

Apparatus for *in situ* x-ray absorption fine structure studies on catalytic systems in the energy range $1000 \text{ eV} < E < 3500 \text{ eV}$

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A new apparatus for *in situ* x-ray absorption fine structure measurements in the medium energy range of 1000–3500 eV has been developed. Measurements can be performed in a gaseous environment (max. pressure 1 bar) at temperatures ranging from 80 to 750 K. Pre-treatments can be performed at 5 bar and 750 K in the same cell, after which XAFS measurements can be done without exposing the sample to ambient air. In a modular set-up several detector systems can be used: fluorescence detection using a gas proportional counter, a photodiode or a microstrip detector. All detectors are highly integrated into the cell, gaining solid angle for detection. Electron yield detection can be used simultaneously using conversion electron yield or total electron yield. The performance of the new apparatus is demonstrated by a study of the *K* edge of Al in Zeolite Beta. The Al content is as low as 2 wt%. It will be shown that octahedral framework Al is formed while adding gaseous water at room temperature after ammonia removal (at 450 °C) of an NH₄-Beta.

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I. INTRODUCTION

X-ray absorption fine structure (XAFS) spectroscopy is a powerful tool to obtain structural information of different types of materials lacking long range order: catalysts, inorganic materials, minerals, organometallic complexes and biological samples like enzymes.¹ The local geometry and electronic state of a specific atom are probed. Material under research can be either in the gaseous, liquid or solid state. *In situ* investigations of catalyst systems² under reaction conditions can be performed routinely on atoms having absorption edges at energies above 3–4 keV. In catalysis, knowledge of the structure of the active site and the interaction between the catalytic sites and the reacting molecules lead to an increased understanding of the processes occurring at the active centers.³ This can eventually result in the development of better catalysts.

XAFS measurements on low *Z* elements ($6 < Z < 19$) with absorption edges in the energy range of $200 \text{ eV} < E < 3000 \text{ eV}$, starting with carbon, can generally only be done in vacuum. Catalytic systems of interest contain elements like Mg, Al, and Si in single or mixed amorphous oxides and in microporous crystallites such as zeolites and clays.⁴ In some cases the above mentioned elements are directly associated with the catalytic active centers. An instrument to study these elements *in situ* during a (pre-) treatment at reaction conditions can give structural and electronic information of the catalytically active site in operation. This will

greatly enhance the understanding of the catalytic behavior of these materials.

Below energies of approximately 3000 eV, air and vacuum windows absorb a substantial part of the photons emitted by the x-ray source. Collecting a spectrum with reasonable signal to noise ratio is not possible without taking special precautions. At the *K* edge of aluminum (1560 eV) absorption in 20 mm of ambient air reduces the photon intensity by 90% (Fig. 1). Only extreme high photon fluxes are able to compensate for the photon loss. However, third generation synchrotrons, like the European Synchrotron Radiation Source, France (ESRF), are designed for high energy photons and generally low energy beamlines at third generation synchrotron sources are usually not designed for XAFS measurements.

An apparatus, which can perform XAFS studies on catalysts under working conditions, must have a very small reaction chamber to minimize absorption of x rays. Recently, an instrument is described in the literature for *in situ* catalyst studies under gas pressures of 10 mbar and maximum temperature of 1000 K in the energy range of 250–1000 eV.⁵ Studies can be performed at the O and C *K* edges. This instrument has a limited pressure range. However, catalysts under realistic working conditions usually require higher gas pressures. Moreover, this apparatus has only electron yield detection and this limits the type of materials, which can be studied to samples having sufficient electric conductance.

