheydt [4] studied the restricted local motion as well as the translational motion of sodium and cesium cations localized on SII and SIII positions in the supercages of these materials and determined activation energies of 52 to 79 kJ/mol. Studying lithium cations in dehydrated zeolites LSX by variable-temperature ^{7}Li MAS NMR spectroscopy, Feuerstein and Lobo [5] obtained an activation energy of 13 kJ/mol for the mobility of cations located at SIII positions in the temperature range of 233 to 313 K. In the present work, the

dynamic behavior of sodium and cesium cations and cesium atoms of guest compounds in dehydrated zeolites LSX, X and Y were investigated by MAS NMR spectroscopy at temperatures up to 773 K.

2. EXPERIMENTAL SECTION

Catalysts. Zeolite Na-LSX with a framework n_{Si}/n_{Al} ratio of 1.06 was synthesized as described in Reference [6]. Zeolites Na-Y and Na-X with n_{Si}/n_{Al} ratios of 2.6 and 1.3, respectively, are commercial materials of Union Carbide Corp., Tarrytown, N. Y., USA. Cation exchange and impregnation were performed as described elsewhere [7]. To ensure a sodium exchange degree of 100 %, the parent zeolites Na-LSX, Na-X and Na-Y were exchanged in a large surplus of a 0.1 M aqueous solution of $NaNO_3$ and, subsequently, washed in demineralised water. In zeolites denoted as CsNa-Y and CsNa-X, ca. 70 % and 55 %, respectively, of sodium cations were exchanged by cesium cations in a 0.4 M aqueous solution of CsCl. To impregnate the cesium-exchanged zeolites X and Y, these materials were suspended in a 0.2 M aqueous solution of CsOH. 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 material, denoted as CsNa-Y/CsOH and CsNa-X/CsOH, were loaded with 16 CsOH/u.c. and 24 CsOH/u.c., respectively. Finally, the zeolites CsNa-Y/CsOH and CsNa-X/CsOH were calcined in a stream of nitrogen gas at 723 K and 773 K, respectively, for 4 hours. All zeolites were characterized by X-ray diffraction, atomic absorption spectroscopy (AAS) and atomic emission spectroscopy with inductively coupled plasma (ICP-AES). ^{29}Si and ^{27}Al MAS NMR spectroscopy was applied to ensure that neither the ion exchange nor the impregnation were accompanied by a dealumination of the zeolite framework. Prior to the variable-temperature NMR investigations, the samples were dehydrated in vacuum for 12 h at 673 K.

Spectroscopy. The NMR investigations were performed on a Bruker MSL 400 spectrometer at resonance frequencies of 105.8 MHz for ^{23}Na and 52.5 MHz for ^{133}Cs MAS NMR spectroscopy. All spectra were recorded after single pulse $\pi/6$ and $\pi/2$ excitation with repetition times of 500 ms and 3 s for ^{23}Na and ^{133}Cs MAS NMR spectroscopy, respectively. The chemical shifts were referenced to 1.0 M aqueous solutions of NaCl and CsCl. The MAS NMR experiments were carried out with sample spinning rates, ν_{rot}, of 22 kHz using a high-speed MAS NMR probe and of 2 kHz applying a 7 mm high-temperature Doty MAS NMR probe. All simulations were performed with the Bruker software WINFIT.

3. RESULTS AND DISCUSSION

The signals contributing to the ^{23}Na MAS NMR spectra of dehydrated zeolites Na-LSX, Na-X and Na-Y were investigated at room temperature applying high-speed sample spinning (ν_{rot} = 22 kHz). The components I1, I2, I3, Q1 and Q2 used to simulate the spectra shown in Figure 1, top, were assigned according to References [8-10]. The quadrupolar parameters obtained by simulation for the different components and the populations of the different cation positions calculated by the corresponding signal intensities are given in Table 1. According to Massiot et al. [11], a correction of the signal intensities could be neglected because of the large sample spinning frequency. Comparing the distribution of sodium cations in zeolites Na-LSX, Na-X and Na-Y, the most important difference is the population of the SIII positions which

