

# Differentiation of strongly bound oxygen on silver

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Understanding the catalytic partial oxidation of methanol to formaldehyde is a long standing problem that is poised to face a resurgence in interest.

Nowadays, formaldehyde is produced industrially by the reaction of methanol over either metal-oxide or silver based catalysts. The two catalysts require different reaction conditions and show different selectivity. For example, it is believed that formaldehyde is produced through both a partial oxidation and dehydrogenation pathway over silver based catalysts, while only the former seems to be important for the metal-oxide catalyst [1]. The existence of multiple pathways on silver is a particularly interesting problem as they give different co-products— $\text{H}_2\text{O}$  or  $\text{H}_2$  for the partial oxidation and dehydrogenation pathway, respectively. Early ex situ studies suggested the two pathways can be attributed to the presence of different adsorbed oxygen species [2], yet other evidence leads to contradictory claims [3]. Our work is motivated by resolving the controversy surrounding the nature of the oxygen species present on silver based catalysts during the catalytic partial oxidation of methanol and determining their roles in the reaction.

The silver oxygen system has been thoroughly investigated in the last decades as it is the basis of important large scale industrial processes such as ethylene epoxidation and methanol oxidation. The identification of different oxygen species was originally carried out by way of TPD measurements. Rehren et al. [4] were the first to identify three different oxygen species with the help of isothermal and isobaric TPD measurements. In addition to the already identified adsorbed atomic oxygen ( $\text{O}_\alpha$ ), and bulk dissolved oxygen ( $\text{O}_\beta$ ), they found a third oxygen species stable up to high temperatures [675-710°C] which they denoted  $\text{O}_\gamma$ . These results were then correlated with XPS performed in ultra-high vacuum (UHV) and later NAP-XPS [5]. Here, the notation and correlated  $\text{O}1s$  binding energies from Rocha et al. [5] were used.

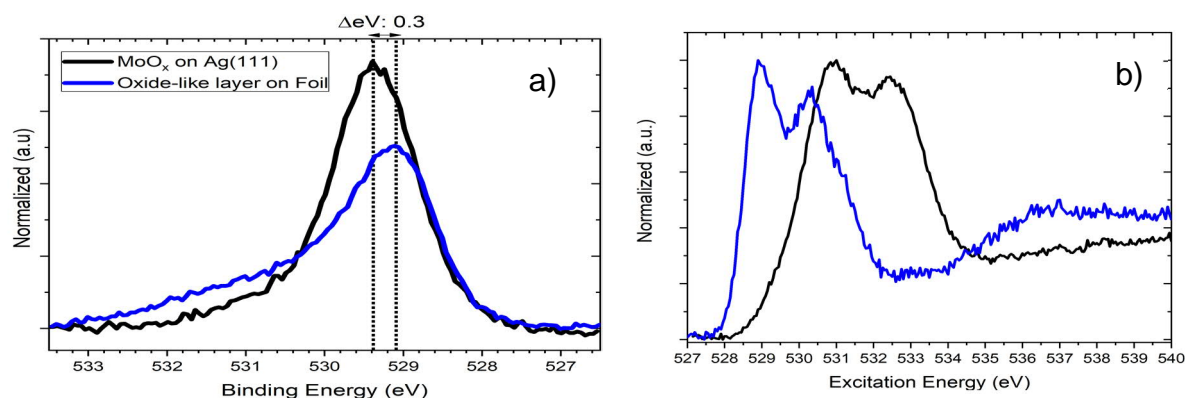


Figure 1: a)  $\text{O}1s$  spectra of oxide-like layers on Ag foil and  $\text{MoO}_x$  on Ag(111) surface measure at 500°C in 0.25 mbar  $\text{O}_2$ .  
b) the, corresponding XA spectra

Due to its thermal stability the oxygen species of interest for the methanol oxidation is  $\text{O}_\gamma$ , with a binding energy of 529.1 to 529.7 eV [5]. It is described as a thin oxide-like-layer on the silver surface. Since at the relevant temperatures silver undergoes faceting to expose Ag (111),  $\text{O}_\gamma$  is thought to form only on the (111) facet. Rocha et al. [5] went on to show two oxygen

species form at 500°C in 0.25 mbar of oxygen,  $O_{\gamma}$  and a second present only under an oxygen atmosphere, which they denoted  $O_{\alpha 2}$ . Reichelt et al. [6] later used UHV techniques to show the strongly bound  $O_{\gamma}$  species could, in some cases, be a molybdenum oxide on the silver surface, but the question remains as to the generality of that finding under in situ conditions. Figure 1 shows the O1s XP and O-K edge XA spectra of molybdenum oxide and oxide-like layers grown on a Ag(111) crystal. The small differences of 0.3 eV in binding energy illustrate the difficulties of distinguishing these species using lab based UHV set-ups. More insights can be gained with synchrotron based NAP-XPS set-ups.

With this it is possible to see the differences in the O K-edge and investigate the stability in different atmospheres (e.g.  $MoO_x$  is stable at 500°C in UHV, the oxide-like layer isn't). When coupled with DFT and computational spectroscopy these results allow us to assign  $O_{\alpha 2}$  to thin pure  $AgO_x$  oxide-like layers [7]. At 500°C in 0.25mbar  $O_2$  we detect a linear correlation between the  $O_{\gamma}$  species and the molybdenum content on the surface ( $O/Mo = 2.3$ ). In addition, the comparison of the reported valence band [5] and measurements on valence band of  $MoO_x$  on silver suggest that molybdenum was present on the surface, which would allow an assignment of  $O_{\gamma}$  to molybdenum oxide.

Furthermore, this technique allows us to investigate the molybdenum oxide (and  $O_{\alpha 2}$ ) under conditions relevant for methanol oxidation. By changing the molar feed ratio from oxygen rich to oxygen lean conditions, differences in the oxidation state of the molybdenum are detectable. This clearly shows that molybdenum oxide is present in different forms depending on the reaction feed.

| Oxygen Species | Binding Energy (eV) | Structure                          | Reference        |
|----------------|---------------------|------------------------------------|------------------|
| $O_{\alpha 1}$ | 528.1-528.4         | Adsorbed oxygen on a p(4x4) phase  | Jones et al. [8] |
| $O_{\alpha 2}$ | 529.1-529.2         | Oxide-like layer                   | This work        |
| $O_{\gamma}$   | 529.5-529.7         | $MoO_x$                            | This work        |
| $O_{\alpha 3}$ | 530.2-530.4         | Adsorbed $SO_4$                    | Jones et al. [7] |
| $O_{\beta}$    | 530.8-531.0         | $SO_4$ on (7x3)rect reconstruction | Jones et al. [7] |

Table 1: Overview of oxygen species present on a Ag(111) surface

The remaining question is, which of the high temperature oxygen species contribute to reported dehydrogenation pathway? It could be that the confusion in literature arises from some groups having studied  $MoO_x$  on silver and others the pure  $AgO_x$  oxide-like layers.

#### References:

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