In this article the development of an apparatus for *in situ* low energy extended x-ray absorption fine structure (ILEX-AFS) measurements for low *Z* elements ($Z \geq 12$) is reported extending the energy range to 3000 eV with a lower limit of

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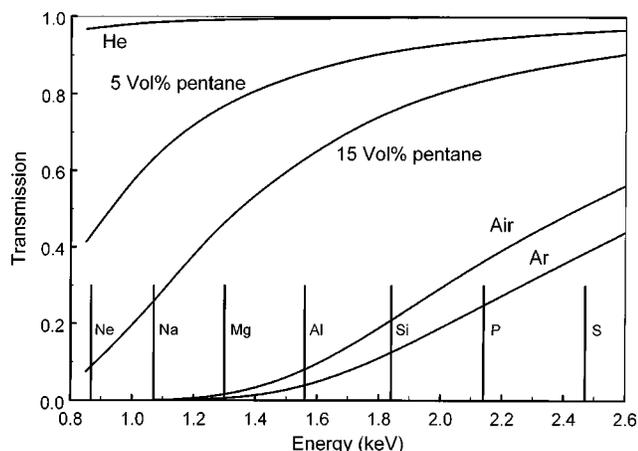


FIG. 1. Calculated transmission of x rays through 20 mm of a gas mixture as a function of the photon energy at 1 bar and 293 K. The vertical lines denote the $K_{\alpha 1}$ absorption lines of the mentioned elements.

about 1000 eV. The vacuum chamber⁶ is constructed to fit on the low energy XAFS beamline 3.4 of the SRS, Daresbury (UK). The *in situ* pressure range is $10^{-4} < P < 1$ bar and the temperature range is $80 \text{ K} < T < 750 \text{ K}$. Pretreatments at 5 bar can be performed. The experimental setup consists of a vacuum chamber, the actual *in situ* cell and several high sensitive fluorescence and electron yield detectors. The *in situ* cell has a modular setup, which has the advantage that several detector systems can easily be changed and used in different compositions simultaneously. The *in situ* cell has optimum cell dimensions by minimizing its volume due to minimizing the distance between sample and vacuum windows, without overheating the windows during sample treatment. The materials used are chosen to be heat resistant and have low or noncatalytic activity. The modular setup gives the cell high flexibility. Nonconducting samples can be measured in the fluorescence mode with a gas proportional counter (GPC) or photodiode. Samples showing sufficient conductivity can be examined simultaneously with fluorescence and electron yield detection.⁷ The angle between the incoming beam and the sample can be varied for specific purposes, like surface sensitive XAFS.

A study of the K edge of Al in zeolite Beta demonstrates the performance of the new *in situ* XAFS cell.

II. DESCRIPTION OF THE APPARATUS

A. The vacuum chamber

A new vacuum chamber is developed and mounted directly onto beamline 3.4 at the SRS, Daresbury, which is designed in such a way that there is space left to install user defined devices. The purpose of the design is (i) blocking as much as possible unfocused photons, (ii) measuring I_0 as close as possible to the cell decreasing beamline influences and (iii) easy assessment for mounting and connecting the *in situ* cell. A schematic drawing of the new vacuum chamber is shown in Fig. 2. The chamber contains a slit holder, a foil holder, two doors, a manipulator onto which the *in situ* cell is mounted and feedthroughs for gas and power supply and electrical signals.

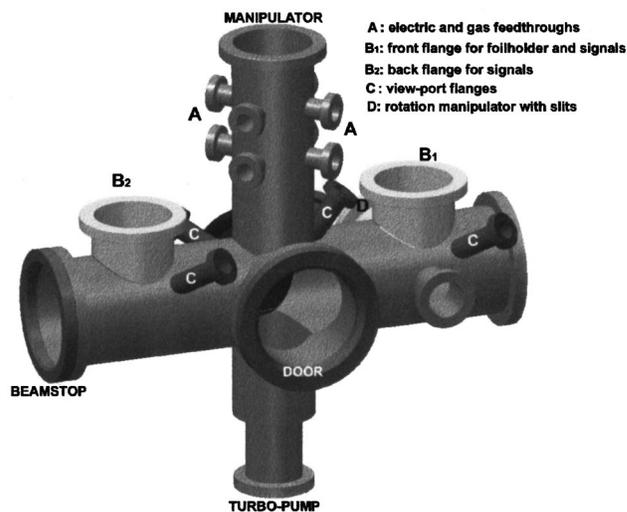


FIG. 2. Schematic drawing of the vacuum chamber; the flanges (A-D) are omitted. The length of the chamber is 90 cm.