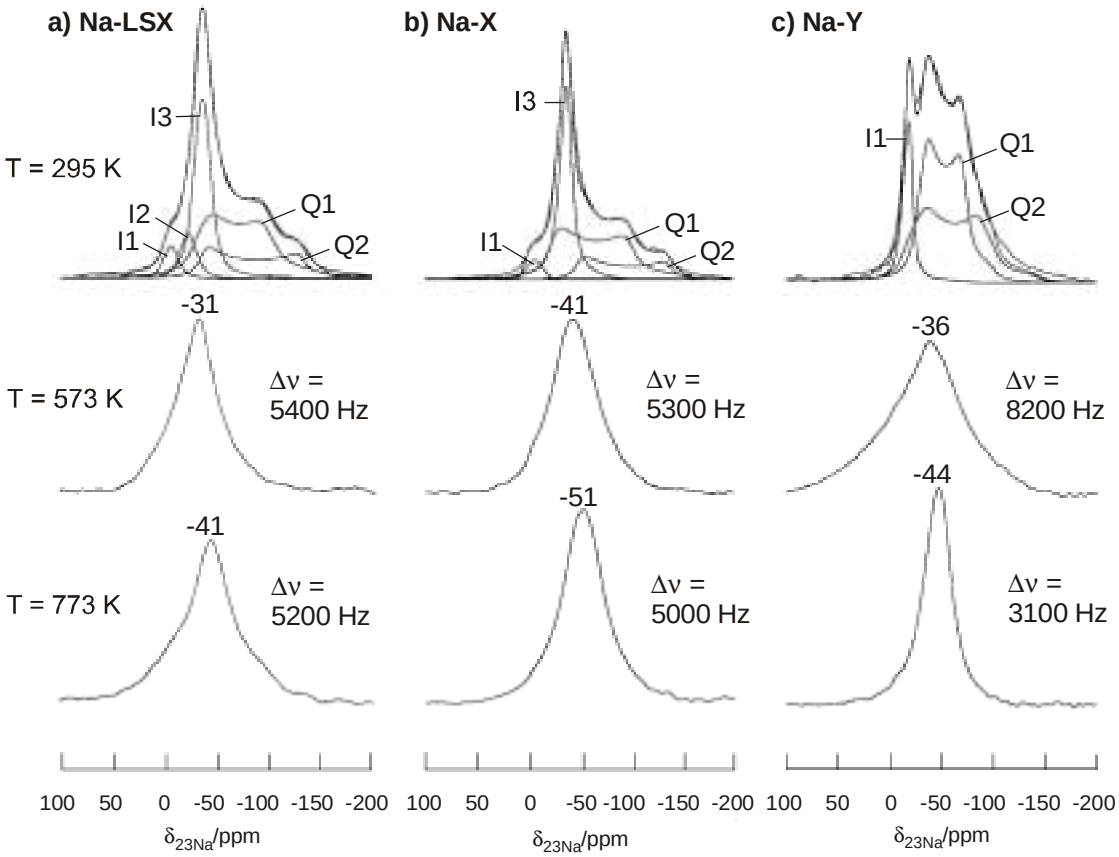

Fig. 1. ^{23}Na MAS NMR spectra of dehydrated zeolites Na-LSX, Na-X and Na-Y, recorded at temperatures of 295, 573 and 773 K. The parameters of the components I1, I2, I3, Q1 and Q2 used to simulate the spectra obtained at 295 K are given in Table 1. The line width Δν was estimated assuming an isotropic line shape.

strongly increases with an increasing aluminium content in the zeolite framework. Variable-temperature experiments were performed using the high-temperature Doty MAS NMR probe in the range from 295 to 773 K raising the temperature in steps of 50 K. In Figure 1, middle and bottom, the spectra recorded at 573 and 773 K are shown. Starting at a temperature of 573 K, signals with isotropic line shape occur in the ^{23}Na MAS NMR spectra of zeolites Na-LSX, Na-X and Na-Y due to a rapid exchange of sodium cations between different cation positions. The centers of gravity of these signals appearing at –31 to –51 ppm indicate that the rapid exchange is not accompanied by an averaging of the quadrupolar interactions of the corresponding sodium cations. In the other case, i.e. if the quadrupolar interactions would be averaged by the rapid exchange, the mean signals would appear in the range of the isotropic chemical shifts from 0 to –17 ppm given in column 5 of Table 1. The variation of the centers of gravity of the mean signals obtained after raising the temperature from 573 to 773 K shows that not all sodium cations are involved in the rapid exchange in a same manner at different temperatures. For all samples under study, the increase of the temperature from 573 to 773 K led to a high-field shift of the mean signal by ca. 10 ppm. Sodium cations located

Table 1. NMR parameters of sodium cations in dehydrated zeolites LSX, X and Y derived by a quantitative evaluation of the high-speed ^{23}Na MAS NMR spectra shown in Figure 1, top. The total amounts of sodium cations given in the first column were determined by ICP-AES. The experimental accuracy of the populations is ± 5 %.

