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Cation Migration in Zeolite LaNaY Investigated by Multi-Nuclear Solid-State NMR

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Cation migration was studied in zeolites LaNaY prepared by lanthanum exchange in aqueous suspension and by contact-induced solid-state ion exchange. In the solid-state exchanged zeolite a hindered lanthanum migration into the sodalite cages was found by ^{139}La NMR and ^{23}Na, ^{27}Al and ^{29}Si MAS NMR spectroscopy. This hindrance is explained in terms of NaCl formation as a result of the $LaCl_3$/NaY solid state exchange and blocking of the six-ring windows of sodalite cages.

1. INTRODUCTION

Cation migration in faujasites brought about by cation exchange and dehydration plays an important role in the preparation of industrial catalysts. The contact-induced solid-state exchange of alkali metal and lanthanum ions into faujasites is now well established [1, 2]. To investigate the cation migration and location in faujasites exchanged in aqueous suspension, MAS NMR spectroscopy was successfully applied [2, 3]. Generally, by ^{23}Na MAS NMR spectroscopy of hydrated faujasites non-localized sodium cations in the large cavities were identified at the chemical shift of -9 ppm [2, 3, 4]. Using two-dimensional ^{23}Na nutation NMR spectroscopy the signal observed at about -13 ppm was attributed to two different types of sodium cations [3]. One type is involved in a quadrupolar interaction characterized by a quadrupole coupling constant QCC = 1.0-1.6 MHz and was attributed to sodium cations locked in sodalite cages. Dehydration and subsequent lanthanum migration into the sodalite cages causes a disappearance of these sodium cations [3]. ^{23}Na MAS NMR spectroscopy of dehydrated zeolites NaY allows a discrimination between sodium cations localized at position SI in the hexagonal prisms and of sodium cations at positions SII and SI' in the large cavities and in the sodalite cages, respectively [5]. While the octahedral oxygen coordination of sodium cations at SI causes a gaussian line at about -13 ppm with a quadrupole coupling constant in the order of 100 kHz, the signals of the latter two types are characterized by high-field quadrupole patterns with QCC = 4.2-4.8 MHz. Hydrated lanthanum cations localized in the large cavities of the faujasite structure were

quantitatively determined by static ^{139}La NMR measurements [4]. By ^{27}Al and ^{29}Si MAS NMR spectroscopy [4, 6] the lanthanum migration to cation positions SI' in the sodalite cages was monitored by chemical shift effects due to the local strain of framework tetrahedra close to the cation position SI'.

The aim of the present paper is the comparison of cation migration in zeolites LaNaY prepared by lanthanum exchange in suspension and by contact-induced solid-state exchange by grinding $LaCl_3$ with hydrated zeolite NaY.

2. EXPERIMENTAL SECTION

The zeolite NaY used in the present study is a commercial product (Union Carbide Corp., Tarrytown, N.Y., USA) with the unit cell composition $Na_{53.3}Al_{53.3}Si_{138.7}O_{384}\cdot H_2O$. The sample denoted LaNaY/s was lanthanum-exchanged in one step using an aqueous 0.3 M $La(NO_3)_3$ solution. After the ion exchange, the zeolite was washed and dried in air at ambient temperature. Analysis by atomic emission spectroscopy with inductively coupled plasma gave a unit cell composition of $La_{11.2}Na_{19.7}Al_{53.3}Si_{138.7}O_{384}\cdot H_2O$. The contact-induced ion exchanged sample (LaNaY/ci) was prepared by grinding $LaCl_3\cdot 7H_2O$ with 2 g hydrated zeolite NaY for 1 hour. The molar ratio of $LaCl_3$ to the framework aluminium was adjusted to 0.33 corresponding to 17.8 La^{3+}/UC. For dehydration 200 mg of the zeolite were heated under vacuum at a heating rate of 10 K/h. After keeping the samples at the final temperature the material was evacuated to below 10^{-2} Pa for 12 hours and sealed. Before the NMR measurements the samples were filled into the MAS rotors under dry nitrogen in a glove box. The NMR experiments were carried out on a Bruker MSL 400 spectrometer with standard probes at resonance frequencies of 105.8 MHz for ^{23}Na, 104.3 MHz for ^{27}Al, 79.5 MHz for ^{29}Si and 56.5 MHz for ^{139}La NMR. The MAS NMR spectra were recorded with single pulse experiments and pulse lengths less than $\pi/(2I+1)$ for quadrupole nuclei. For the ^{139}La NMR investigations the echo sequence proposed by Kunwar et al. [7] was applied. All chemical shifts are referenced to external standards: tetramethyl silane for ^{29}Si, crystalline NaCl for ^{23}Na and aqueous 0.1 M $Al(NO_3)_3$ solution for ^{27}Al NMR.