The new vacuum chamber is connected to the beamline using a CF 250 flange. The chamber is cross shaped and has a horizontal length of about 90 cm and a height of 80 cm. A turbopump and a rotary vacuum pump maintain the pressure in the vessel better than about 10^{-6} mbar, measured by Pirani and Penning pressure gauges. The vacuum chamber is mounted onto a frame, which is adjustable in the x , y , z directions for accurate alignment of the setup with regard to the x-ray beam. On top is a rotation and linear x , y , z precision manipulator mounted onto which the *in situ* cell can be connected. The manipulator makes precise positioning of the *in situ* cell in the x-ray beam possible.

Each flange on the B position (Fig. 2) has a linear four position manipulator, equipped with a foil holder. The purpose of the front foil holder in B1 is to define the intensity of the initial beam (I_0 signal) and for alignment of the chamber. The second foil holder in B2 can optionally be used for REFLEXAFS (reflection EXAFS) or other experiments needing an I_t signal. The four positions of the front foil holder can be adjusted so that the x-ray beam passes freely or through a gold mesh, a copper mesh, or onto phosphorous paint. The phosphorous paint can be used for alignment of the vacuum chamber. The linear manipulator makes a fast interchange between these positions possible. At the back of the horizontal tube, near flange B1, a flange (D in Fig. 2) containing a rotation manipulator is situated to which a slit holder is mounted. By rotation of this manipulator the beam spot can be reduced to any size desired.

The vertical tube has eight flanges (CF 70), denoted A in Fig. 2, for electrical and gas feedthroughs. For supply of gas into the vessel, five gas feedthroughs including valves are present. Flexible metal tubes transport the gases to the *in situ* cell and the GPC. These are connected to the *in situ* cell and GPC by vacuum tight quick couplings with Viton O rings. Moreover, feedthroughs for liquid nitrogen or other coolants, if desired, are connected. Double walled flexible metal tubes are used to transport the coolant inside the chamber, which are connected to the cell using silver plated gaskets.

Electrical feedthroughs are divided over several flanges.

Power supplies for preamplifiers, furnace and IR lamps are on a flange having 20 separate electrical feedthroughs. A separate thermocouple feedthrough is present to which three *k*-type thermocouples can be connected. A separate feedthrough is mounted through which a high voltage can be supplied, to prevent interference with other electrical signals. All experiment signals are lead to *N*-type feedthroughs, positioned on flanges B_1 and B_2 . All signal wiring inside the chamber is shielded (Imp. 50 Ω) to prevent electrical noise take up as much as possible.

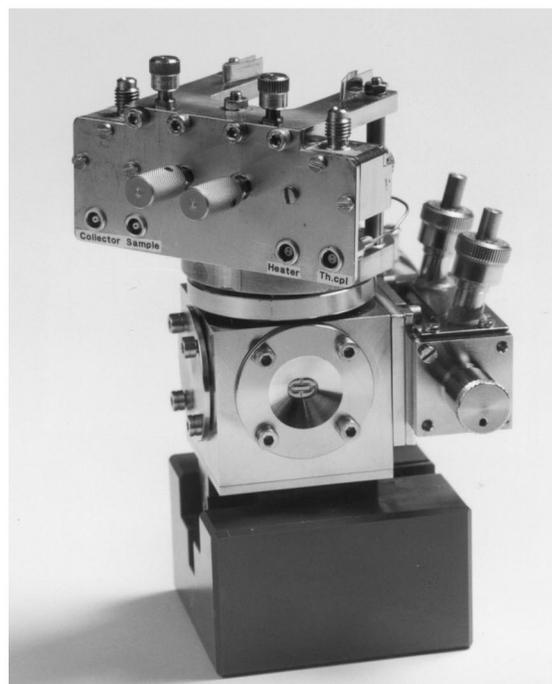
Safety vacuum gauges supplied by the SRS are mounted onto the chamber to prevent the x-ray beam from entering the chamber unless the chamber is closed and well below atmospheric pressure.

