More Insights into Fundamental Aspects of Au Catalysis:
From Idealized In Situ Characterization to Operando Spectroscopy

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The high activity and selectivity of supported Au catalysts under mild reaction conditions for a wide range of oxidation and reduction reactions has motivated intense research on Au catalysis for over two decades.[1] Nevertheless, fundamental aspects of the underlying reaction mechanisms are still under debate and far from being resolved. Understanding the physical origin of the activity and selectivity of these catalysts entails in particular a rigid structure-reactivity correlation under realistic reaction conditions, which includes also the role of the interface between Au nanoparticles and support. Particular helpful for these purposes are operando spectroscopy techniques, which allow for simultaneous monitoring of the reactivity and probing of the catalyst structure (e.g. using X-ray absorption spectroscopy XAS) or of the adlayer (FTIR or Raman spectroscopy). In the present contribution we report some key examples where operando / in situ spectroscopy has been successful for understanding the catalytic performance of the respective supported Au catalysts.

In a first example this is illustrated for methanol synthesis from CO$_2$/H$_2$ on Au/ZnO catalysts, which was explored both under idealized and realistic reaction conditions by a combination of operando FTIR (DRIFTS), near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) and X-ray absorption spectroscopy (XAS) at the O K-edge, in addition to temporal analysis of products (TAP) measurements. DRIFTS measurements performed at pressures between 1 and 50 bar using CO, which is formed during methanol synthesis via the RWGS reaction (CO$_2$ + H$_2$ => CO + H$_2$O), as probe molecule revealed the formation of strongly adsorbing negatively charged gold sites (CO$_\text{ad}$@Au$^{3+}$).[2,3] Kinetic, NAP-XPS and XAS (O K-edge) measurements point to a close correlation between i) the methanol formation rate, ii) the formation of O-vacancies (defects) and iii) the adsorption strength on the Au$^{3+}$ species.

In another example we aimed at the identification of the nature of the active Au species during the low-temperature water gas shift (WGS) reaction on highly active Au/CeO$_2$ catalysts.[3] XAS measurements on differently pretreated Au/CeO$_2$ catalysts indicate that independent of the initial oxidation state of Au, the exposure to H$_2$-free idealized reformate (1% CO, 2% H$_2$O, balance N$_2$) results in the rapid formation of completely metallic, sub-nanometer sized Au clusters. The presence and formation / depletion of oxidized Au$^{3+}$ species could not be correlated with the different activities of different catalysts and their changes with time. In situ DRIFTS measurements showing no indication of CO adsorption on Au$^{3+}$ sites are in full agreement with the above findings.

As a third example, the combination of EXAFS measurements at the Au LIII edge with electron microscopy (HAADF-STEM) and XRD helped us to map out correlations between changes in the size of the Au NPs of Au/CeO$_2$ catalysts during CO oxidation at 80°C and the observed deactivation of the catalyst.[4,5] Obviously, the long-term deactivation is dominated by a modest but irreversible Au particle size growth. Combining these measurements with in situ DRIFTS measurements helped us to decouple Au particle size effects from possible surface poisoning by the accumulation of oxygenated carbon containing surface species.

Insights from these operando measurements will be discussed and compared with results from temporal analysis of products (TAP) on the dynamics of formation / refilling of active surface oxygen vacancies,[6] which we consider to be a key-element in the reaction pathway for different reactions, despite their different role in different reactions.[6-8]

References