

Flexible Aluminium Coordination of Zeolites as function of Temperature and Water content, an *in-situ* method to determine Aluminium Coordinations

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The aluminium coordinations in zeolites H-Beta and H-Y have been quantitatively investigated as a function of temperature in the presence and absence of water. *In-situ* Al K edge X-ray Absorption Spectroscopy shows that a framework tetrahedrally coordinated aluminium is stable in inert to at least 725 K. However, in the presence of water, already at room temperature, part of the framework tetrahedral aluminium is converted to an octahedral coordination. This octahedral aluminium is not stable in inert at 375 K, where it quantitatively reverts to the tetrahedral framework coordination.

1. INTRODUCTION

The importance of the aluminium coordination in zeolites for the development of active and selective catalysts for many reactions has been well documented. A generally used method for zeolite activation is acid or base leaching and / or steaming. Processes occurring during these treatments greatly affect activity and selectivity. Nonetheless, limited information on the aluminium coordinations during these treatments are reported, due to lack of clear methods to do this. Here we report the application of Al K edge XAFS spectroscopy on zeolites that allow direct structural information about the aluminium atoms during a zeolite treatment. The aluminium coordination is determined as a function of temperature in the presence and absence of water.

Al K edge X-ray Spectroscopy allows the quantitative determination of aluminium coordinations by recognition of coordination-specific features in the near edge spectra. Spectra can in principle be obtained at high temperature and pressure. It takes about 5-10 minutes to take a near edge scan, allowing the detection of changes in structure at such time scale.

The applicability of the quantitative determination under *in-situ* conditions is a great advantage over ^{27}Al MAS NMR, which is the dominant method to determine the aluminium coordination. Although recently serious progress has been made in the quantitative determination of aluminium coordinations in zeolitic samples and use of multiple quantum magic-angle spinning (MQ MAS) increased significantly the resolution^{1,2}, still a set-up allowing the determination of *in-situ* data is not readily available. Normally, before a (^{27}Al

MAS) NMR measurement, samples are pretreated (hydrated) in a controlled water environment in order to decrease the so-called quadrupolar couplings constant (QCC). Certainly, under these conditions, the resolution in ^{27}Al MQ MAS NMR spectra is very high. However, increasing the temperature in a dry environment causes a very large increase in QCC, resulting in a loss of resolution or even of the signal itself³. As Al K edge spectroscopy allows the quantitative determination of aluminium coordinations at any temperature, we have developed a set-up enabling measurements at high temperature under controlled gas-environment⁴. Here, the combination of the two techniques provides unique information on the changing aluminium coordination in zeolites as function of treatment. ^{27}Al MAS NMR is used under standard (and hydrated) conditions, providing high resolution information on samples, whereas Al K edge X-ray Spectroscopy is used to determine the changing aluminium coordinations under non-ambient conditions.

We will show how the aluminium coordinations are changing as a function of treatment conditions. The influence of temperatures up to 725 K and the presence of water are shown to affect the aluminium coordinations.

2. EXPERIMENTAL

2.1. Samples

Zeolite NH_4 -Beta was obtained from Delft University. Template removal has been done very carefully in order to prevent decomposition of the zeolite during this treatment, using a method developed by Kunkeler et al.⁵. The heat-treatment of NH_4 -Beta with heating rate of 10 K per minute (max T = 725 K) is followed in-situ with Al K edge XAS. The obtained H-Beta was exposed to water in Helium and subsequently to gaseous NH_3 and measured with ^{27}Al MAS NMR and Al K edge XAS.

NH_4 -Y was obtained via BP-Amoco. ^{27}Al MAS NMR showed no octahedral Al was present. Both samples were checked for crystallinity using XRD, nitrogen physisorption and transmission electron microscopy. The formation of octahedral aluminium in a calcined sample was followed by XAS at room temperature by treatment in Helium saturated with water. The stability of the octahedral aluminium was investigated by treating the sample in inert at 400 K.