The chamber is designed with six small viewports (C in Fig. 2) along with leaded windows. In this way, view of the interior is possible and alignment of the chamber and the *in situ* cell can be done easily. Moreover, to view the interior of the chamber, a leaded window is mounted at the end the horizontal tube and in the front door. In the front and at the back, doors are situated with a Viton O-ring sealing. The front door has an open area with a diameter of 200 mm, for placing and replacing the *in situ* cell and making all connections. The back door is used for a microstrip detector, which is still in development.

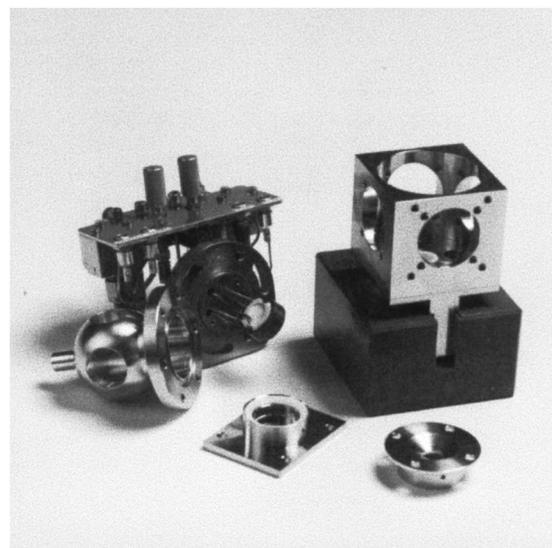
B. The *in situ* cell

This cell is designed to perform XAFS measurements under catalytic reaction conditions or during (pre) treatment of the catalyst on elements having absorption edges in the range of $1000 < E < 3000$ eV. The beam spot is focused on the sample position and usually has dimensions smaller than 10×3 mm. In practice a variety of experiments in the gas phase under reducing or oxidizing atmospheres with pressures $10^{-4} < P < 1$ bar and temperatures up to 750 K can be performed. Moreover, to decrease influence of the Debye–Waller factor, samples can be cooled to liquid nitrogen temperature. The pressure under measuring conditions is limited to 1 bar, due to the ultrathin windows. *Ex situ* pretreatment of the catalyst, without exposure of the sample to ambient prior to the measurement, is possible at pressures up to 5 bar, due to the rotation possibility of the inner part of the cell, which is explained below.

The dimensions of the interior of the cell are kept as small as possible in order to minimize the absorption of x rays of the incident beam and of the fluorescence radiation by the atmosphere inside the cell. The effect of the gas on the intensity of the x rays and the fluorescence radiation is shown in Fig. 1. The small size of the cell and the integration of the GPC in the exit window decrease the distance of the fluorescence detector to the sample, increasing the solid angle for the fluorescence radiation detection. The *in situ* cell has a modular setup, which makes changes in the setup easy and adaptation of other detectors possible. The major parts of the *in situ* cell are made of stainless steel. A photograph is shown in Fig. 3 and a schematic drawing in Fig. 4. As indicated in Fig. 4, the reaction chamber (B) is constructed like a hollow ball valve, positioned in a cube shaped body (A) with



(a)



(b)

FIG. 3. (a) A photograph of the *in situ* cell. At the front in the middle a window holder is visible, with a window glued in. On the front panel the electrical connections are visible, and the gas connections are situated on the top. On the right, the integrated GPC is partly visible. (b) A photograph of the parts of the cell, with the cube, the reaction chamber, the top flange and the window holders. A BN cup is implemented in the sample holder on the top flange.

outer size of 56 mm. The top flange (C) consists of the heater/cooler incorporated into the sample holder and diverse feedthroughs for gases and signals. The top flange fits on the reaction chamber (B) with a Viton O ring.

