SO_x on Ag catalysts and its role in alkene epoxidation

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The direct partial oxidation of ethylene to ethylene oxide (EO) over Ag highlights the tremendous potential of heterogeneously catalyzed partial oxidation reactions. Ag catalysts can be made to favor ethylene epoxidation by ca. 90% over the thermodynamically favored total combustion, but this performance is not ubiquitous. The Ag catalysts that are so useful for EO production fail dramatically when used to produce another important feedstock epoxide, propylene oxide (PO). This failure may appear surprising owing to the structural similarity between EO and PO, yet extensive studies of Ag-based catalysts in the direct epoxidation of propylene demonstrate Ag favors total combustion. Thus, PO is currently mainly produced by either environmentally unfriendly or costly process.[1]

We have recently identified the nature of the oxygen species that can produce EO on Ag catalysts. This oxygen originates from adsorbed SO_4 ($SO_{4,ads}$) which is part of a non-stoichiometric two-dimensional Ag/SO_4 phase where the sulfur is formally S(+V). [2] On a surface free of oxygen SO_4 forms an unreactive $SO_4(7 \times \sqrt{3})$rect surface reconstruction. When oxygen induced surface reconstructions are formed on such a surface, however, the Ag/SO_4 reconstruction is partially lifted resulting in the formation of $SO_{4,ads}$. TPR experiments and DFT calculations show $SO_{4,ads}$ can produce EO.[2] NAP-XPS experiments demonstrated that the EO selectivity tracks the coverage of $SO_{4,ads}$, and that $SO_{4,ads}$ is present on the Ag surface for steady state ethylene epoxidation.[2] A significant population of $SO_{3,ads}$ is only observed under a pure ethylene atmosphere, when complete titration of $SO_{4,ads}$ occurs due to the absence of the adsorbed O necessary to sustain the $SO_{4,ads}$ population by re-oxidation of $SO_{3,ads}$.[2]

Following this result, we used NAP-XPS to study the Ag surface under propylene epoxidation conditions. We find that as opposed to ethylene epoxidation, $SO_{4,ads}$ is not present under steady state propylene oxidation conditions (Figure 1a). $SO_{4,ads}$ can, however, be formed by introducing an SO_2 pulse to the reaction feed, resulting in an increase in selectivity to PO (Figure 1b). However, $SO_{4,ads}$ is rapidly titrated under reaction conditions and PO selectivity decreases with time following the decrease in $SO_{4,ads}$ coverage. During this process we observe the formation of $SO_{3,ads}$ (Figure 1c). As for ethylene epoxidation, it seems that $SO_{4,ads}$ is also responsible for

propylene epoxidation and $SO_{3,ads}$ is seen as a titration product. However, NAP-XPS demonstrates atomic O has a low coverage under propylene epoxidation conditions compared to those for ethylene epoxidation. As a consequence, $SO_{4,ads}$ is continuously titrated under propylene epoxidation conditions, resulting in a low steady state coverage. In addition, low coverage of adsorbed atomic O precludes the formation of oxygen induced surface reconstructions[3], necessary to partially lift the Ag/SO_4 reconstruction and make the active species $SO_{4,ads}$.

It appears that the O coverage on Ag has a critical role in mediating the coverage of the active species $SO_{4,ads}$ under steady state conditions. The co-existence of SO_4 and atomic O on the Ag surface appear to dictate the (high) EO and (low) PO selectivity.

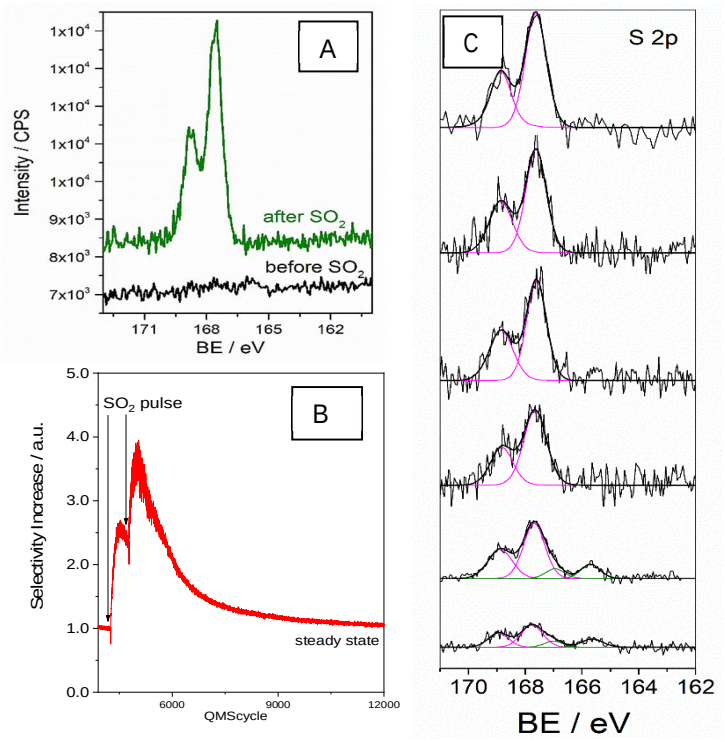

Figure 1: S 2p measures in O_2:C_3H_6 at 270 °C before and after a SO_2 pulse (A).). PO selectivity increase measured by QMS (B). S2p evolution with time under reaction (C).

References

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