Application Note #000384

KeyWords
XPS, Catalysis, Minerals, Zeolite, Measurements, Surface Analysis, Charge Compensation

XPS surface analysis of Zeolites with EnviroESCA

This application note presents how EnviroESCA can be used to analyze the surface of Clinoptilolite, a natural zeolite. Charge compensation of this porous and insulating material is accomplished by Environmental Charge Compensation allowing measuring of X-ray photoelectron spectra on this challenging material with ease.

Motivation

Zeolites are molecular sieves, microporous aluminosilicate minerals. They are being used for filtration of water, as adsorbents or catalysts.

Because of their wide usage in the petrochemical industry as a catalyst, the interaction of its surface and the surrounding atmosphere is of great importance for the optimization of these processes.

Fig. 1 Blocks of natural occurring Clinoptilolite used as samples in this study

Method

EnviroESCA utilizes X-ray Photoelectron Spectroscopy (XPS) as its main analytical technique.

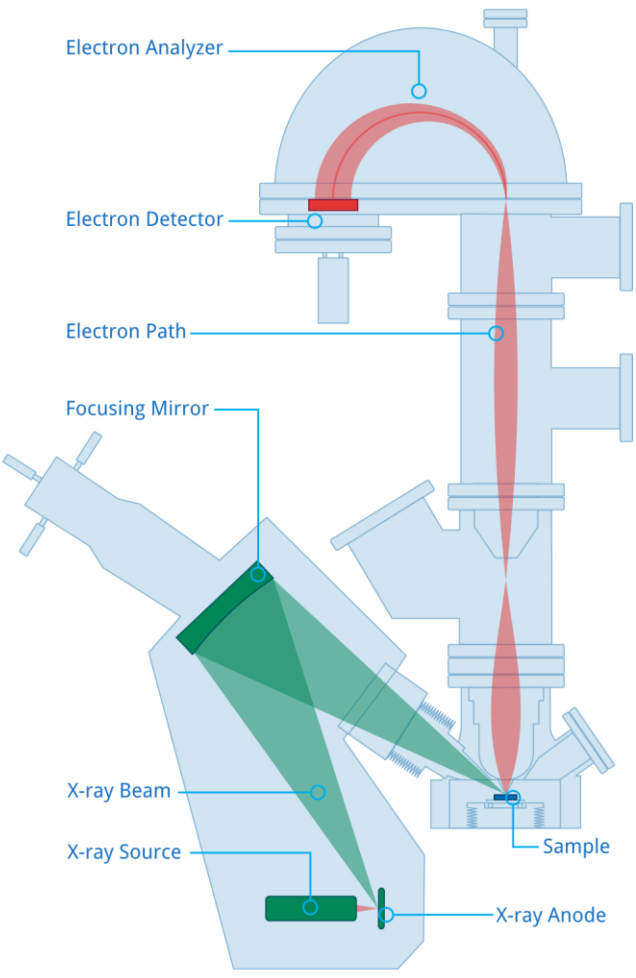

Fig. 2 XPS with EnviroESCA

Hereby an electron beam is generated inside the X-ray source and focused onto an X-ray anode made of aluminum. The deceleration of the electrons on the anode leads to the production of X-rays. This X-ray beam is monochromated and focused onto the sample.

X-ray photons impinging the sample excite electrons in the material which are subsequently emitted with specific kinetic energy determined by their binding energy and the photon energy of the x-rays. Thereby only electrons from atoms up to a depth of approx. 10nm are able to leave the surface. These electrons propagate through the lens system of the Electron Analyzer into the hemisphere which acts as a spherical capacitor forcing the electrons onto circular paths with radii depending on their kinetic energy. The electron paths end at an electron sensitive detector where the electrons are amplified and measured as an intensity in counts / second. Sweeping the voltage of the spherical capacitor while measuring the number of electrons per second on the detector results in a photoelectron spectrum. From these spectra a quantitative analysis of the atomic composition of the sample surface can be done.

Experimental Section

Zeolites confine molecules in small spaces which makes it difficult to investigate them in classical XPS systems that require ultra-high or high vacuum working conditions. The trapped molecules will outgas during pump down cycles and will desorb continuously from the surface of the specimen.