The reaction chamber (B) has two openings at an angle of 90° for x rays entering the chamber and fluorescence radiation leaving the chamber. Alignment and fixation of the reaction chamber in the cube are established by four window holders (W) and a centering rod fixed in a hole with a poly-

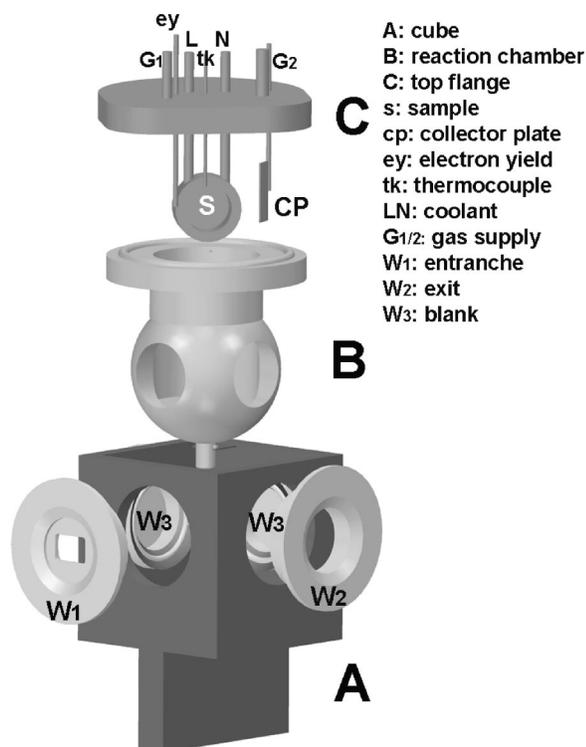


FIG. 4. Schematic drawing of the *in situ* cell assembly. A: stainless steel cube with window holders; B: the reaction chamber; C: the flange containing the sampleholder and all feedthroughs.

tetrafluoroethylene (PTFE) liner in the bottom plate of the cube. Two window holders, with open ports, are mounted at an angle of 90° for the entrance (W_1) and exit (W_2) windows. The other window holders (W_3) are blank. The entrance port has a $7\text{-}\mu\text{m}$ -thick gas and light tight beryllium window of a diameter of 13 mm fixed to a support with an aperture of 12×8 mm. The exit windows are chosen to have an optimum between the thickness of the window and the diameter of the aperture. A bigger aperture implies a big solid angle, which is preferable above an ultrathin window. A $13\text{-}\mu\text{m}$ -thick beryllium window with a diameter of 23 mm is placed in a mount with an aperture of 22 mm and has proven to withstand a pressure difference of 1 bar. The exit window holder can be integrated with several fluorescence yield detection systems, like a GPC or photodiode. Also supported polyimide windows as entrance and exit windows have been tested. The fixation of the windows in the port is done with a two component adhesive, fit for use in high vacuum at high temperatures (>600 K). The epoxy remains flexible after a mild hardening treatment. The four window holders have PTFE O rings, which position the reaction chamber of the *in situ* cell like a ball valve. The Teflon closure rings are used for sealing the reaction chamber toward the surrounding vacuum chamber by attaching the window holders to the cube. The rings are pressed against the reaction chamber, sealing the open areas in the sphere from the vacuum.

The reaction chamber (B) of the *in situ* cell is a sphere welded to a flange. The chamber has a vertical blind hole and two horizontal ports at an angle of 90° . The hollow center is the reaction chamber where the sample holder will be situ-

ated. With this design, it is possible to rotate the reaction chamber in the cube. When the two ports in the reaction chamber are in front of the windows a measurement can be performed. Rotating the reaction chamber by 180° will protect the fragile windows as the ports of the reaction chamber are now in front of the blank window holders. In this configuration treatments can be performed in the reaction chamber with $P < 5$ bar and $T < 750$ K, without exposing the fragile windows to these extreme conditions. This unique reactor design allows a thorough pretreatment to the sample while the fragile windows are protected from these conditions.

A flange (C) on top of the sphere incorporates the complex sample holder (s). This flange can be bolted onto the reaction chamber and closes the reaction chamber with a Viton O ring. The top flange is equipped with feedthroughs from the interior of the vacuum chamber to the reaction chamber. There are two tubes ($G_{1,2}$; 1/16 in., Fig. 3) mounted with valves for gas inlet and outlet and two tubes (LN; 1/8 in.) for liquid nitrogen or another coolant inlet and outlet. For the furnace, a sheeted resistance wire is used and for temperature control a sheeted thermocouple (tk; *k*-type) is used. Electrical feedthroughs for the electron yield signal from the sample (ey) and collector plate (cp) for bias purposes are isolated from the body by ceramic isolated conductors. All feedthroughs are vacuum soldered into the top flange.