3. RESULTS AND DISCUSSION

3.1. ^{23}Na MAS NMR

The ^{23}Na MAS NMR spectrum of the hydrated parent zeolite NaY (Fig. 1a) consists of a line at -9 ppm and a shoulder at about -13 ppm which are caused by hydrated non-localized sodium cations in the large cavities and hydrated sodium cations near SII and SI', respectively [4]. The exchange of cations in suspension (LaNaY/s) causes a distinct decrease of the non-localized sodium cations at -9 ppm. Two-dimensional nutation NMR and investigations using two different magnetic field strengths yielded [4] that the signal at about -13 ppm originates from two components, a non-quadrupolar component at -12 ppm and a component which is shifted by second-order quadrupolar interaction (Fig. 1b). The residual amount of 19.7 sodium cations per unit cell at the chemical shift of

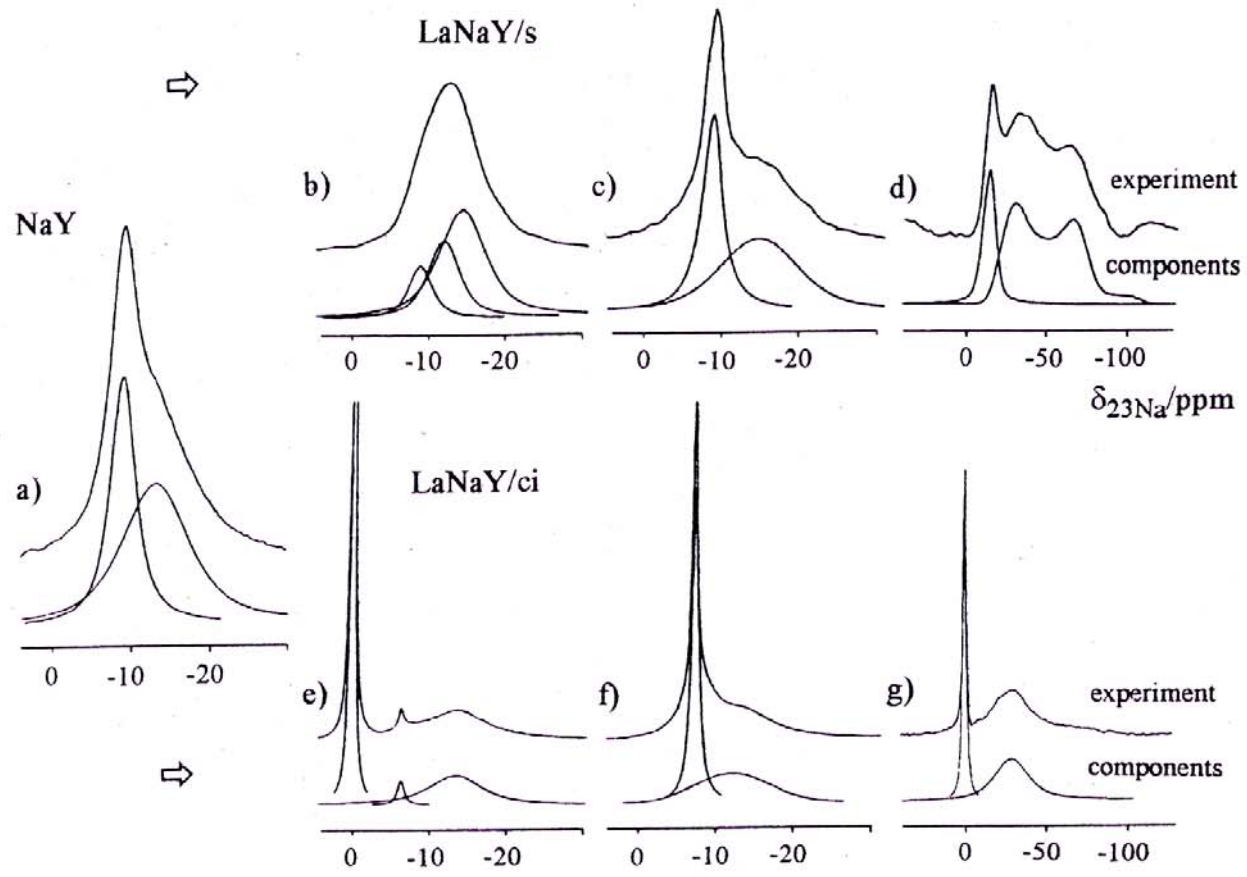


Figure 1. ^{23}Na MAS NMR spectra of the hydrated parent zeolite NaY (a) and the zeolite LaNaY prepared by lanthanum exchange in suspension (b, c, d) and by contact-induced exchange (e, f, g) in the hydrated state (b, e), after thermal treatment at 433 K and rehydration (c, f) and after dehydration at 673 K (d, g).

about -13 ppm corresponds to cations localized near positions SI' and SI in the hexagonal prisms since hydrated lanthanum ions (radius of 3.96 Å [8]) cannot diffuse through six-ring windows with a diameter of about 2.4 Å. After thermal treatment of zeolite LaNaY/s at 433 K and rehydration the ^{23}Na MAS NMR signal of sodium cations located in the sodalite cages at about -13 ppm decreases and the above-mentioned quadrupolar component