Figure 3 shows a photograph taken with the "Through the Lens" digital microscope of EnviroESCA's SampleExplorer of the surface of Clinoptilolite, a natural zeolite used as a specimen. The visible area in this picture is about 400 by 300 µm and resembles the analysis area underneath the analyzer nozzle in the EnviroESCA.

EnviroESCA can work in pressures up to several dozens of mbar and therefore does not necessarily require vacuum conditions which overcome the problem of outgassing of almost all samples.

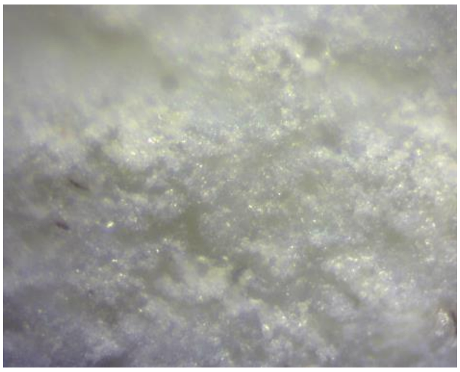

Fig. 3 Microscopic image of the surface under investigation (visible area: 400x300µm)

In classical XPS systems zeolites tend to quickly charge up under X-ray illumination which makes charge compensation inevitable. In classical XPS low energy electron and ion sources are being used in addition to the X-ray source to compensate the surface charge of the surface.

In EnviroESCA an intrinsic charge compensation method which we call Environmental Charge Compensation makes additional electron or ion sources unnecessary. The gas atmosphere that is surrounding the sample delivers all the free charges, when illuminated with the soft X-rays, that is needed to compensate for surface charging (see figure 4 for an illustration).

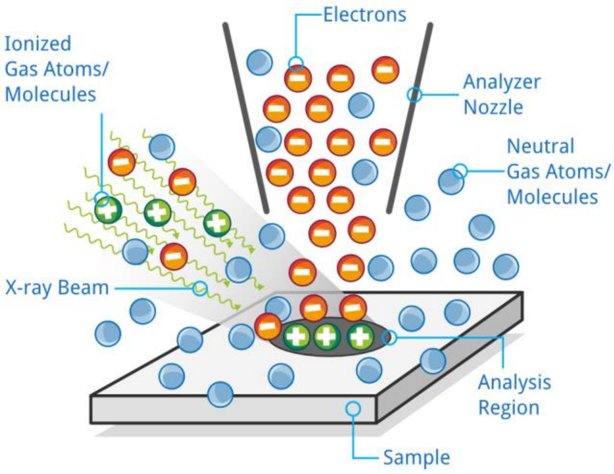

Fig. 4 Environmental Charge Compensation

In this study the surface of Clinoptilolite chunks, normally being used for water filtration, were investigated with the EnviroESCA.

Because of the charge up of the surface in vacuum a working pressure of 1 mbar ambient air was chosen for this study.

Results

In the following we are presenting unmodified raw data taken with EnviroESCA. The data was not smoothened or shifted on the energy scale unless otherwise mentioned.

A chunk of about 8x5x5 mm was selected and mounted onto the sample holder with carbon tape. No additional masking or electrical contacting was performed.

