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Design and construction on an *in situ* cell for catalytic studies on elements with $12 < Z < 20$

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An *in-situ* cell for catalytic studies on elements with X-ray absorption edges between 1300 eV < E < 3000 eV (Mg to Cl) has been designed and constructed at beamline 3.4 of SRS Daresbury (UK). The apparatus consists of a vacuum vessel, that contains a replaceable sealed *in-situ* cell. Dimensions of the *in-situ* cell are small, which results in a low absorption of the X-ray beam.

Keywords: soft X-ray, instrumentation, *in-situ* XAFS, catalysis

1. Introduction

In catalysis the study of the relationship between local and electronic structure on the one hand and catalytic performance on the other hand is of great importance for the understanding of catalytic behaviour and for further development of improved catalysts. Since XAFS probes the local and electronic structure and it allows *in-situ* measurement, XAFS spectroscopy is frequently used in the investigation of catalysts.

In the literature *in-situ* XAFS studies on elements starting from (roughly) the third row in the periodic table are reported. Due to the strong absorption of X-rays at low energy, *in-situ* XAFS on the low Z elements is much more complicated (D.C.Koningsberger and R.Prins, 1988). However, many catalysts and catalyst supports (like zeolites) contain low Z elements and therefore, it is necessary to extend the range where *in-situ* measurement is possible.

Here we report the design and construction of a new cell, which makes *in-situ* XAFS studies possible for elements with $12 < Z < 17$. We are particularly interested in the investigation of zeolite catalysts where aluminum and silicon are reoccurring elements. Their K edges lie at 1559 and 1839 eV respectively. XAFS measurement at elevated temperatures in a gas environment at these elements can now be performed in the new constructed apparatus. The design is suited for simultaneous detection of fluorescence and electron yield.

2 The Vacuum Vessel

The apparatus exists of a big vacuum vessel, which contains a replaceable *in-situ* cell. The vacuum vessel has many feedthroughs, which make temperature-control as well as gas treatment during XAFS measurement possible. Several windows are present, which allow visible control of the interior of the vessel. A picture of the vacuum vessel is shown in Figure 1. Two

large tubes are connected in a cross shape, with on top a sample manipulator. In the middle the door is visible. The vacuum vessel is attached to beamline 3.4 at the SRS in Daresbury (UK). A turbo pump maintains a vacuum lower than 10^{-6} mbar. The vacuum of the beamline is protected from the atmosphere in the vessel by a supported 3 μ mylar window. During sample change, the vacuum vessel is brought to atmospheric pressure using dry nitrogen. The time needed to bring the vessel from atmospheric pressure down to vacuum is about 5 minutes. The vacuum vessel is placed on top of a frame which itself has a possible x,y,z-movement, so the vacuum vessel can be aligned such that the beam goes through the centre of the horizontal central tube.

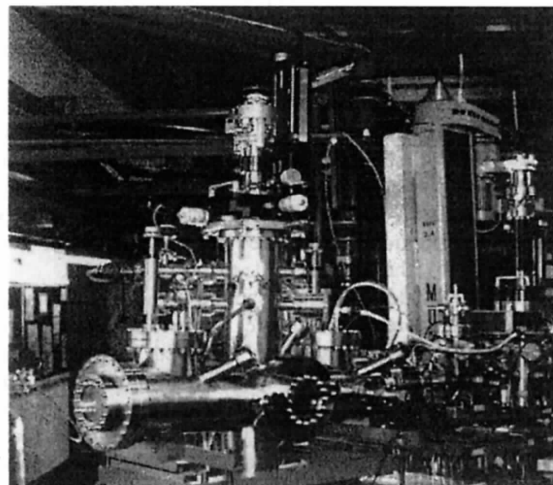


Figure 1. The vacuum vessel as installed at beam line 3.4 at the SRS Daresbury (UK).

On top of the tank a manipulator is placed, which makes accurate x,y,z-movement of the *in-situ* cell possible. This *in-situ* cell is placed inside the vessel through the door at the front of the vessel.

During measurement, the initial intensity is determined by measuring the drain current from a copper (4 μ m, 88% aperture) or gold (6 μ m, 60% aperture) mesh by choice. These meshes are connected to a linear manipulator, which makes an easy change possible between both meshes. A third position on the linear manipulator contains phosphorescing paint, which is used for alignment of both the vacuum vessel and the *in-situ* cell.

3 The *In-situ* Cell

The *in-situ* cell itself consists of three parts. The central part is the sample holder, which is placed inside a sphere. This sphere itself is vacuum tight positioned in a cube. The sphere can be rotated in the cube. The cube holds fragile X-ray transparent windows, which protect the vacuum in the vessel from the pressurizable environment around the sample inside the sphere. These windows are held in specially designed window-holders, in which teflon rings seal the environment in the *in-situ* cell from the vacuum of the vessel. Figure 2 gives a picture of the *in-situ* cell. In the middle a window-holder is visible.

