

In situ photoelectron spectroscopy studies of the structure-activity relationship

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The investigation of the structure-activity relationship (SAR) in heterogeneous catalysts has a fundamental role to identify active sites and design reaction mechanisms.[1] Because active sites have to be characterized while exposed to the reaction environment, in situ and/or operando spectroscopies are required.[2] Over the last 20 years, the development of differentially pumped electron analyzers equipped with electrostatic pre-lenses has enabled X-ray photoelectron spectroscopy (XPS) measurements in the mbar range at synchrotron facilities as well as in laboratory setups.[3] Since 2019, the in situ spectroscopy (ISS) beamline at the Swiss light source allows ambient pressure (AP) XPS measurements in the fields of catalysis, surface and environmental chemistry.[4,5] The facility is designed to investigate solid-gas and solid-liquid interfaces.[6,7] Thanks to its surface sensitivity and the possibility to reproduce reactive gas environments, APXPS allows the identification of active sites involved in a reaction.

In my presentation, I will introduce the technique, describe the ISS beamline and the end stations available. After such a technical introduction, I will focus on the characterization of Pt/CeO₂ catalysts for the low temperature water-gas shift reaction. This is a clear example of how in situ XPS, together with high-resolution electron microscopy, allows identifying the structure of active sites, differentiating atomically dispersed species from nanoparticles, and how they affect the reactivity. The new approach proposed brings the direct quantification of different types of platinum sites under working condition. Catalytic tests, carried out in parallel and reproducing the reaction conditions adopted during spectroscopy measurements, provide relevant information about the catalytic performance, thus bridging the pressure gap between techniques.

A triangular connection between morphology, electronic structure and performance of actual Pt/CeO₂ catalysts is proposed. Metallic coordinatively unsaturated sites on platinum nanoparticles are the dominant active sites, and they positively correlate with WGS activity. Other sites on nanoparticles and atomically dispersed species are less active. The approach is generally applicable and enables the understanding of reaction mechanisms in heterogeneous industrial catalysts.

References:

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