disappears (Fig. 1c). The simultaneous increase of the line at -9 ppm is a hint for the migration of sodium cations from the sodalite cages into the large cavities. Figure 1d shows the ^{23}Na MAS NMR spectrum after dehydration of zeolite LaNaY/s at 673 K. As observed in the spectrum of dehydrated zeolite NaY [5] the low-field gaussian line at -13 ppm corresponds to sodium cations localized at SI. The peaks at -30 ppm and -63 ppm originate from singularities of the quadrupole patterns of sodium cations localized at SII and SI'. Simulation of the spectra and correction of the experimentally observed ^{23}Na MAS NMR intensities with the method proposed by Massiot et al. [9] yield cation populations of 1.2 Na^+/UC localized at SI and 18.5 Na^+/UC localized at SII and SI' (accuracy of determined populations ±20%). The same procedure yields a sodium population in the dehydrated (673 K) parent zeolite NaY of 3.2 Na^+/UC at SI and of 50.1 Na^+/UC at SII and SI' [5].

The contact-induced lanthanum exchange (LaNaY/ci) causes a disappearance of the non-localized sodium cations at -9 ppm and the appearance of a strong line

at 0 ppm and a small signal at about -7.0 ppm (Fig. 1e). The signal at -13 ppm indicates the existence of sodium cations near SI' which cannot be exchanged by hydrated lanthanum cations. After thermal treatment at 433 K and rehydration (Fig. 1f) the low-field range of the spectrum is dominated by a signal at -7.0 ppm. In the spectrum of LaNaY/ci dehydrated at 673 K the low-field signal is shifted to -0.5 ppm while in the high-field range a broad signal at about -23.0 ppm can be observed (Fig. 1g).