In order to prevent loss of intensity by adsorption of the X-rays by the gas-environment in the cell, sizes are kept as small as possible. The sphere is 45 mm in diameter, the sample holder is a disc of 25 mm in diameter and 12 mm thickness.

The sphere contains two openings of 20 mm diameter at an angle of 90 degrees at the center of the sample, for incoming X-

rays and outgoing fluorescence radiation. The window-holders in the cube exactly fit onto these openings. The sample holder can be connected inside the sphere in such a way that the angle of the incoming X-rays on the sample can be freely chosen. This is done by connecting a flange in the desired position on top of the sphere. In Figure 2 this flange is visible directly above the cube. The second flange, connected on top of the previous contains the electrical and gas feedthroughs.

The sample holder is used for heating and cooling the sample. Inside a resistance heating wire has been coiled, which makes rapid heating of the sample possible up to 500°C. Special care has been taken, that this heating wire induces at no time any electrical field at the position of the sample. This is done by exactly reversing the direction of coiling halfway along the wire, so any electrical field created is cancelled out by a field in opposite direction. In addition, direct current is used.

The sample holder also contains a hollow tube, which can be connected to a liquid nitrogen supply outside the vacuum vessel. This makes rapid cooling of the sample possible. By combining the heater and the supply of liquid nitrogen any temperature starting from -198°C to 500°C can be maintained. A k-type thermocouple continuously measures the temperature at 2 mm behind the centre of the sample inside the sample holder.

In the sample holder a pressed sample with 13 mm diameter can be placed. In order to be able to perform electron yield detection, the sample is electrically shielded from the sample holder by use of BN or Makor cups, making heat transfer possible between sample holder and sample, while any electrical current is suppressed. The sample is electrically connected through the top flange of the *in-situ* cell by a shielded feedthrough to a shielded wire. This wire can be connected directly to a preamplifier in the vacuum or to a signal amplifier outside the vacuum vessel in order to measure the electron yield signal.



Figure 2. The *In-situ* cell. At the front a window holder is visible.

As already mentioned, the sphere is contained in a cube which has four window holders, which shield the environment in the sphere from the vacuum in the vessel by teflon rings, pressed against the sphere. These teflon rings in the window-holders make rotation of the sphere inside the cube possible, while the inside of the sphere is pressurised and vacuum exists in the vessel. Two of the window holders are blind and two contain thin X-ray transparent windows. The entrance and exit window are placed under an angle of 90 degrees. The openings in the sphere exactly coincide with the positions of the window holders in the

cube. The sphere in the cube can be rotated by hand (in order to pre-treat the sample while in the laboratory) or by using the manipulator on top of the vacuum vessel (in order to pre-treat the sample, while inside the vacuum vessel, just before measurement). During these treatments the openings in the sphere are placed in front of the blind windows. At this position the fragile and expensive windows are protected from the gas environment in the sphere, hence making more severe pre-treatment conditions possible. In this way we have reached 5 bar pressure at 550°C. After such a treatment the sample holder can be rotated back to the measuring position and the sample is exposed to X-rays. In this position the fragile windows limit the gas-treatment conditions which can be reached during XAFS measurement. We have tested the windows (beryllium and polyimide) under a sample treatment of 450°C at 1 bar gas pressure. Under these conditions we are able to take EXAFS data on the Al K edge. While not in the vessel, the window-holders can be easily changed, which makes the cell flexible for choice of window material. The entrance window is 4*8 mm, the exit window for fluorescence detection is spherical with a diameter of 20 mm. The thickness of the entrance Beryllium window (4*8mm) is 7.6µm and the exit window (diameter 20 mm) is 13µm. The supported polyimide window is 0.5µm thick and supported.

4 Detection in ILEXAFS

Electron yield and fluorescence detection can be performed simultaneously. The sample is electrically connected via shielded wires and shielded feedthroughs to a Keithley, or to a preamplifier inside the vacuum vessel. The latter amplifies the small drain current in the protecting Faraday cage of the vacuum vessel. A platinum collector plate can be positioned opposite the sample. This makes conversion electron yield (CEY) possible by applying voltages on sample and collector plate (Schroeder, S.L.M. 1996). Currents from both the sample and the collector plate can be measured.

Due to the strong absorption of X-rays at low energies a solid angle as large as possible must be obtained to measure fluorescence. Therefore, much effort has been given to the positioning of fluorescence detector(s) with respect of the sample. A fluorescence detector can be placed as close as 20 mm from the sample. Depending on the application, several fluorescence detectors can be installed: a gas proportional counter or a photodiode by choice. A microstrip detector is currently under construction. To increase the yield in fluorescence, the exit window is in both cases integrated with the detector. By applying a GPC, the exit window of the *in-situ* cell is at the same time used as window for the GPC itself. This integration of the detector window with the window-holder reduces the number of windows, thereby increasing solid angle on the detector. In addition, this positions the detector very close to the sample, hence obtaining a large solid angle. If a photodiode is used, it is positioned inside the gas-environment of the *in-situ* cell. If corrosive gasses are used, or a heat treatment is given to the sample, the detector will be placed behind an exit window, protecting the photodiode.