Zeolite Population	signal	Position	QCC/MHz[1)]	η[2)]	δ_{iso}/ppm[3)]	Na^+/u.c.[4)]
Na-LSX	I1	SI	1.2	0.1	0	4
93.2 Na^+/u.c.	I2	SIII'(3)	2.0	0.8	-1	13
	I3	SIII'(1,2)	2.2	0.5	-13	26
	Q1	SII	5.1	0.2	-12	32
	Q2	SI'	5.9	0.1	-6	18
Na-X	I1	SI	1.2	0.1	-1	4
83.5 Na^+/u.c.	I3	SIII'	2.6	0.5	-17	31
	Q1	SII	4.8	0.2	-16	32
	Q2	SI'	5.9	0.1	-10	16
Na-Y	I1	SI	1.2	0.1	-3	7
53.3 Na^+/u.c.	Q1	SII	3.9	0.2	-7	30
	Q2	SI'	4.8	0.2	5	16

1) Quadrupole coupling constant QCC = $3 \cdot e^2 \cdot q \cdot Q/h$. The parameters $e \cdot q$ and $e \cdot Q$ are the z-component of the electric field gradient and the electric quadrupolar moment of the nuclei, respectively.

2) Asymmetry parameter, $\eta = (V_{xx} - V_{yy})/V_{zz}$.

3) Isotropic chemical shift, δ_{iso}.

4) Number of sodium cations, obtained by a separation of the high-speed MAS NMR signals and the total amounts of Na^+/u.c. determined by ICP-AES.

at SI' positions in the sodalite cages cause the quadrupolar pattern with a center of gravity occuring at the highest field (signal Q2). Hence, it can be assumed that the observed temperature-dependent resonance shift of the mean signals is due to an increasing involvement of sodium cations located at SI' positions in the rapid exchange. To determine the line width $\Delta\nu$ given in Figure 1, middle and bottom, isotropic signals were assumed. However, an accurate fitting was possible for the spectra of zeolite Na-Y only. The high-temperature ^{23}Na MAS NMR signals of zeolites Na-LSX and Na-X show deviations from an isotropic line shape and only a weak dependence of the line width of the mean signals on the temperature. For zeolites Na-LSX and Na-X, an increase of the temperature from 573 to 773 K led to a decrease of the line width from ca. 5300 to ca. 5100 Hz while for zeolite Na-Y a decrease of the line width by a factor of about 0.4 was found.

In Figure 2, top, the high-speed ^{133}Cs MAS NMR spectra of dehydrated zeolites CsNa-X and CsNa-Y, recorded at 295 K are shown. Due to the weak quadrupolar interactions of cesium cations (spin I = 7/2) in zeolites with faujasite structure [12], the spectra can be simulated using isotropic line shapes. The assignment of the signals given in Table 2 was made according to References [13,14]. The cesium populations of the cation positions were calculated using the relative ^{133}Cs MAS NMR intensities of the corresponding signals and the total amounts of cesium cations obtained by AAS. Comparing the distribution of cesium cations in the zeolites under study, the most significant difference is the strong cesium

population of the SIII positions in the supercages of zeolite CsNa-X. In contrast to this finding, in zeolite CsNa-Y about the same amounts of cesium cations are located at positions