Since the isotropic chemical shift of sodium cations in NaCl-sodalites is -1.1 ppm [10] the signal at -0.5 ppm observed in Figure 1g is attributed to NaCl species in zeolite cavities. The corresponding sodium cations are coordinated to one chlorine atom and three framework oxygens of six-ring windows [10, 11]. The rehydration of these NaCl species shifts their resonance position to that of aqueous NaCl solution which explains the occurrence of the low-field line at -7.0 ppm in Figure 1f. ^{23}Na MAS NMR studies carried out at resonance frequencies of 105.8 MHz and 198.4 MHz proved that the sodium cations causing the high-field line at -23 ppm are not involved in a quadrupolar interaction. Since the rehydration of the calcined (673 K) zeolite NaY causes a gaussian line at about -24 ppm [4], the -23 ppm signal in Figure 1g may be explained by a residual amount of hydrated sodium cations. It is interesting to note that after washing the calcined (673 K) zeolite LaNaY/ci and an additional calcination at 673 K the ^{23}Na MAS NMR spectrum corresponds to the one in Figure 1d, i.e. no lines appear at -0.5 ppm and -23 ppm. Hence, the above-mentioned NaCl species are not occluded in sodalite cages.

3.2. ^{139}La NMR

The application of ^{139}La NMR spectroscopy allows a discrimination between hydrated lanthanum ions located in the supercages and lanthanum ions which, upon dehydration, migrated into sodalite cages [5, 12]. While the signal of the former lanthanum ions is characterized by a line broadening of about 12 kHz (line (i)), the quadrupolar interaction of the latter type of ions causes a line broadening of 150-190 kHz (line (ii)). Studies of a homologous series of lanthanum-exchanged faujasites [5] demonstrated that the ^{139}La NMR intensity of line (i) can be used for a quantitative determination of hydrated lanthanum cations in the large cavities. Comparing the intensity of line (i) in Figure 2a with that of an external standard, the number of hydrated lanthanum ions in the large cavities of LaNaY/s was determined to 9.9 La^{3+}/UC (accuracy ±10%). After thermal treatment at 433 K and rehydration a second broad line (ii) appears (Fig. 2b) which is caused by lanthanum cations in the sodalite cages. The observed intensity of line (i) corresponds to a residual amount of 2.1 La^{3+}/UC located in the large cavities. Since the second-order quadrupolar interaction is the main line broadening mechanism of lanthanum cations in zeolites, the quadrupole coupling constant of these nuclei can be estimated by the width of line (ii) to about 30 MHz [13]. This value agrees with the quadrupole coupling constant of lanthanum cations localized at position SI' calculated by a point charge model [14]. In agreement with this result in previous pulsed-field-gradient NMR studies [15] of unsaturated hydrocarbons in faujasites the

lanthanum ions were found predominantly located in the sodalite cages. Hence, the decrease of line (i) in the spectrum of zeolite LaNaY/s is caused by the migration of 7.8 La^{3+}/UC from the large cavities to the cation position SI' in the sodalite cages.

For $LaCl_3 \cdot 7H_2O$ salt Herreros et at. [12] found a ^{139}La NMR quadrupole pattern with QCC = 24 MHz and strong singularities split over a range of about 80 kHz. Contrary to this line shape, the ^{139}La NMR spectrum of the sample LaNaY/ci consists of one signal of type (i) only, the intensity of which corresponds to about 18 La^{3+}/UC. The decrease of line (i) observed upon thermal treatment at 433 K and rehydration corresponds to a migration of about 4.5 La^{3+}/UC from the large cavities into the sodalite cages. Consequently, the number of lanthanum ions which migrate into the sodalite cages of zeolite LaNaY/ci is distinctly smaller than for zeolite LaNaY/s.