5 Measurement in ILEXAFS

As an example of the performance of *in-situ* EXAFS a study to the coordination of aluminium in zeolite Beta is given. The Beta

has a Si/Al ratio of 11.6. Fluorescence detection, using a gas proportional counter has been used.

^{27}Al magic angle spinning NMR (de Ménorval, 1996) suggests the framework of Beta contains some tetrahedrally coordinated aluminium which can be converted to octahedrally coordinated aluminium after a temperature treatment of 450°C during 1 hour (sample called H-Beta). However, an ammonia treatment at 100°C for one

octahedrally co-ordinated Al (van Bokhoven, 1997), thus confirming the ^{27}Al MAS NMR of the formation of octahedrally coordinated aluminium after the heat treatment at 450°C.

An *ex-situ* ammonia treatment yields the spectrum (top) given in Figure 4. For comparison the original NH_4 -Beta spectrum (bottom) has been given. The ammonia treated spectrum has been given an offset, since both spectra are within the limits of the noise identical. This indicates a quantitative reversal of coordination after the ammonia treatment. Moreover, the peaks at 5 and 10 eV are unaltered, which means long range order around the tetrahedral aluminium exists. Therefore it must be concluded this tetrahedral aluminium after subsequent short heat and ammonia treatment is placed in identical positions as before these treatments. This must be in the framework, which implies the octahedrally coordinated aluminium after the short steam treatment must somehow be attached to the framework, hence the full reinsertion into the framework is possible.

6 Conclusions

The use of the *in-situ* catalyst cell has made it possible to measure at *in-situ* conditions at the Al K edge. Conditions at which the cell can be used are 1 bar pressure at a temperature of 450°C. More severe pre-treatment conditions, with pressures up to 5 bars and maximum temperatures of 550°C can be reached.

Electron yield and fluorescence can be detected simultaneously.

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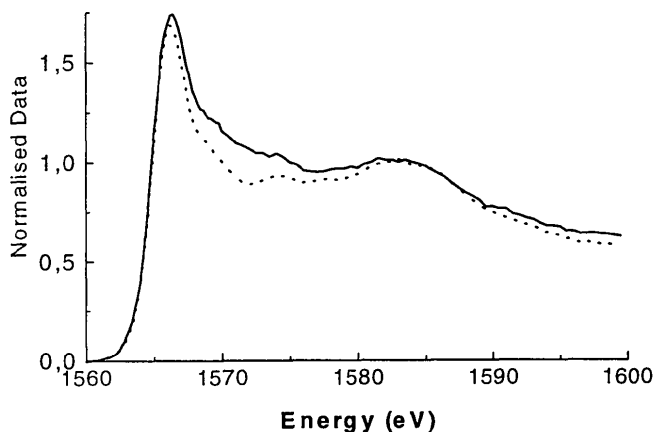


Figure 3. Al K edge of NH_4 -Beta (dots) and H-Beta (solid).

day forces the Al to return to their original coordination. A difficulty in the ^{27}Al MAS NMR measurements is the fact that some aluminium escapes detection and hence the results are not quantitative.

We used the ILEXAFS apparatus to follow the coordination of Al in zeolite Beta as a function of treatment of the zeolite. The heat treatment has been performed *in-situ*. In Figure 3 Al K edge spectra of NH_4 -Beta (the parent material) and the sample after short heat pulse (H-Beta) are given. The NH_4 -Beta shows the characteristic features of a tetrahedrally coordinated aluminium (van Bokhoven, 1997): a sharp whiteline and a broad shape-

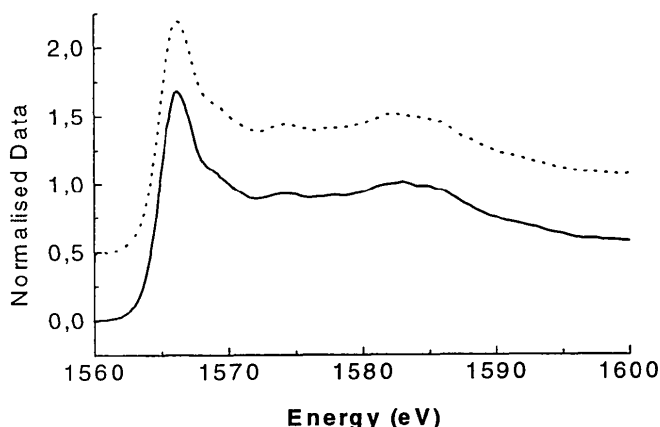


Figure 4. Al K edge of H-Beta, ammonia treated (dotted) and NH_4 -Beta (solid).

resonance at 20 eV above the edge. At 5 and 10 eV above the edge small features are present, which find their origin in long range order (15 Å) (Cabareth, 1996)ⁱ.

The treated sample shows increased intensity at 5-10 eV above the edge. A difference spectra (not given) between the H-Beta and the NH_4 -Beta shows the characteristic spectrum of an