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Influence of Adsorbed Molecules on the Configuration of Framework Aluminum Atoms in Acidic Zeolite- β . A ^{27}Al MAS NMR Study

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The formation of octahedral framework aluminum sites in acidic zeolite- β depends on the adsorption of water. This could be shown by ^{27}Al MAS NMR spectroscopy under controlled atmosphere conditions. The ^{27}Al MAS NMR spectrum of the hydrated zeolite shows two lines corresponding to tetrahedral and octahedral Al sites, respectively. These NMR lines disappear on dehydrated samples. The adsorption of methanol or pyridine as probe molecules on the dehydrated zeolite samples restores only the tetrahedral (framework) aluminum sites in the ^{27}Al MAS NMR spectrum due to the relaxation of the distorted zeolite lattice by the adsorbed molecules. The acid-catalyzed reaction (470 K) of adsorbed methanol molecules on zeolite- β , which supplies water, brings back the ^{27}Al MAS NMR signal caused by the octahedral framework aluminum sites.

Introduction

The ^{27}Al nuclei in NMR of solids is often subjected to strong quadrupole interactions. The corresponding line width of these signals can be so broad that in some cases they cannot be observed in the spectrum. These quadrupolar interactions due to electric field gradients at the site of the aluminum nuclei are the main source of line width in zeolites. Thus the loss of the environmental symmetry around an aluminum atom can lead to a strong broadening of the ^{27}Al NMR signals.^{1,2}

The detection of the aluminum species in zeolites by the NMR technique depends therefore strongly on the level of relaxation of the framework (flexibility) and on the nature of guest molecules or counteranions.^{3–5}

Despite a great number of NMR studies, there is still debate concerning the exact nature of the aluminum species in zeolites. Usually, the visibility of these species in the ^{27}Al NMR spectra depends strongly on the presence of water, as it has been reported for instances in refs 6 and 7, and in particular for acidic zeolite- β .^{8,9}

The structure of acidic zeolite- β is such that each aluminum ion is surrounded by four close-packed oxygen ions. The presence of a field gradient at the site of the aluminum ion will be determined largely by the deviation of the four oxygen ions from an exact tetrahedral configuration. There is also evidence that some of the aluminum may be converted from tetrahedral to octahedral species when the ammonium form of as-synthesized material is calcined to produce the acid form and then hydrated.^{8,10} In other zeolites this would be attributed to the formation of extraframework aluminum species, but for acidic zeolite- β , the tetrahedral–octahedral interconversion appears to be reversible under mild treatment conditions.

In this work we investigated the fate of aluminum in acidic zeolite- β by ^{27}Al MAS NMR spectroscopy using a specially designed NMR probe, in the presence of adsorbed molecules

such as methanol and pyridine in sealed NMR tubes. In situ reaction of methanol at 470 K in sealed NMR tubes was also performed in order to study the influence of nascent water molecules on the transformation of tetrahedral into octahedral framework aluminum species.

Experimental Section

An acidic (H-form) zeolite- β with a silicon-to-aluminum ratio of 12.8 (4.8 aluminum atoms/64 tetrahedra) has been prepared by calcination in air at 820 K of a parent zeolite synthesized in the presence of tetraethylammonium hydroxide, ion exchange of the calcined zeolite with a 2 M solution of ammonium nitrate at reflux temperature, and a final calcination in air at 820 K. Preservation of the crystallinity was checked by XRD, FT-IR spectroscopy, and nitrogen adsorption.⁸

Several samples were prepared in 5 mm precision NMR tubes equipped with a resealable valve suitable for attachment to a vacuum line. The samples were loaded as powders to a height of 10 mm and then, when necessary, evacuated for 1 h at ambient temperature, heated 1 K/min to 570 K under vacuum (10^{-6} Torr) and maintained at this temperature for 8 h. Two samples were equilibrated at room temperature with 10 Torr of methanol or pyridine, respectively, which were previously purified several times by freeze–pump–thaw cycles and then stored over 3A zeolite as drier agent.

After sealing the tubes, NMR measurements were performed on a Bruker CXP 200 MHz spectrometer using a specially designed homemade NMR probehead that could spin the sealed tubes at speeds up to 4 kHz.¹¹ The ^{27}Al MAS NMR spectra were acquired at 52.1 MHz for the ^{27}Al nucleus. Two millisecond pulses with a repetition time of 1 s and a sweep width of 25 000 Hz have been used to obtain the ^{27}Al MAS NMR spectra. All the NMR spectra were obtained at room temperature. The Al chemical shifts were referenced relatively to a 1 M solution of $\text{Al}(\text{NO}_3)_3$. The signal corresponding to the aluminum coming from the glass tube has been subtracted in the presented spectra.

In a specific experiment the NMR sealed tube containing the zeolite sample loaded with methanol has been heated to 470 K

