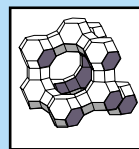


High-temperature MAS NMR investigation of the mobility of cations and guest compounds in zeolites X and Y



M. Hunger, A. Buchholz and U. Schenk

Institute of Chemical Technology, University of Stuttgart, D-70550 Stuttgart, Germany

Summary

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. 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 $E_a = 20$ 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 (85 to 115 kJ/mol).

Introduction

Cations in zeolites act as adsorption sites for adsorbate molecules 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 depends 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 ^7Li MAS NMR spectroscopy, Feuerstein and Lobo [5] obtained an activation energy of 13 kJ/mol for the mobility of cations 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.

Experimental Section

Zeolite Na-LSX ($n_S/n_A = 1.06$) was synthesized as described in Ref. [6]. Zeolites Na-Y and Na-X ($n_S/n_A = 2.6$ 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]. 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 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. Prior to the variable-temperature NMR investigations, the samples were dehydrated in vacuum at 673 K for 12 h.

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. 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 of up to 22 kHz at 295 K.

Results and Discussion

High-temperature ^{23}Na MAS NMR spectroscopy of dehydrated zeolites

The ^{23}Na MAS NMR spectra of dehydrated zeolites Na-LSX, Na-X and Na-Y recorded at room temperature ($\nu_{\text{rot}} = 22$ kHz) consist of components I1 (SI), I2 (SIII'(3)), I3 (SIII'(1,2)), Q1 (SII) and Q2 (SI') [8-10]. Comparing the distribution of sodium cations in zeolites Na-LSX, Na-X and Na-Y, the most important difference is the sodium population of the SIII positions which 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

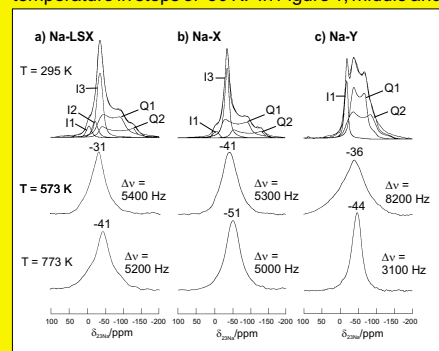


Fig. 1: ^{23}Na MAS NMR spectra of dehydrated zeolites Na-LSX, Na-X and Na-Y recorded at temperatures of 295, 573 and 773 K. The line widths were determined assuming isotropic signals.

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. 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 at SI' positions in the sodalite cages cause the quadrupolar pattern with a center of gravity occurring 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 yielding an accurate fitting only for the spectra of dehydrated zeolite Na-Y. For zeolites Na-LSX and Na-X, an increase of the temperature from 573 to 773 K led only to a weak 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.

High-temperature ^{133}Cs MAS NMR spectroscopy of dehydrated zeolites

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. The assignment of the signals was performed according to Refs. [11,12]. After raising the temperature to 473 K and higher, a significant narrowing of the signals occurred. Comparing the line widths $\Delta\nu$ of the signals at -90 to -92 ppm, only a weak decrease was found for zeolite CsNa-X after raising the temperature from 473 to 773 K, while for zeolite CsNa-Y a narrowing by a factor of ca. 0.15 occurred in the same temperature range.

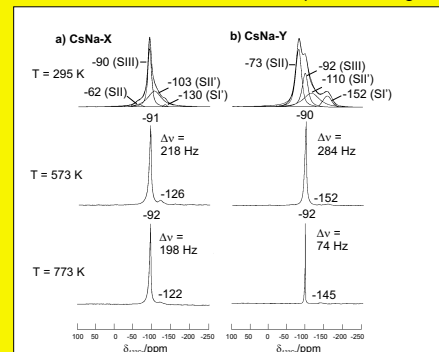


Fig. 2: ^{133}Cs MAS NMR spectra of dehydrated zeolites CsNa-X and CsNa-Y recorded at 295, 573 and 773 K.

In Figure 3, the line widths $\Delta\nu$ of the ^{23}Na MAS NMR signals of sodium cations in dehydrated zeolite Na-Y and of the ^{133}Cs MAS NMR signals of cesium cations in dehydrated zeolite CsNa-Y are plotted as a function of the temperature T . The plots show a linear dependence of $\ln(\Delta\nu)$ on T^{-1} for sodium and cesium cations yielding an activation energy of $E_a = 20 \pm 2$ kJ/mol. This value is significantly lower than the activation energy of 85 to 115 kJ/mol obtained for oxidic guest compounds in dehydrated zeolites CsNa-X/CsOH and CsNa-Y/CsOH (see Ref. [10]).

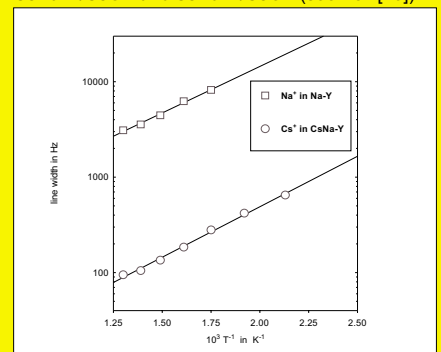


Fig. 3: Arrhenius plot of the line widths $\Delta\nu$ determined by variable-temperature ^{23}Na and ^{133}Cs MAS NMR spectroscopy.

Acknowledgements:

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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 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 influences cation exchange processes.
- Cation mobility in zeolite Y is significantly higher than the mobility of oxidic guest compounds.