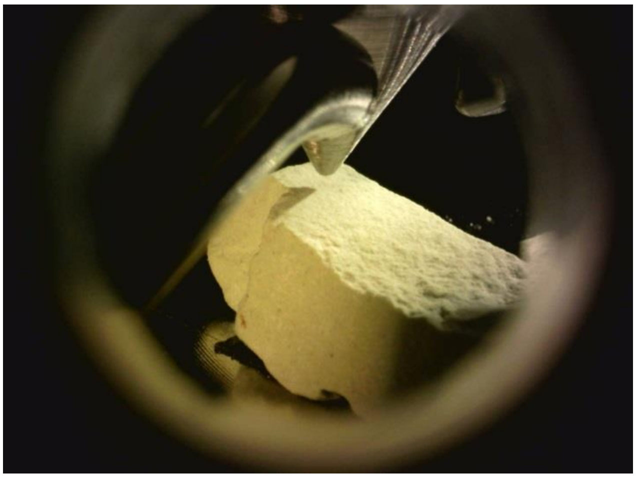

Fig. 5 Camera view onto the analysis area

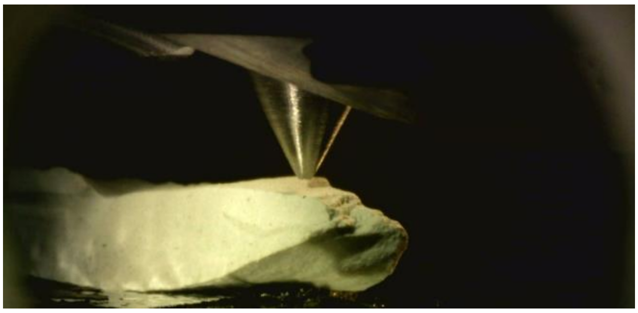

Fig. 6 Side view onto the analysis area

A survey scan was acquired less than three minutes after starting the pump down of the SampleEnvironment to 1 mbar.

Figure 7 displays the result of that scan which was measured with a total acquisition time of 2 minutes and 29 seconds (1 eV step width).

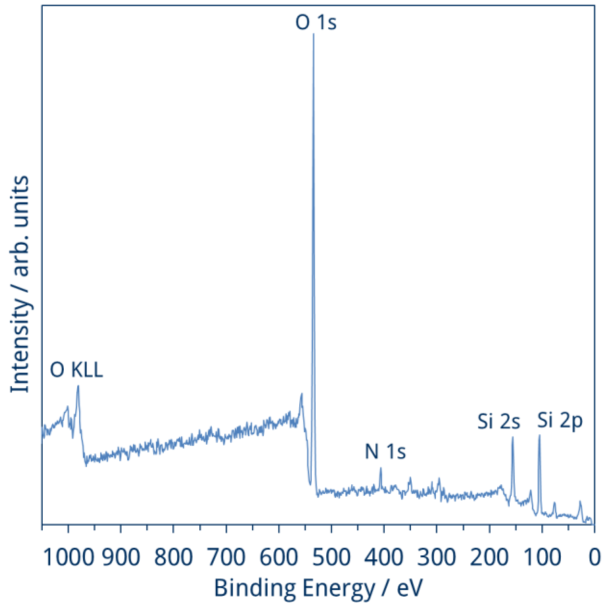

Fig. 7 XPS survey spectrum of Clinoptilolite

Taking a closer look gives a peak position of 534.5 eV of the O 1s. Which means the spectrum is shifted about 3.5 eV to higher binding energies when comparing the measured O 1s position to the literature value [1].

A spectrum taken in the energy range 0 to 200 eV clearly shows peaks from Silicon (2s and 2p), Aluminum (2p) and the 2s peak of Oxygen (see figure 8 for details).

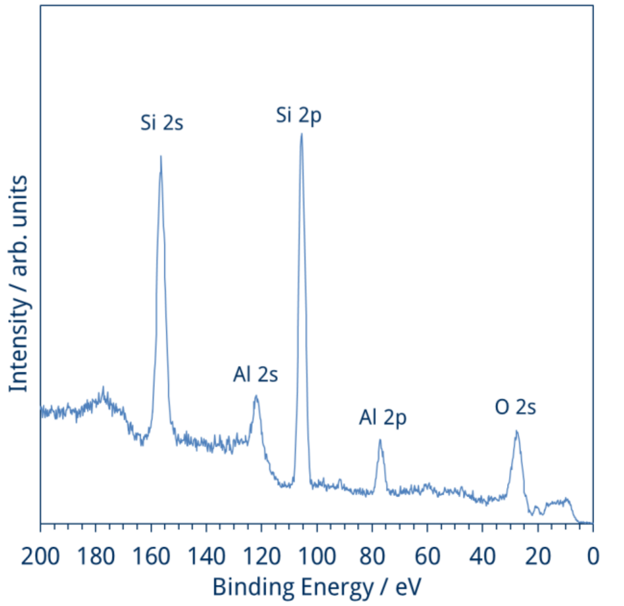

Fig. 8 XPS spectrum of the energy range 0-200 eV (spectrum recorded with a step width of 0.2 eV in about 22 minutes)

Figure 9 displays a detail spectrum of the region between 260 and 510 eV where signals from Calcium, Potassium, Carbon and Nitrogen can be identified.