2.2. Al K edge X-ray Absorption Spectroscopy

The recently developed *in-situ* set-up, ILEXAFS (*In-situ* Low Energy X-ray Absorption Fine Structure Spectroscopy), has been used⁴. It consists of a large vacuum vessel in which a small stainless steel *in-situ* chamber, containing the sample, is placed. A sample is pressed in a wafer and placed in a boronitride cup that can be heated up to 800 K under a maximum gas-pressure of 1 bar. The vacuum in the large vessel is protected from the gas-pressure in the *in-situ* chamber by thin supported (7-15 μm) beryllium or Kapton windows. The design allows simultaneous fluorescence and (total) electron yield detection. Here, only fluorescence detection, via a gas proportional counter (GPC), integrated with the *in-situ* chamber to increase the solid angle of detected fluorescence radiation, has been used.

The initial intensity of the X-ray beam has been measured via the drain current of either a thin 6 μm Au or 4 μm Cu mesh (with apertures of 60 and 88% respectively) positioned in the large vacuum vessel. A double crystal monochromator with YB66 crystals has been used. Measurements are performed at station 3.4 at the SRS, Daresbury (UK).

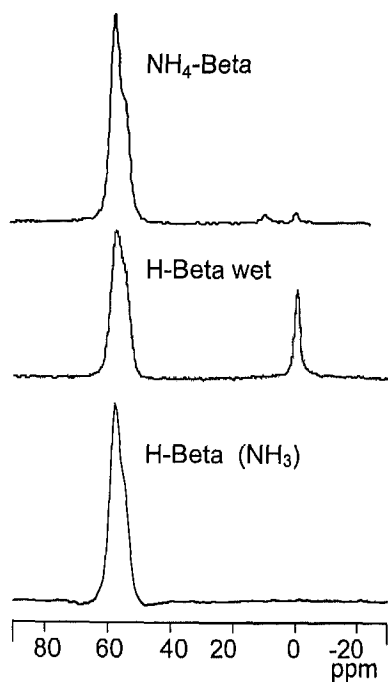


Figure 1. ^{27}Al MAS NMR spectra of zeolite Beta, showing a reversible and quantitative transition of tetrahedral Al (~ 55 ppm) into octahedral (0 ppm).

2.4. ^{27}Al MAS NMR

^{27}Al MAS NMR was performed on a Chemagnetics Infinity 600 with a magnetic field strength of 14.1 T. Magic angle spinning was performed at a rotation speed of 27 kHz using a Chemagnetics 2.5 mm HX MAS probe. To circumvent saturation of the signal and ensure a linear response, $\pi/18$ pulses using an RF field strength of 36 kHz were used. Chemical shifts were taken relative to aqueous $\text{Al}(\text{NO}_3)_3$. The relaxation delays were 0.5 s, which was determined to be sufficient for quantitative analysis. 1000 Scans were recorded.

3. RESULTS / DISCUSSION

As-synthesized zeolites contain tetrahedrally coordinated aluminium in the framework. In Figure 1, the ^{27}Al MAS NMR spectrum of zeolite NH_4 -Beta is shown. This spectrum shows two partly overlapping peaks in the range 50-60 ppm, that have been interpreted as tetrahedral coordinated aluminium at different crystallographic framework T-positions using multiple quantum (MQ) MAS NMR⁸. (For an explanation of the spectra of H-Beta and H-Beta (NH_3) *vide infra*). Figure 2 shows the corresponding Al K near edge spectrum of the same sample. It shows the characteristic features of a tetrahedrally coordinated aluminium: A sharp whiteline

2.3. Al coordinations from Al K edge spectroscopy

Near edge spectra at the Al K edge show features that are characteristic for different aluminium coordinations. Using a fingerprint of these features⁶, different aluminium coordinations can be recognized in a sample. By altering the conditions of a measurement, such as temperature and / or gas-environment, (small) changes in aluminium coordination are readily detected by comparing the differences between spectra.