The center of the *in situ* cell is the sample holder (s). It is a closed hollow stainless steel cylinder with a heating element and tube connections for coolant feed and exhaust (LN1, LN2, Fig. 3). The furnace is constructed with a counter wound heating element to prevent any electrical and magnetic field on the sample. Changing electric and magnetic fields might introduce extra noise on the electron yield signal, which is avoided in this setup. Also stabilized dc power for the furnace is used during the EXAFS measurements for the same purpose. A flow of liquid nitrogen or another cooling liquid through the sample holder is possible. By combined use of coolant and heater the sample can be maintained at any temperature between 90 and 750 K.

The sample holder is equipped with a pressed replaceable boron nitride cup to hold a self-supporting sample wafer with a diameter of 13 mm. Boron nitride (BN) is an electrical isolator and has good heat conductivity. The sample is mounted into the BN cup and is thus electrically isolated from the body. Sample wafers are pressed onto a thin stainless steel disk, which is connected to a spot-welded electrical lead. Any electron yield signal from the sample is transported via the stainless steel disk through the isolated wire to the conducting feedthrough. A second isolated electrical feedthrough is connected to the collector plate. With a bias potential on the collector plate conversion electron yield measurements are possible, making use of the gas amplification of the signal.⁷ Also two gas ports for flushing a gas mixture through the cell during the *in situ* treatments are connected onto the top flange. The top flange can be mounted in several positions onto the reaction chamber, so that the sample can be positioned at an angle between 0° and 90° with respect to the incident beam. This feature makes it

possible to perform surface XAFS measurements with only a small penetration depth of the incident beam in the sample.

III. X-RAY DETECTION

In an EXAFS experiment, the intensities of the initial x-ray beam and the absorbed photons by the element under investigation in the sample need to be recorded. The measurement of the initial beam intensity (I_0) is performed by measuring the drain current from a foil or mesh in the foil holder on flange B1 (Fig. 2). The current setup is equipped with a copper mesh of 4 μm thickness and an aperture of 88% and a gold mesh of 6 μm and aperture of 60%. The drain current is amplified by a current amplifier.

Dependent on the element and its dilution, detection of the absorbed photons is most directly done by detection of the transmitted beam behind the sample (I_t). For low energy photons this is not possible, because the x-ray beam is completely absorbed by the sample. Among other phenomena that are quantitatively related to the absorption of photons by the atoms under investigation are fluorescence radiation and Auger electron emission.

A small cylindrical gas proportional counter (GPC), for detection of the fluorescence radiation is developed by SRON (Stichting Ruimte Onderzoek Nederland). The GPC is incorporated into the exit window holder of the *in situ* cell. Although there is normally only a small pressure difference over the beryllium window between the *in situ* cell and the GPC, because both operate at 1 bar, the window is strong enough to hold 1 bar pressure difference. It is possible to evacuate the reaction chamber during a treatment in this setup. The counting gas (10% CH_4 in helium) has a flow rate of approximately 3 ml/min. The operating voltage is 1200–1400 V.

The primary signal is preamplified in the vacuum chamber close to the gas proportional counter using a charge sensitive amplifier, fit for use in vacuum, developed by SRON. The advantage is that the low signal is amplified before it picks up noise from the surroundings. Although the vacuum chamber is a complete metal box, experience has taught that the very small signals are easily distorted. By preamplifying and shielding the wiring, noise is limited as much as possible. For fluorescence detection, a silicon photodiode is also tested. The photodiode is integrated into the internal part of an exit window and has therefore an increased solid angle. Although a photodiode is not energy specific, it was possible to gain excellent data, in a light tight vacuum chamber at room temperature. A preamplifier directly mounted on the photodiode is used for signal amplification. The background is a stable and continuous signal. The photodiode cannot be used at elevated temperatures without taking precautions to protect the diode from overheating and photons created by the heat.

