Stability and mixing behavior of vanadium-iron oxide monolayers on Pt(111) and Ru(0001) substrates

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Cation mixing is a well-recognized mean to obtain oxides of desired functionality with predetermined structure and stoichiometry, which yet has been only little analyzed at the nanoscale. Recently, with the help of DFT modelling, we have shown that the low dimensionality of the oxide film and its interaction with a substrate may induce cation mixing characteristics and charge states, which differ from those present in the corresponding bulk oxides [1,2].

In this context, we have performed a comparative analysis of the stability and mixing properties of O-poor and O-rich two-dimensional V-Fe oxide layers grown on Pt(111) and Ru(0001) surfaces, based on high resolution STM imaging and DFT modelling, with the aim of gaining an insight into the role of substrate and oxygen conditions on the accessible Fe contents and distributions [3-5]. We find that due to the high oxygen affinity of the Ru substrate, the mixed O-rich layers are highly stable while the stability of O-poor layers is limited to inaccessibly oxygen-poor environments. In contrast, on the Pt surface, O-poor and O-rich layers may coexist with, however, a lower Fe content in the O-rich phase.

We show that cationic mixing (formation of mixed V-Fe pairs) is favored in all considered systems. It results from local cation-cation interactions, reinforced by a site effect in O-rich layers on the Ru substrate. However, in O-rich layers on Pt, Fe-Fe repulsion is so large that it precludes the possibility of a substantial Fe content. These findings highlight the subtle interplay between structural effects, oxygen conditions, and substrate characteristics (work function and affinity towards oxygen), which governs the cationic mixing in complex 2D oxide phases on metallic substrates. Such versatility opens a way toward a thorough fundamental understanding of the principles that underlie oxide alloying in 2D and its possible use in various applications.

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[3] P.I. Wemhoff, N. Nilius, C. Noguera, J. Goniakowski, J. Phys. Chem. C 126, 5070-5078 (2022).
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