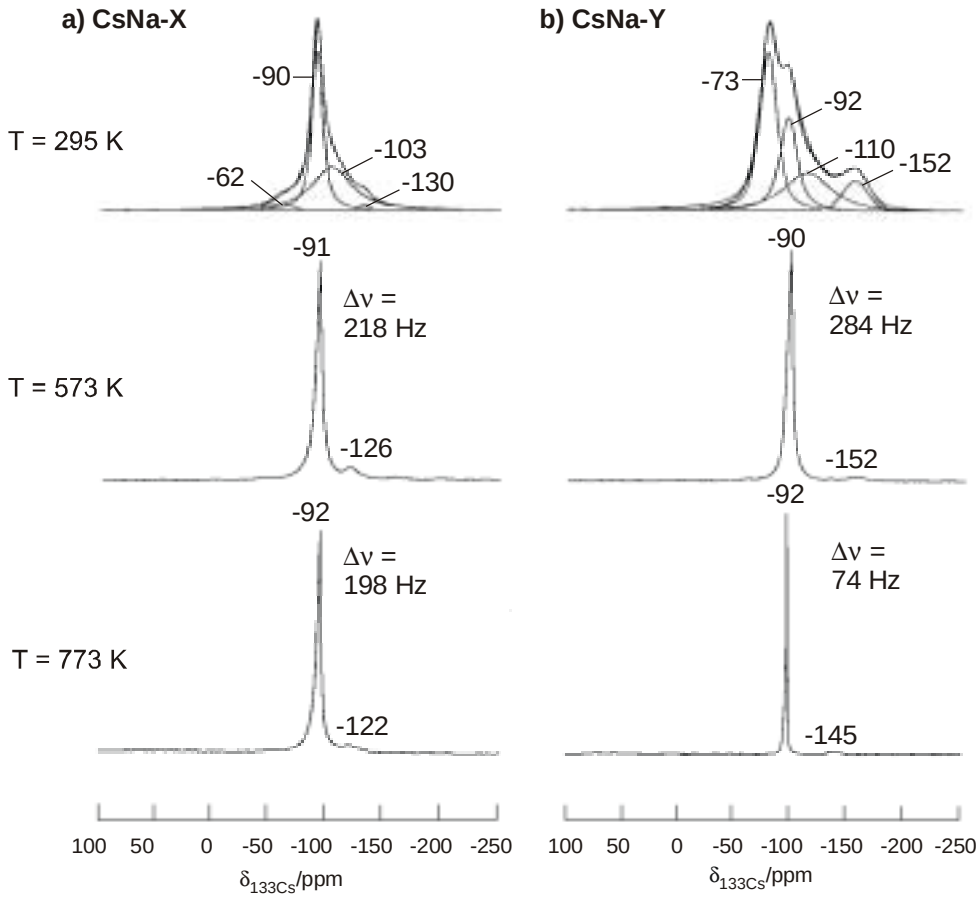

Fig. 2. ^{133}Cs MAS NMR spectra of dehydrated zeolites CsNa-X (a) and CsNa-Y (b), recorded at temperatures of 295 K, 573 K and 773 K. The parameters of the components used to simulate the spectra obtained at 295 K are given in Table 1. The line width Δν was estimated assuming an isotropic line shape.

Table 2. Assignment of the ^{133}Cs MAS NMR signals of dehydrated zeolites CsNa-X and CsNa-Y and populations of cesium cations in these materials, calculated by their relative signal intensities in the high-speed MAS NMR spectra in Figure 2, top, and the total amounts of cesium cation obtained by AAS. The experimental accuracy of the populations is ± 5 %.

Cation position	SII	SIII	SII'	SI'
Zeolite **CsNa-X**				
δ_{133Cs}/ppm	-45 to –62	-84 to –90	-103	-128 to –130
Cs^+/u.c.	3	26	15	2
Zeolite **CsNa-Y**				
δ_{133Cs}/ppm	-73	-92	-107 to –115	-152 to –155
Cs^+/u.c.	14	9	10	3

in sodalite cages (SI', SII') and supercages (SII, SIII). After raising the temperature to 473 K and higher, a significant narrowing of the ^{133}Cs MAS NMR signals occurred. The centers of gravity of the signals observed in the high-temperature spectra can be explained by a rapid exchange of all cesium cations excluding the cesium cations located at SI' positions [10]. The latter cations are responsible for the weak high-field signals appearing at –122 to –126 ppm and –145 to –152 ppm in the high-temperature ^{133}Cs MAS NMR spectra of zeolites CsNa-X and CsNa-Y, respectively (Fig. 2, middle and bottom). Comparing the line width $\Delta\nu$ of the signals at –90 to –92 ppm, only a weak decrease from 218 to 198 Hz was found for zeolite CsNa-X after raising the temperature from 573 to 773 K. On the contrary, for zeolite CsNa-Y a narrowing of the signal at –90 to –92 ppm by a factor of ca. 0.15 occurred in the same temperature range. This dynamic behavior of cesium cations in zeolites X and Y is similar to that of sodium cations in these materials (*vide supra*). The mean signals show a stronger temperature-dependent narrowing in the high-temperature ^{23}Na and ^{133}Cs MAS NMR spectra of sodium and cesium cations in zeolite Y than in zeolite X. This may be due to the smaller concentration of cations in zeolite Y and, therefore, the larger amount of non-occupied cation positions which are accessible for rapid cation processes in this zeolite in comparison with zeolite X.