Simultaneously with fluorescence yield, the drain current or total electron yield signal can be recorded. This signal is also preamplified close to the cell in the vacuum chamber using the same type current to voltage preamplifier as for the photodiode. The amplified signal is led outside the vacuum chamber through shielded wiring and an *N*-type feedthrough.

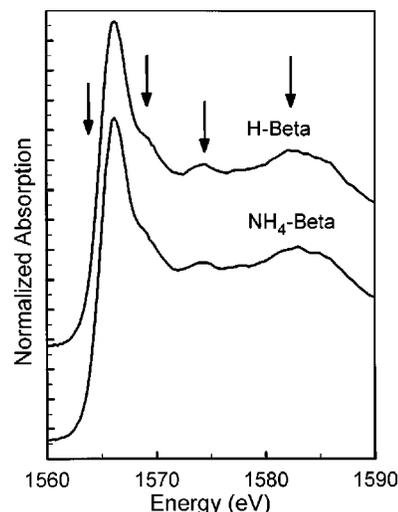


FIG. 5. The fluorescence Al *K* edge spectra of NH_4 -Beta (bottom) and H-Beta (top). The arrows indicate the typical tetrahedral features.

Stable signals can only be derived when the sample is sufficiently electrically conducting. Experience has taught that although zeolites are electrical isolators, in general good total electron yield signals are generated. Each sample should be tested for this type of detection.

IV. PERFORMANCE OF ILEXAFS

A. Introduction

As an example of the performance of ILEXAFS, the Al coordination in zeolite Beta is studied as a function of the activation treatment carried out *in situ* in the newly built cell. Beta is Si-Al crystalline material with Si/Al molar ratio of 11.3. Zeolite Beta is activated before use in catalysis by a calcination—or steaming procedure—at high temperature. It is known that the Al coordination is changing due to these treatments.⁸ In order to be able to determine the relationship between the structure of the zeolite and the catalytic activity, a detailed structural knowledge is a necessity.⁹ The low Al content and the two structure types of Al will show low detection limits of the ILEXAFS cell.

B. Samples

Starting material [NH_4 -Beta] is a synthesized Beta¹⁰ with a NH_4 -group as charge-balancing species. Calcination in the *in situ* cell at 450 °C (heating rate 1 °C / min) under a flow of dry He removes NH_3 and creates protons forming an acidic zeolite beta [H-Beta]. This sample is treated in a He flow saturated with water for 4 h [H-Beta(w)].

Another batch of NH_4 -Beta has been treated in the laboratory at 450 °C for 1 h under inert gas. This material is treated in the laboratory in a He flow saturated with water and thereafter with a flow of NH_3 at 100 °C for one day [H-Beta(NH_3)]. The last sample is treated *ex situ*, because of the long ammonia treatment.

From each named sample the EXAFS spectrum is measured at room temperature on beamline 3.4 of the SRS, UK. The SRS was running at 2 GeV and the ring current was 100–200 mA. The beamline was equipped with a YB₆₆

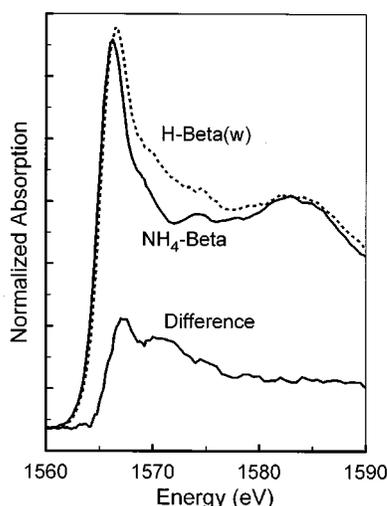


FIG. 6. Normalized absorption spectra of NH_4 -Beta and H-Beta(w). Also the difference spectrum is shown.

double crystal monochromator.¹¹ The counting time for each point in the edge region is 2 s. The measurements are performed under a He flow and fluorescence detection has been used, either using a gas proportional counter or a photodiode.

