ZnO Thin Films on Pt (111), an Inverse Oxide/Metal Nanocatalyst : Fabrication and Characterizations by STM, LEED, STS and XPS

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The inverse oxide/metal catalysts have been suggested to present remarkable catalytic performances in the CO oxidation and represent a promising highly active and stable catalytic system [1,2]. Recently, Zn, an affordable metallic material, has emerged as one of the most promising element in heterogeneous catalysis owing to the stability of ZnO under reducing conditions and its greater “affinity” to oxygen compared with that of Pt [2, 3]. Indeed, ZnO/Pt is active for CO oxidation and promotes catalytic reactions relevant for fuel cells [3].

In our experiment, well-ordered ZnO thin films, from sub-monolayer up to several monolayers, were prepared in ultrahigh vacuum by electron beam evaporation on Pt (111). The structure and morphology of ZnO films on Pt (111) were studied by scanning tunnelling microscopy (STM) and LEED. The ZnO islands, at low coverage, appear to be flat with a step height of 2.0 Å, corresponding to one monolayer (1ML) thick islands. The ZnO film grows seemingly in layer-by-layer mode. When the ZnO film reaches multilayers, triangular islands are observed on the surface which is a characteristic of the ZnO (0001)-Zn-terminated surface. From high-resolution STM investigations, the Moiré structure on the surface were observed, which is assigned to a coincident lattice formed at the interface of ZnO and Pt (111). The LEED patterns of the ZnO films correspond to ZnO(5×5)/Pt(6×6) structure. As the ZnO film grows thicker, a set of six spots begins to appear around the ZnO spots, which is in agreement with the Moiré structure observed on the surface of ZnO films. The current-voltage (I-V) measurements on the ZnO films were performed using scanning tunneling spectroscopy (STS) as a function of the ZnO film thickness. The electronic local density of states (LDOS) of ZnO exhibited a gradual transition from a metallic behavior to the n-type semiconducting behaviour, illustrating the charge transfer from the Pt across the thin ZnO film. The CO oxidation on ZnO/Pt were observed under a (CO: O_2=1:4) mixture at 1 mbar using synchrotron based near-ambient pressure XPS (NAP-XPS), starting at 380K. The morphology of ZnO films, as investigated by STM in the same conditions, indicates dewetting with the formation of nanoclusters (see arrows in Figure). In addition, the Moiré structure has disappeared in accordance with the LEED patterns. The present study demonstrates the growth evolution of ZnO films from the structural and electronic points of view, and the effectiveness of NAP-XPS in the study of complex catalytic processes at work on ZnO/Pt nanocatalysts.

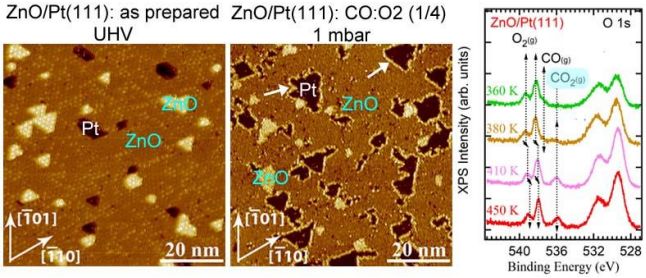

Figure: left: STM images of a ZnO thin film (~1 ML) deposited on Pt(111) in UHV and after exposure to CO:O_2 gas mixture at 1 mbar pressure. Right: in situ NAP-XPS O 1s core-level spectra under 1 mbar CO:O_2 (ratio 1/4)

References:

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[2] A. Naitabdi, R. Fagiewicz, A. Boucly *et al*. Top. Catal. 59, 550-563 (2016).
[3] A. Naitabdi, A. Boucly, F. Rochet *et al*. Nanoscale (2018) accepted: DOI: 10.1039/C7NR07981H.