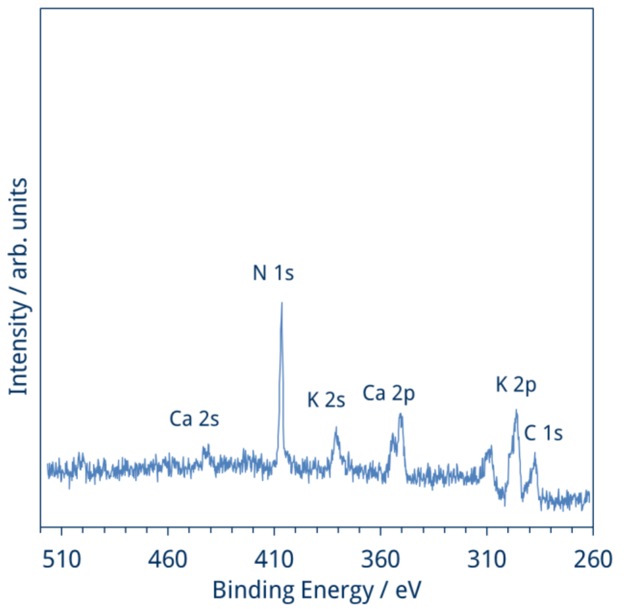

Fig. 9 XPS spectrum of the energy range 260-510 eV

In Figure 10 and 11 high resolution spectra are presented. They show detailed views on the Calcium 2p and on the Potassium 2p spectral regions.

The spectrum of Figure 10 clearly shows the splitting of the Calcium 2p peak whereas Figure 11 displays the splitted Potassium 2p together with the Carbon 1s peak.

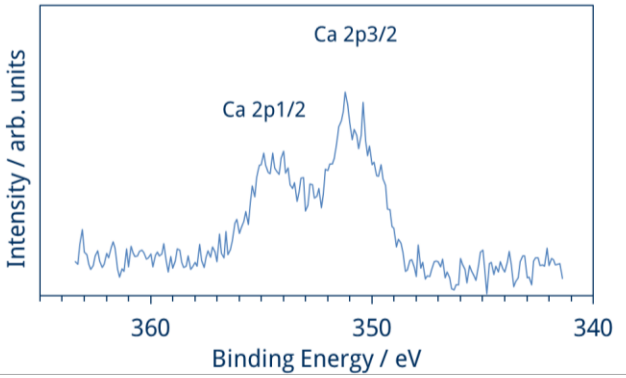

Fig. 10 High resolution spectrum of the Ca 2p region (recorded with a step width of 0.1 eV in 19 minutes)

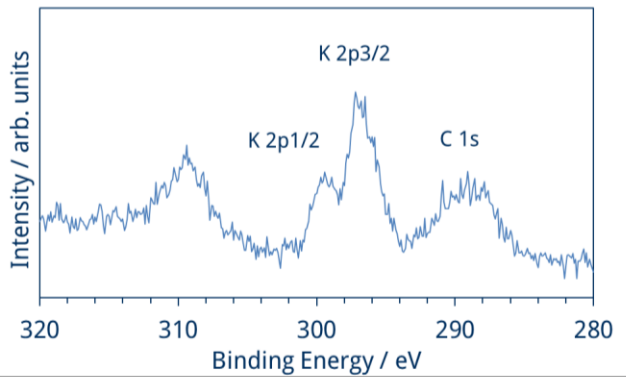

Fig. 11 High resolution spectrum of the K 2p region (recorded with a step width of 0.1 eV in 30 minutes)

Conclusion

EnviroESCA has proven to be a powerful tool to investigate the surface of zeolites with XPS. Because of the intrinsic charge compensation of the gas environment high resolution and high quality spectra are recordable. With an overall charge up of 3.5 eV of the surface in an atmosphere of 1 mbar the Environmental Charge Compensation is working properly for these sample types. Also the outgassing of the sample itself presents no problem for EnviroESCA.

[1] Handbook of X-ray Photoelectron Spectroscopy, Physical Electronics, 1995, ISBN 0-9648124-1-X