The activation energy E_A of a thermal exchange process with the correlation time τ can be obtained by an Arrhenius plot $\tau = \tau_o \exp(E_A/RT)$ without to assume a special model [15]. Due to the linear relation between the correlation time τ and the line width $\Delta\nu$ observed for nuclei involved in a thermally activated exchange process, E_A can be determined by the dependence of $\Delta\nu$ on the temperature T. In Figure 3, the line width $\Delta\nu$ of the ^{23}Na MAS NMR signal of sodium cations in dehydrated zeolite Na-Y and of the ^{133}Cs MAS NMR signal of cesium cations in dehydrated zeolite CsNa-Y are plotted as a function of the temperature. The plots show a linear dependence of $\ln(\Delta\nu)$ on T^{-1} for both sodium cations in the temperature range

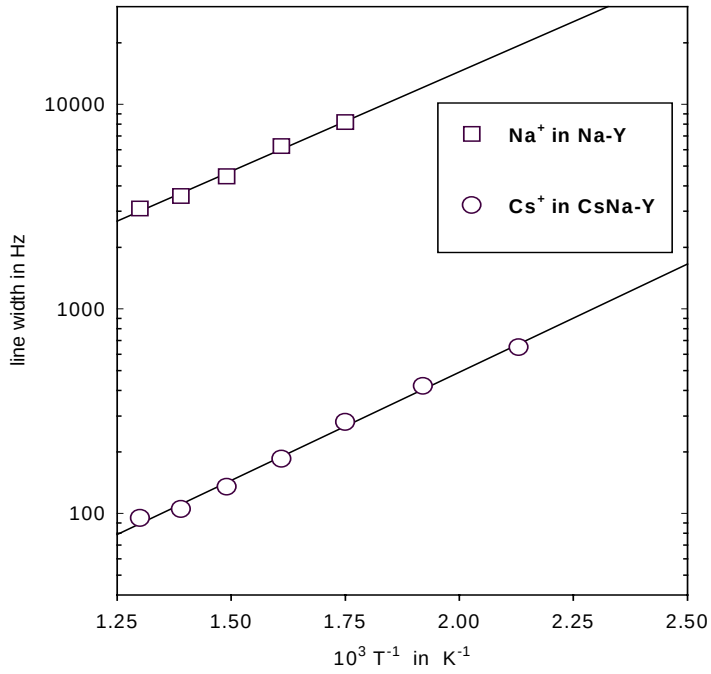

Fig. 3. Arrhenius plot of the line width $\Delta\nu$ of the ^{23}Na MAS NMR (□) and ^{133}Cs MAS NMR signals (○) due to sodium and cesium cations in dehydrated zeolites Na-Y and CsNa-Y, respectively.

from 573 to 773 K and cesium cations in the temperature range from 470 to 773 K. The rise of the curves for both the rapid exchange process of sodium and cesium cations in dehydrated zeolite Y corresponds to an activation energy of E_A = 20±2 kJ/mol. The activation energies of the rapid sodium and cesium exchange in dehydrated zeolite Y determined by variable-temperature MAS NMR spectroscopy are significantly lower than those obtained by Mortier and Schoonheydt [4] applying dielectric spectroscopy (E_A = 52 to 79 kJ/mol), but, agree well with the value of 13 kJ/mol determined for lithium cations in zeolite X [5].

