

Model catalysts for reforming and oxidation reactions: ultrathin films of zirconium oxide and cobalt oxide

Günther Rupprechter, Hao Li, Kresimir Anic, Christoph Rameshan, Andrey Bukhtiyarov

Institut für Materialchemie, Technische Universität Wien, A-1060 Wien, Austria
(corresponding author: G. Rupprechter, e-mail: guenther.rupprechter@tuwien.ac.at)

It is well accepted that surface science based planar model catalysts are well-suited for fundamental studies of surfaces processes, despite the inherent differences between model and technological catalysts [1-3]. Classical ultrahigh vacuum (UHV) based experiment are still indispensable but methodological developments also allow to examine active functioning model catalysts under operando conditions, at (near) atmospheric pressure and at elevated temperature. Frequently applied methods encompass polarization-modulation infrared reflection absorption spectroscopy (PM-IRAS), sum frequency generation (SFG) laser spectroscopy and near atmospheric pressure X-ray photoelectron spectroscopy (NAP-XPS). Most of the current operando studies were performed at synchrotron sources (BESSY (DE), MaxLab (SE), SLS (CH)), and in lock-step with theory. In the current contribution two oxides that are relevant for Solid Oxide Fuel Cell (SOFC) technology are discussed: (i) Ni-ZrO₂ SOFC „cermet“ anodes for CH₄ reforming to H₂ and/or H₂ oxidation, and (ii) Co₃O₄, a potential catalysts for cleaning H₂ feeds from CO traces via preferential CO oxidation (PROX).

In order to model SOFC anodes well-ordered ultrathin films of ZrO₂ were grown in UHV by oxidation and annealing of Pt₃Zr(0001) single crystals [4,5]. Ni was deposited by physical vapor deposition. Low Energy Electron Diffraction (LEED), Scanning Tunneling Microscopy (STM), high resolution X-ray Photoelectron Spectroscopy (XPS) and Density Functional Theory (DFT) indicated the formation of a well-structured ZrO₂ trilayer film, corresponding to the (111) facet of cubic ZrO₂. Whereas the interaction of the film with CO or CO₂ was very weak (desorption temperatures of 155 and 117 K, respectively), its interaction with water was very strong (desorption temperature of 485 K). NAP-XPS was thus applied to examine water adsorption and the hydroxylation of the film (Fig. 1, left). Once hydroxylated the film exhibited exceptional activity for reaction with CO₂ (whereas the non-hydroxylated film did not). IRAS, using formic acid (HCOOH) and formaldehyde (HCHO) as reference, was then used to identify the functional groups of the formed species. CO₂ and H₂O codosing induced the formation of formaldehyde, dioxymethylene and formate on hydroxylated ZrO₂.

Low temperature fuel cells rely on clean hydrogen, since CO traces in the feed would poison the catalyst. Cobalt oxide is highly active for low temperature CO oxidation and PROX and holds potential for replacing noble metals and/or rare earth oxides. Nevertheless, the origin of the high cobalt oxide activity is still not thoroughly understood. Thin cobalt oxide films,

$\text{Co}_3\text{O}_4(111)$ or $\text{CoO}(111)$, with well-defined structure were thus grown on $\text{Ir}(100)$ by Co physical vapor deposition in O_2 background and subsequent post-oxidation [6].

The interaction of 6 ML thick $\text{Co}_3\text{O}_4(111)$ or $\text{CoO}(111)$ films with CO was again examined by TPD, XPS and PM-IRAS (200 to 700 K, UHV to 100 mbar). Upon CO exposure, weakly bonded CO, carbonates and elementary carbon were observed. Upon desorption and repeated adsorption/desorption cycles, (partial) reduction of cobalt oxide occurred. Interestingly, for CO oxidation (mbar pressure, up to 650 K) operando NAP-XPS in the valence band region revealed the same active state of the catalyst, independent of the original composition (Co_3O_4 or CoO), which is in line with corresponding operando studies on technological „powder“ Co_3O_4 catalysts that were also performed by our group [7].

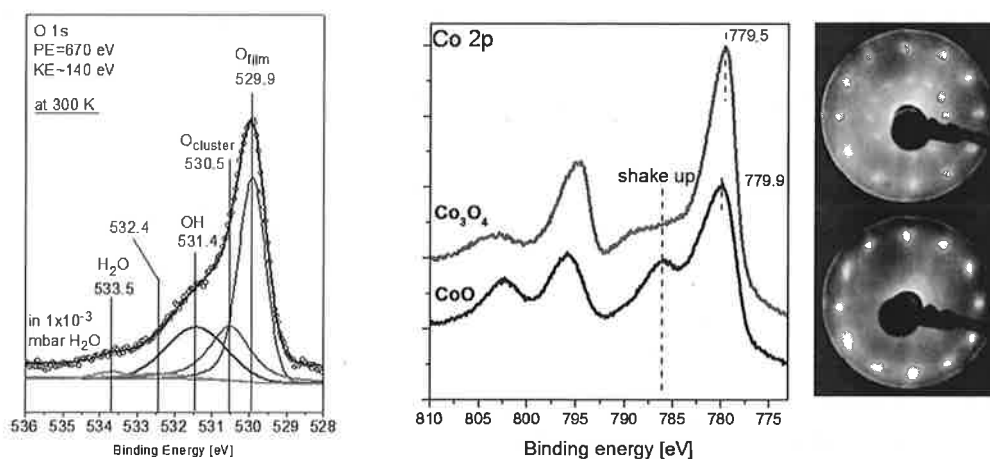


Figure 1. (NAP-) XPS spectra of hydroxylated ZrO_2 (left) and of cobalt oxide thin film model catalysts (right). For the latter, LEED patterns are included.

For both oxide model catalysts, ZrO_2 and Co_3O_4 , potential reaction mechanisms and their relevance for technological catalysis will be discussed.

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