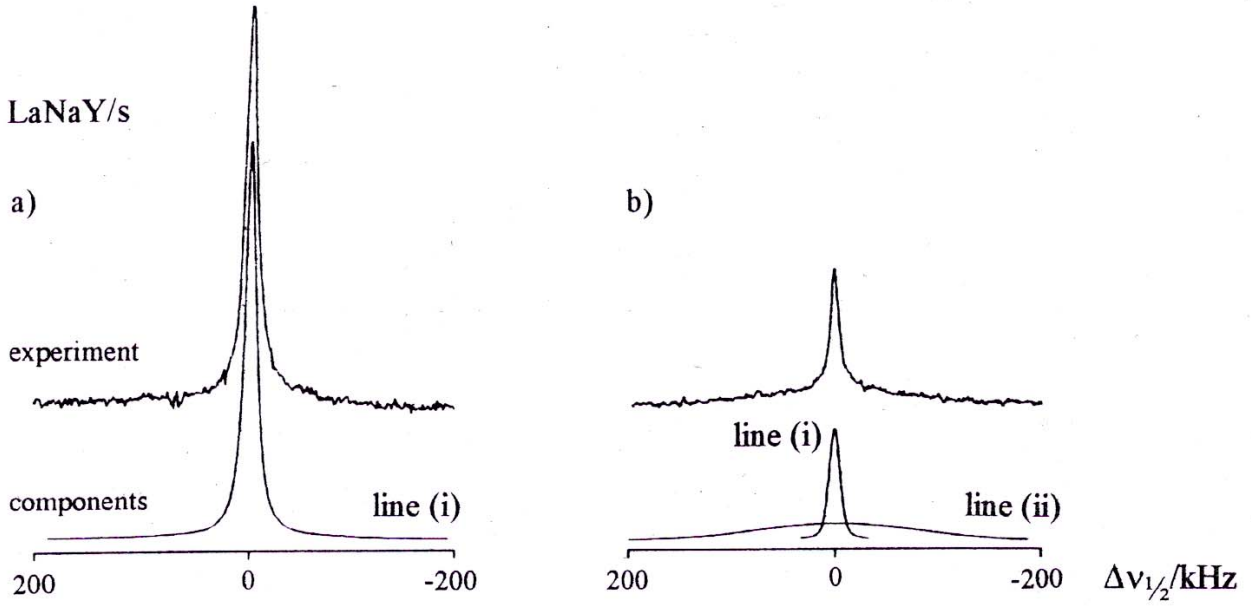


Figure 2. ^{139}La NMR spectra of the as-exchanged zeolite LaNaY/s before (a) and after (b) thermal treatment at 433 K and rehydration.

3.3. ^{27}Al MAS NMR

At variance to results of Lee and Rees [8], the ^{27}Al MAS NMR spectra of zeolite LaNaY/s and LaNaY/ci recorded after thermal treatment at 433 K show no signal of extra-framework aluminium at about 0 ppm (Fig. 3a and 3b). On the other hand, the spectra of both samples consist of the line of tetrahedrally coordinated framework aluminium at 58 ppm and a second signal at 45 ppm with a line broadening of about 3 kHz. Fourier transformation in the absolute intensity mode proved that the total intensities of the signals at 58 ppm and 45 ppm in the spectra of the thermally treated zeolites agrees with the intensity of framework aluminium atoms at 58 ppm in the spectra of the as-exchanged samples. Simulation of the spectra in Figure 3 yields an intensity contribution of the broad high-field signal of 26% and 14% for the zeolites LaNaY/s and

