Bridging the Material Gap between Model and Practical Au/TiOx Catalysts Using X-ray Spectroscopies

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Introduction

The physical basis for the low-temperature activity of supported Au particles remains controversial [1-3]. The oxide support influences both morphology and electronic structure of the Au particles [4,5], and hence their catalytic activity [6,7]. We have probed the electronic structure of a highly active Au/TiOx powder catalyst in situ under reaction conditions by synchrotron X-ray spectroscopies (XAFS, XPS) and found that the electronic structure of the Au component is dynamically responding to environmental conditions.

Methods and Materials

The Au/TiOx catalyst with low gold loading was prepared by deposition-precipitation [8] from HAuCl4. CO-oxidation turnover frequencies per Au atom at 353 K (space velocities of 20,000 h-1) were approximately 1 s-1. After characterisation by standard techniques (XRD, TEM, XPS) and reaction rate measurements we measured in situ fluorescence-yield XAFS (X1, Hasylab, Germany; 9:2, SRS Daresbury, UK) at the Au L3-edge at 1 atm, and by in situ synchrotron XPS (U49/2-PGM1, BESSY, Germany) at 1 mbar [9].

Results and Discussion

XANES and EXAFS indicate that only very small, metallic Au particles are catalytically active towards low-temperature CO oxidation. For example, as catalytic activity increased at elevated temperatures, near-edge features of in situ XA spectra associated with lower-coordinated Au species became more pronounced (fig. 1). In situ XP spectra of the Au/TiOx catalyst additionally revealed reversible electronic structure changes as a function of the composition of the gaseous environment (fig. 2) [9]. We found that CO and O2 appear to cooperatively influence the electronic structure of Au and likely also its morphology. Higher oxidation activity may thus be associated with the formation of raft-like Au particles (schematic fig. 2). An influence on adjacent sites of the TiOx support was not detectable by Ti photomission. CO and O2 have been found to disrupt and re-disperse Au clusters on planar model systems [4, 10]. The influence of the gas-phase environment on the XA and XP spectra of the Au particles is reminiscent of these observations and suggests that the origins of activity in planar model systems and practical Au catalysts might be similar. The results underline the dynamic nature of supported Au, and the importance of in situ experimentation for the elucidation of gas/surface reaction mechanisms.

Acknowledgements

This project was supported through DFG contract SCHR677/2.