The impregnation of zeolites CsNa-X and CsNa-Y with cesium hydroxide is an often applied method to improve the basic properties of zeolite catalysts [16]. In the ^{133}Cs MAS NMR spectra of zeolites CsNa-X/CsOH and CsNa-Y/CsOH (Fig. 4) signals occur at –15 to 28 ppm due to the guest compounds [7,13]. After raising the temperature to 423 K (Fig. 4, middle), a rapid exchange of cesium atoms contributing the guest compound and of cesium cations located at cation positions occurred. In the ^{133}Cs MAS NMR spectra recorded at 773 K (Fig. 4, bottom), signals appear at –33 and –52 ppm which can be explained by a rapid exchange of all cesium atoms and cations, excluding those located at SI' positions. As described in Reference [10], the temperature dependence of the chemical exchange of cesium atoms and cations in dehydrated zeolites CsNa-X/CsOH and CsNa-Y/CsOH allows to estimate an activation energy of 85 to 115 kJ/mol. Hence, the chemical exchange process of cesium

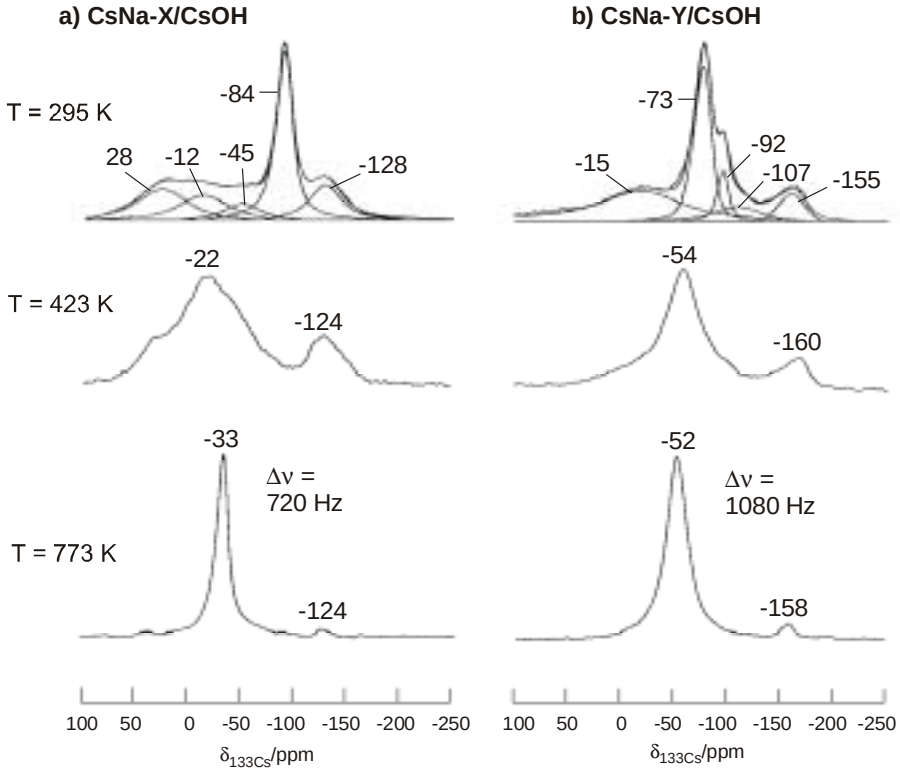

Fig. 4. ^{133}Cs MAS NMR spectra of dehydrated zeolites CsNa-X/CsOH (a) and CsNa-Y/CsOH (b), recorded at temperatures of 295, 423 and 773 K. The parameters of the components used to simulate

the spectra obtained at 295 K are given in Table 2. The line width $\Delta\nu$ was estimated assuming an isotropic line shape.

atoms contributing to the guest compounds and of cesium cations located at cation positions in the zeolite lattice has a significantly higher energy barrier than the rapid exchange of the cations only. On the other hand, it indicates that the alkali oxide guest compound is well dispersed inside the zeolite pores in the neighborhood of zeolite cations allowing the above-mentioned chemical exchange processes.

4. CONCLUSIONS

High-temperature MAS NMR spectroscopy is a suitable method to investigate rapid cation exchange processes in dehydrated zeolites. By the temperature dependence of the rapid exchange of sodium and cesium cations in dehydrated zeolite Y, an activation energy of 20±2 kJ/mol could be determined. For cations in dehydrated zeolites LSX and X, only a weak temperature dependence of the MAS NMR signals was found which indicates that the amount of non-occupied cation positions in the zeolite lattice strongly influence cation exchange processes.

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