The characteristic features used to distinguish different coordinations are summarized below⁶: The K edge of aluminium metal is located at 1560 eV, while the spectra of tetrahedrally coordinated aluminium oxides show an edge at 1566 eV and octahedrally coordinated at 1568 eV. Moreover, an octahedrally coordinated aluminium shows a doublet (4 eV split) as whiteline (first intense peak in the spectrum) and displays a small pre edge feature at 1566 eV, except when a perfect octahedron⁶. In addition, tetrahedral aluminium shows a very characteristic broad peak at ~ 20 eV above the absorption edge. The position of this peak is sensitive to the Al-O bondlength⁷. In spectra of octahedrally coordinated aluminium, a comparable peak is visible at ~ 50 eV above the absorption edge.

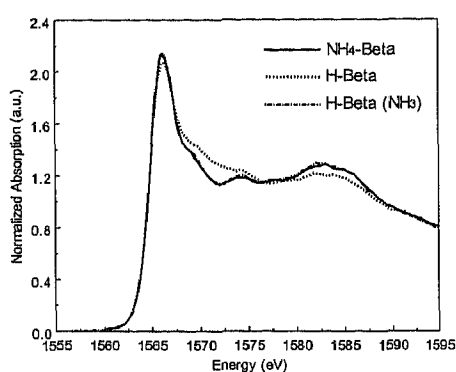


Figure 2. Al K edge spectra of zeolite Beta: NH_4 -Beta (Solid-line), calcined H-Beta wet (dotted) and H-Beta treated with NH_3 (dash-dotted), strongly overlapping with NH_4 -Beta.

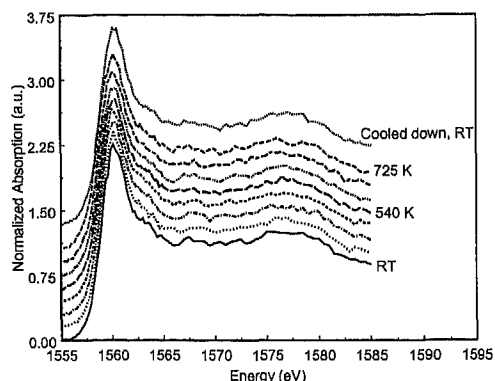


Figure 3. Al K edge spectra of NH_4 -Beta, while heated in inert. Every spectrum corresponds to an increase of about 60 K. Some respective temperatures are provided.

is visible at 1567 eV, a broad peak at ~ 20 eV above the edge and in between some fine-structure.

Figure 3 shows the near edge spectra of NH_4 -Beta while heating to 725 K in vacuum. Each spectrum represents a temperature interval of about 60 K. It is obvious that no clear changes in the spectra occur as function of temperature and upon removal of NH_3 . It is therefore inferred that all tetrahedral aluminium in the framework of zeolite Beta is stable in inert to a temperature of 725 K. No octahedral, penta- or tri-coordinated aluminium is formed under these conditions. After cooling down the sample to room temperature and exposing the sample to He, saturated with water by bubbling it through water at room temperature, changes in the spectra occur. In Figure 2 (spectrum H-Beta wet), it is obvious that an increase in intensity in the range 3-10 eV is observed. Previously we have decomposed similar spectra and concluded that this variation in intensity is due to the creation of octahedral coordinated aluminium. This conclusion is also found by the ^{27}Al MAS NMR spectrum (Figure 1) of a sample that has been treated in the laboratory under identical conditions. This spectrum (of a hydrated sample) shows a loss of one of the two tetrahedral aluminium framework peaks and the appearance of octahedral coordinated aluminium. The total intensity under the spectra of NH_4 -Beta and H-Beta are identical, showing no 'NMR-invisible' aluminium or other coordinations are present in the samples. Both NMR and the Al K near edge show an identical change in variation from tetrahedral into octahedral, without the creation of any other coordination. From the Al K near edge data it is concluded that the transition from tetrahedral to octahedral takes place at room temperature, induced by the presence of water in the gas-phase.

