In Situ Surface Characterization of Technical Catalysts by Synchrotron Based Near Ambient Pressure X-ray Electron Spectroscopy

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The surface of functional materials like catalysts responds to the ambient conditions. X-ray photoelectron spectroscopy (XPS) and soft X-ray absorption spectroscopy (XAS) are one of the most versatile methods for the investigation of surfaces on the atomic scale providing quantitative information about the elemental composition and chemical specificity. Surface sensitive *in situ* spectroscopy, i.e. in the presence of a reactive environment allows studying the formation of the interface (gas/solid or liquid/solid) of a catalyst with time. Examples for the dynamic formation of the electronic surface structure by interaction with the ambient gas under equilibrium studied by near ambient pressure XPS (NAP-XPS) and variable pressure soft-XAS (vP-XAS) will be presented.

We characterized the surface of the alkane oxidation catalyst vanadyl pyrophosphate $(VO)_2P_2O_7$ (VPP) with NAP-XPS in the mbar pressure range and with vP-soft XAS in the electron yield mode at pressures up to 1000mbar at various gas compositions at temperature up to 400°C. Analysis of NAP-XPS spectra provides evidence that details of the electronic structure like core level binding energies, valence band, work function, and electron affinity of the technical catalyst VPP do respond systematically on the gas phase. This indicates the formation of a dynamic surface/subsurface space charge region that has an impact on the charge transport properties of the active catalyst [1]. Additionally, the vanadium oxidation state has been extracted from the V L_3-edge XAS under O_2, C_4H_{10}, and C_4H_{10}+O_2 feed in a variable pressure XAS experiment (vP-XAS). It was found that the vanadium oxidation state changes both with the gas composition and the total pressure. The observed pressure gap is understood in terms of Gibbs free energy of the surface and its dependence on the oxygen partial pressure of the surrounding gas phase [2].

Finally, an outlook on future activities at HZB/BESSY to develop further synchrotron based ambient pressure characterization methodologies will be given. Recently, the advent of reaction cells based on electron transparent membranes at low kinetic energy (i.e. high surface sensitivity) has found much interest [3]. First results of the application of this type of cells allowing performing XPS studies at 1000mbar gas pressure and in liquids will be presented. Currently, HZB and FHI are establishing EMIL, The Energy Materials In-Situ Laboratory Berlin at BESSY II. This novel facility includes a new laboratory building hosting beamlines providing an unusual broad photon energy range from 80eV – 8000eV in one spot and (among others) a NAP-high kinetic energy XPS endstation capable to operate at kinetic energy of photoelectrons up to 7000eV that allows studying buried layers and liquid/solid interfaces [4]. Prospects of this new facility for catalysis research will be discussed.

References

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