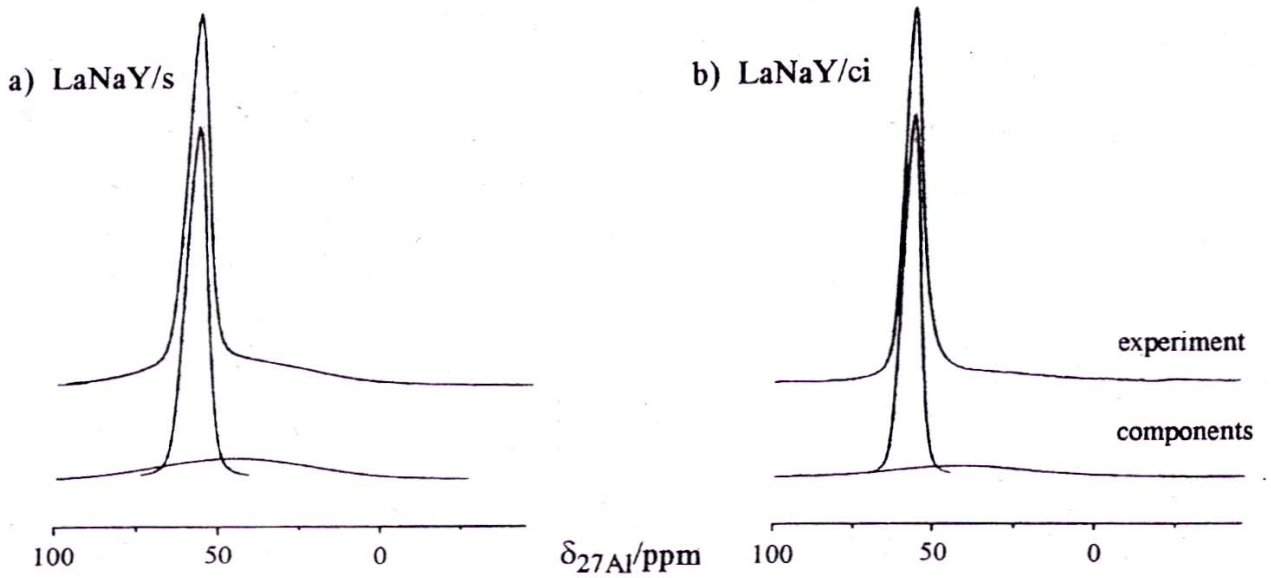


Figure 3. ^{27}Al MAS NMR spectra of thermally treated (433 K) and rehydrated zeolites LaNaY/s (a) and LaNaY/ci (b).

LaNaY/ci, respectively. As shown below the migration of lanthanum ions to position SI' is responsible for a framework strain causing the high-field shift of the resonance position for a corresponding number of [AlO_4] tetrahedra.

3.4. ^{29}Si MAS NMR

Like the ^{29}Si MAS NMR spectrum of the parent sample NaY (Fig. 4a), the spectra of both as-exchanged zeolites (not shown) consist of lines at the chemical shifts of -89.2 ppm, -94.5 ppm, -100.5 ppm and -105.0 ppm corresponding to Si(3Al), Si(2Al), Si(1Al), and Si(0Al) [16], respectively. The thermal treatment of zeolite LaNaY/s at 433 K results in a strong decrease of the lines in the shift range between -89 ppm and -94 ppm and the appearance of a new peak at -97.2 ppm. Considering the fact that no dealumination was observed by ^{27}Al MAS NMR the simulation of this spectrum yields a high-field shift of about 30% of the intensity of the Si(nAl) lines with n = 3, 2 and 1. Using the correlation between the ^{29}Si MAS NMR chemical shifts and the mean SiOT bond angle $\bar{\alpha}$ of zeolites given in reference [17] the observed high-field shift of 3 ppm corresponds to a variation of $\bar{\alpha}$ = 4°. The number of Si(nAl) units contributing to six-ring windows close to lanthanum cations localized at position SI' agrees well with the determined amount of 30% of strained [SiO_4] tetrahedra. It is interesting to note that the percentage of the broad high-field component at 45 ppm observed by ^{27}Al MAS NMR spectroscopy corresponds also to the mean number of [AlO_4] tetrahedra in six-ring windows close to lanthanum ions localized at SI'.

The ^{29}Si MAS NMR spectrum of LaNaY/ci in Fig. 4b shows a similar high-field shift of Si(nAl) lines as observed for zeolite LaNaY/s. However, the contribution of strained [SiO_4] tetrahedra of 16% indicates a significantly smaller number of lanthanum cations localized at SI'.

