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X-Rays sight active sites: Dynamics of catalytic surfaces under reaction conditions

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Our realisation is outlined in Fig. 1. A sample chamber with a cooled thin silicon nitride window for the photon beam houses pellets of heterogeneous catalysts that are placed on a sample stage ca. 1 mm in front of the

The Japanese symbol for a catalyst means appropriately 'marriage broker', i.e. a catalyst offers an active site for a reaction to take place without being changed itself. In this way, a park bench can be regarded as a 'marriage broker' for twosomes. Without the catalyst the reaction would not or only slowly take place. 95% of the value produced in chemical industry is done with the help of catalysts, but their optimisation is normally done by a trial- and error approach.

Our group has built an instrument to follow the dynamics of catalytic surfaces under reaction conditions. The system is dedicated for the investigation of gas-surface reactions of single and polycrystalline solids. Such in-situ studies allow establishing structure-function correlations without having to make assumptions about the relevance of a specific species detected by surface analysis. X-ray photoelectron spectroscopy is here the key method as it can detect all elements besides hydrogen, exhibits pronounced chemical sensitivity and when used with synchrotron excitation can be used in highly specific modes of depth and energy resolution. Its greatest disadvantage as photon in – electron out technique is the required (ultra)-high vacuum operation to detect the photoelectrons.

Attempts to overcome this limitation use the concept of a small aperture and multiple differential pumping between sample and electron energy analyzer. It is only the incorporation of self-tuning electron optical elements that focus the electrons from the exit aperture into the hemispherical electron energy analyser that provides a useful count rate over a wide range of kinetic energy for electron spectroscopy ranging from about 100 to 1,000 eV.

aperture of 1 mm diameter of the first differential pumping stage. Depending on gas composition and the exact distance sample-aperture pressures of typically 5 mbar can be reached at the sample which can be heated with a ramp-controlled laser beam system between 300 K and 1,000 K. Reactive and corrosive gases including hot water vapour, oxygen and organic solvents can be used provided that the window is not attacked. A flowing gas atmosphere with on-line compositional gas detection can be used. Liquids, solutions and dispersions can be studied with a precision temperature regulation limiting the vapour pressure between ca. 0.1 mbar and 5.0 mbar. Additionally, gas phase analysis is possible with a conventional quadrupole mass analyzer and with a high sensitivity proton-transfer ion molecule reaction mass analyzer.

The spectral analysis of data is similar to that of conventional XPS with two prominent exceptions: in all relevant core level regions the spectra of the gas phase atoms occur besides those from the surface. The resulting complex spectral shapes can be analysed taking into account that the work function shifts the gas phase components relative to those of the solid and adsorbates. The emitted photoelectrons interact heavily with the surrounding gas phase giving rise to composition-specific strong alterations in the element specific photoelectron yields. The modifications reach up to an order of magnitude changes relative to the cross sections used for UHV surface analysis and need to be carefully calibrated for each system.

References:

H. Bluhm et al., *J. Phys. Chem., B* **108**, 14340 (2004)

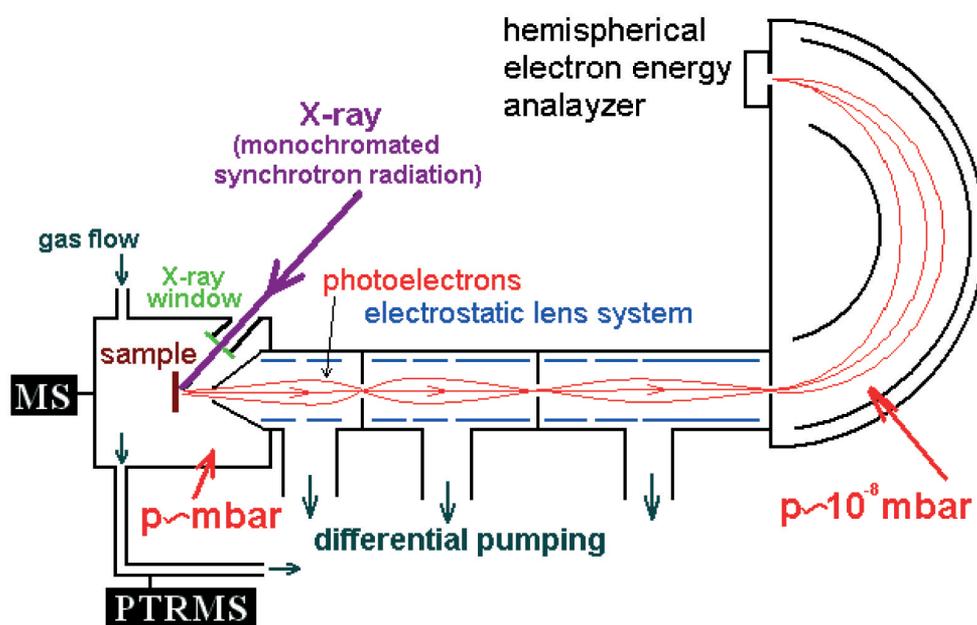


Fig. 1: Schematic representation of the high pressure XPS instrument at BESSY.

An example is presented in Fig. 2 showing a polycrystalline silver surface active in the epoxidation of ethylene. This much studied reaction proceeds according to surface science via the formation of one species of atomic oxygen being present as electrophilic oxygen at the catalyst surface. The data in Fig. 2 reveal, however, that a mixture of species is present under steady state reaction conditions and that their relative abundance depends critically on the operation conditions. No peroxide or molecular species is present as often speculated in the literature. The difference spectra at 470 K reveal the presence of a smaller abundance of surface atomic oxygen (3 - 4) and a larger contribution from sub-surface species (4) which are catalytically inactive. This new finding and the fact that the unwanted nucleophilic oxygen species that burns ethylene to carbon dioxide is present as unavoidable companion of the desired oxygen species at high pressure explain the limited selectivity and why no other molecules than ethylene can be reacted to its epoxide over silver: all other molecules are C-H activated by nucleophilic oxygen and undergo thus additional reaction pathways leading to undesired products. The unambiguous detection of the desired and undesired oxygen species on the working catalysts surface gives now a unique handle to test for strategies to suppress the undesired species currently executed as an industrial cooperation between BESSY and a large epoxide producer.

The now smooth operation of the system permits the study of a wide variety of applications in material science. The possibilities range from charge neutralisation in polymer surface analysis by the addition of water vapour over the melting of ice and the effect of solutes on the kinetics of the solid liquid transition of this environmentally relevant system to surface analysis of biological systems in their native wet state and the study of electrochemical cells without the need for emersion.

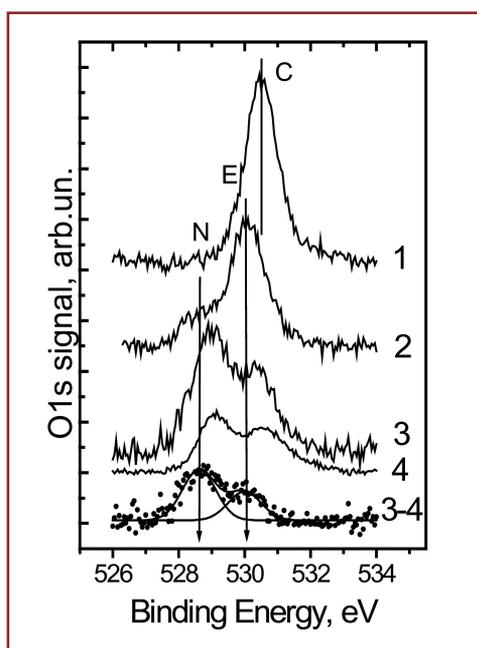


Fig. 2: Oxygen 1s spectra during ethylene epoxidation at 0.5 mbar total pressure: (1) at 300 K, no reaction, (2) at 420 K, stable conversion, (3) at 470 K deactivating, (4) at 470 K without oxygen in the gas phase. The three oxygen species are carbonate (spectator, C), electrophilic (wanted, E) and nucleophilic (unwanted, N) atomic oxygen.

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