C. Results

Figures 5, 6, 7, and 8 demonstrate the good quality Al *K* edge spectra. Figure 6 presents the difference spectrum of NH_4 -Beta and NH_4 -Beta(w). The data quality allows us to assign the features in this difference spectrum to octahedral Al in NH_4 -Beta(w) (see below).

Figure 5 shows the fluorescence Al *K* edge spectra of NH_4 -Beta and H-Beta, giving all characteristic features of tetrahedral Al, as is indicated by the arrows.⁹ This is in accordance with ²⁷Al magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra that only show a resonance corresponding to tetrahedral Al.¹² After heating this sample to 450 °C and cooling down to room temperature,

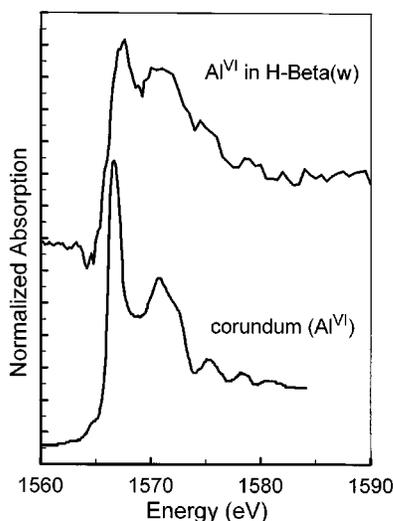


FIG. 7. Comparison of octahedral Al in H-Beta(w) and corundum (an octahedral reference compound).

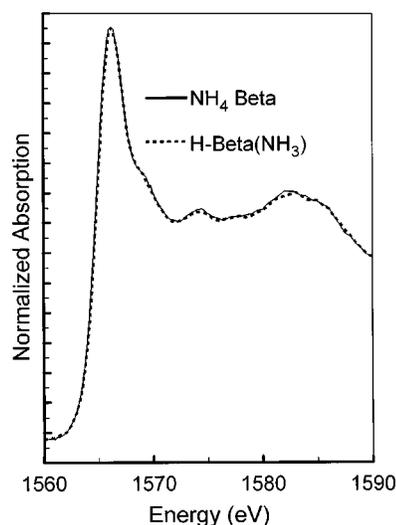


FIG. 8. Comparison of parent NH_4 -Beta and the ammonia treated, calcined H-Beta (NH_3).

H-Beta, a very similar spectrum is found. It is therefore concluded that the calcination did not induce any changes in the Al coordination.

However, after adding water to the sample, the Al *K* edge spectrum shows differences from the parent sample. Figure 6 compares the spectra of NH_4 -Beta and H-Beta(w). The spectrum of H-Beta(w) shows a surplus in intensity in the range 5–15 eV above the absorption edge. The difference between the two spectra is given at the bottom. This spectrum shows characteristic features of octahedral Al, which is emphasized in Fig. 7, where the normalized difference spectrum is compared to the spectrum of a standard octahedral compound, corundum. Both spectra show the typical split white line and edge position of octahedral Al. This prompts the conclusion that octahedral Al is present in H-Beta(w), besides the presence of the tetrahedral Al.

The spectrum of the ammonia treated calcined sample H-Beta(NH_3), is compared to the spectrum of NH_4 -Beta in Fig. 8. These spectra are identical. The octahedral coordination present after calcination and addition of water is lost and reversed to the original tetrahedral coordination. The estimated accuracy is about 2%.

Moreover, it is known that spectral shape in the near edge, that is 0–15 eV above the absorption edge, is determined by multiple scattering over a medium-range (~ 15 Å) ordering around the absorber. Since both spectra in Fig. 8 are identical in this region, it is concluded that the tetrahedral Al coordinations are identical up to medium-range order in both samples. This can only occur if the octahedral Al is connected to its original framework position where it can be converted back into its original tetrahedral state. In conclusion, the octahedral Al can be quantitatively reversed to tetrahedral Al, with the preservation of medium-range ordering. The implications of these changes in coordination on the catalytic activity are discussed elsewhere.¹²

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