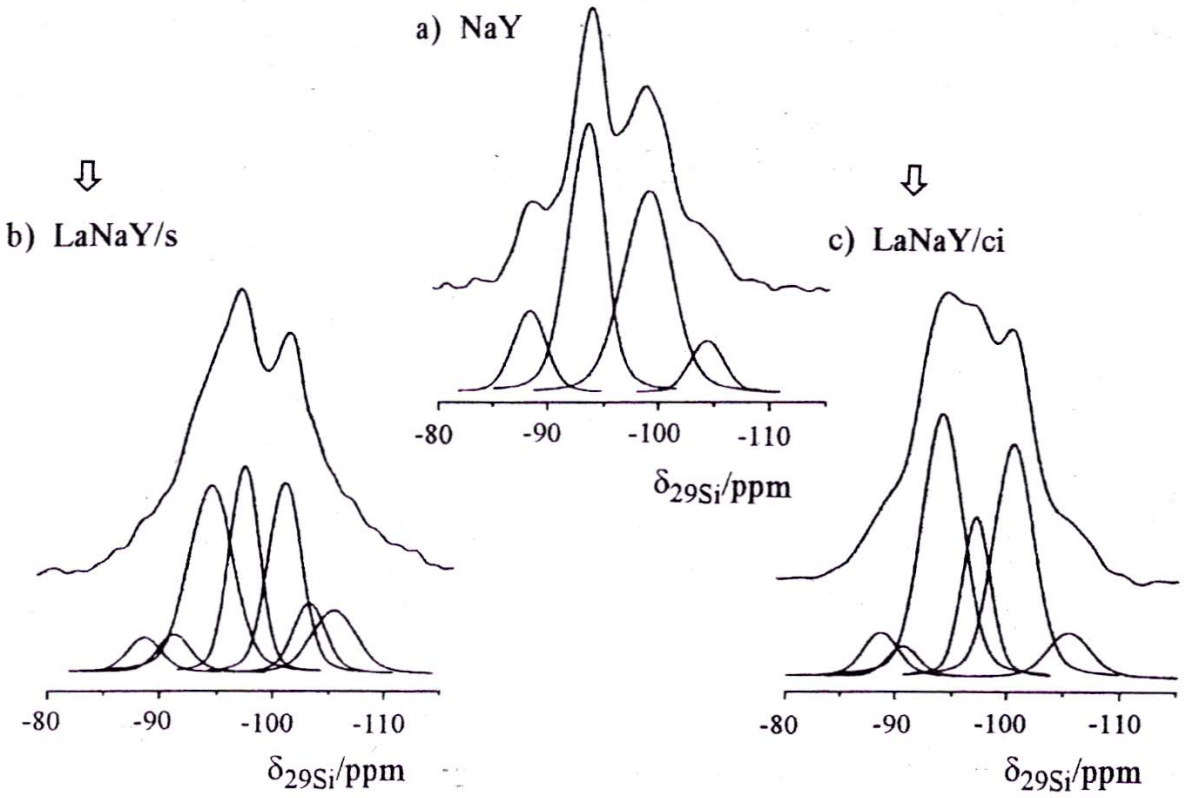


Figure 4. ^{29}Si MAS NMR spectra of the parent zeolite NaY (a) and the thermally treated (433 K) and rehydrated zeolites LaNaY/s (b) and LaNaY/ci (c).

4. CONCLUSIONS

Multi-nuclear solid-state NMR spectroscopy is demonstrated to be a useful tool for investigating cation migration in lanthanum-exchanged faujasites. The present study compares lanthanum exchange of zeolites NaY carried out in aqueous suspension (LaNaY/s) and by a contact-induced solid state $LaCl_3$/NaY exchange (LaNaY/ci). In both cases lanthanum cations exchange at first non-localized sodium cations in the large cavities. In zeolite LaNaY/ci this process is coupled with the formation of NaCl species which corresponds to sodium cations coordinated to one chlorine atom and three framework oxygens of six-ring windows. Although the number of lanthanum cations per unit cell in zeolite LaNaY/ci was 1.5 times higher than in zeolite LaNaY/s, the number of lanthanum cations migrating after dehydration into the sodalite cages is distinctly smaller in zeolite LaNaY/ci. This fact was established by ^{139}La NMR spectroscopy of lanthanum cations and using ^{29}Si and ^{27}Al MAS NMR by the number of strained framework tetrahedra in six-ring windows close to lanthanum cations localized at position SI' in the sodalite cages. The hindrance of lanthanum migration in zeolite LaNaY/ci can be explained by NaCl blocking of the six-ring windows of a certain part of sodalite cages.

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