The reversible transition of tetrahedrally coordinated aluminium to octahedrally coordinated has been well-documented for zeolite Beta⁹, but is also reported for other zeolites¹⁰. Moreover, different crystallographic T-sites have reportedly a different tendency to dealuminate⁸. In order to investigate the behavior of aluminium coordination in other zeolites, a sample NH_4 -Y zeolite was investigated. Figure 4 shows the near edge spectra of this sample. A calcined sample (at 725 K), called H-Y dry, shows all characteristics of a tetrahedrally coordinated aluminium. When this sample is exposed at room temperature to He saturated

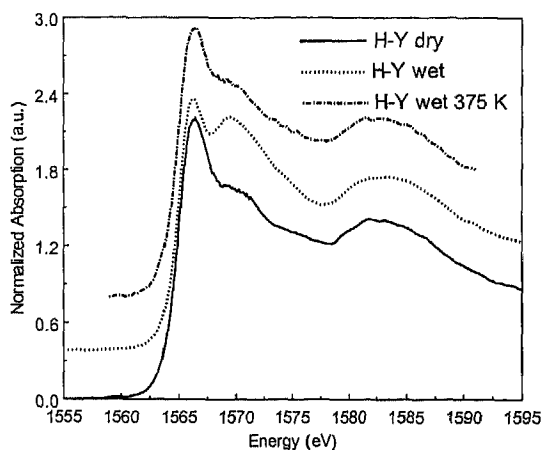


Figure 4. Al K edge spectra of zeolite Y: H-Y (Solid line), H-Y wetted (dotted) and H-Y wetted at 375 K (dash-dotted).

can be reverted into a tetrahedral coordinated aluminium by ion exchange with an alkali-ion or by the addition of NH_3 in the gas phase at elevated temperature⁹. The ^{27}Al MAS NMR and XAS spectra of zeolite H-Beta treated with NH_3 (at 375 K), are given in Figures 1 and 2 respectively, and are both identical to the spectrum of the parent NH_4 -Beta. This confirms a complete reversal of aluminium coordination into the original tetrahedral framework coordination. We have previously shown that for zeolite H-Beta, a treatment with NH_3 in the gas-phase, completely recovers the tetrahedrally coordinated aluminium, yielding identical isotropic chemical shifts⁸. This strongly suggests that an identical aluminium coordination is recovered and the framework is completely intact, as shown here by both NMR and Al K edge XAS.

In order to investigate the stability of the octahedral aluminium in zeolite Y, we evacuated the gas-environment of the H-Y_{wet} sample. Only after heating the sample to ~ 375 K (in vacuum), the octahedral coordinated aluminium completely disappeared and a spectrum of a tetrahedral coordinated aluminium is recovered (Figure 4). This experiment shows that the octahedral coordinated aluminium is not stable to a slight heat treatment in vacuum. It is reverted into a tetrahedral aluminium by removing H_2O from the gas-phase at ~ 375 K. This process can be repeated during several cycles.

4. CONCLUSIONS

The combination of *in-situ* Al K edge with ^{27}Al MAS NMR provides unique structural information on the changing aluminium coordinations in zeolites. *In-situ* Al K edge X-ray Absorption Spectroscopy allows the quantitative determination of aluminium coordinations under non-ambient conditions. ^{27}Al MAS NMR under hydrated conditions yields high resolution spectra, especially when MQMAS is applied.

A study on zeolites shows that part of the tetrahedral framework aluminium shows a high flexibility and is able to transform -reversibly- into an octahedral aluminium. In an acidic

with water, a clear increase in intensity in the range 1567 – 1675 eV is visible, while the whiteline and the broad peak at 1583 eV decrease in intensity. This is indicative of the creation of octahedral coordinated aluminium at the cost of tetrahedrally coordinated aluminium. The same phenomenon is observed, as with zeolite Beta. In an acidic zeolite H-Y, the addition of water at room temperature results in the formation of octahedral coordinated aluminium.

It has been reported that this octahedral coordinated aluminium, that is established to be connected to the framework,

zeolite (H-Beta and H-Y), octahedrally coordinated aluminium is formed at room temperature, only when water is present in the gas-phase. This octahedral aluminium is unstable in vacuum at slightly elevated temperatures and completely reverts to a framework tetrahedral aluminium. This process can be cycled several times.

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