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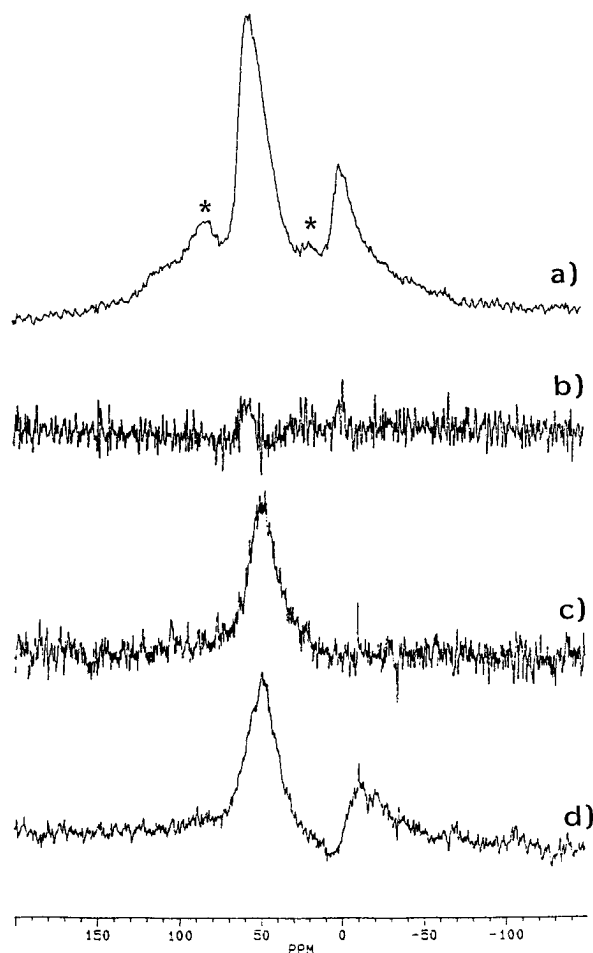


Figure 1. : ^{27}Al MAS NMR spectra taken at 52.1 MHz, with spinning of the sample at 1.6 kHz (a) of hydrated acidic zeolite- β . Asterisks show spinning sidebands, (b) of acidic zeolite- β dehydrated at 570 K under vacuum, (c) of dehydrated acidic zeolite- β with adsorbed methanol (the spectrum obtained is the same after pyridine adsorption, spectrum not shown), and (d) after heating (c) in the sealed NMR tube (with the methanol probe) at 470 K for 30 min.

in an oven for 30 min, and then the ^{27}Al MAS NMR spectrum was recorded at room temperature.

Results and Discussion

Figure 1a presents the ^{27}Al MAS NMR spectrum of the hydrated zeolite- β sample. Two signals at 55 and around 0 ppm corresponding to tetrahedrally and octahedrally coordinated aluminum species, respectively, can be observed. These signals are generally attributed to framework and nonframework aluminum species. However Bourgeat-Lami et al.⁸ have suggested from their studies of the state of the aluminum species in zeolite- β that the signal at 0 ppm could be generated as well by aluminum atoms in framework positions linked to four lattice oxygens, the oxygen of a hydronium ion, and the oxygen of a water molecule. Accordingly these atoms are not part of extraframework aluminum species, but despite their octahedral symmetry, they belong to the zeolite framework.

Due to the high density of defects in the structure of zeolite- β ,^{12,13} generating silanol groups, the determination of the framework aluminum content in the zeolite by ^{29}Si MAS NMR and FT-IR of lattice vibrations is questionable.⁸ The absence of extraframework aluminum species in this sample was nevertheless ascertained by repeated back-exchange treatments of the protons by ammonium and potassium cations. In all cases, the cation to aluminum molar ratios were equal to 1.00

± 0.02 , indicating that all aluminum atoms of the solid led to an exchangeable site; in other words, that they were all associated with framework atoms.

To form the octahedral symmetry, the presence of water is necessary. The sample was then dehydrated by activating the zeolite at 570 K for 8 h. This treatment led to a broadening of the ^{27}Al MAS NMR resonances so that the signals at 0 and 55 ppm were no longer detectable (Figure 1b). In the case of the tetrahedrally coordinated species, this effect can be explained by an important increase of the quadrupolar coupling constants during the removal of the water molecules, which cause a certain distortion of the electric field symmetry around the aluminum of the zeolite lattice.^{1,7} The ^{27}Al resonance line was then broadened beyond detection in a MAS experiment. The disappearance of the peak at 0 ppm on drying the samples can be explained not only by the above arguments but also by a possible transformation of the octahedrally coordinated aluminum atoms in the presence of water molecules into atoms with tetrahedral surrounding, as suggested by Bourgeat-Lami et al.⁸

The adsorption of methanol or pyridine molecules on the dehydrated samples regains only a resonance line at 55 ppm (Figure 1c). These probe molecules have a very different interactions with the zeolite. This means that upon adsorption of these probe molecules the zeolitic framework relaxes and then the aluminum tetrahedral sites become again more symmetrical and the quadrupolar coupling constant decreases. These observations agree well with recent work of Hunger et al.^{4,5} on Y, ZSM-5, and mordenite dehydrated zeolites containing adsorbed molecules (pyridine, methanol).

The heating of the sample loaded with methanol at 470 K led to the dehydration of the alcohol on the acidic sites of the zeolite and the formation of dimethylether and water.² This nascent water was adsorbed in part on tetrahedral aluminum sites as ligands and the octahedrally coordinated aluminum line could be again observed at a chemical shift around 0 ppm, the tetrahedrally coordinated aluminum line is still present as shown in Figure 1d. These NMR experiments reinforce therefore the previous proposal⁸ concerning the origin of octahedral aluminum in protonic zeolite- β . The later appears associated more probably to framework aluminum atoms coordinated to 4 lattice oxygens, the oxygen of an hydronium ion and the oxygen of a water molecule.

Conclusion

Our preliminary results show the potential of ^{27}Al MAS NMR studies under well controlled sample conditioning in the determination of the origin of the tetrahedral and octahedral framework aluminum species in acidic zeolite- β .

By reacting methanol molecules on zeolite- β , which provides nascent water into the sealed system, we have shown that the octahedral aluminum species can effectively be associated with a tetrahedral framework aluminum species, modified by the presence of water.

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