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INVITED: Rational design of selective epoxidation catalysts

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Epoxides are cyclic ethers used to manufacture plastics, solvents, and surfactants[1,2]. The simplest epoxide, ethylene oxide (EO), is produced through the direct partial oxidation of ethylene over silver at 220-280°C. In this process EO is formed by the addition of a single oxygen atom across ethylene's C=C double bond, and while combustion is thermodynamically favorable, EO can be produced with 90% selectivity[1]. Despite the technological importance of such a process to selectively produce propylene oxide (PO), no selective direct oxidation route to PO is known[2]. A major focus in efforts to understand why has been uncovering what drives EO selectivity.

APXPS has revealed the active catalyst contains two types of oxygen, nucleophilic and electrophilic, which are distinguishable by their O1s binding energies (BE) of ca. 528 eV and 530 eV, respectively[3-5]. Only electrophilic oxygen is known to produce EO[6]. Its atomic structure has been debated[7-9]. This ambiguity has hampered mechanistic understanding. By combining APXPS with density functional theory (DFT) calculations we demonstrated electrophilic oxygen is related to trace sulfur impurities[9] that can produce O-SO₃ adsorbed on unreconstructed silver. DFT shows this species has the spectroscopic fingerprints of electrophilic oxygen, and it is predicted to participate in EO formation. APXPS appears to confirm the DFT results, showing surface the coverage of SO_x species correlates with EO selectivity[9]. This knowledge has made it possible to gain insights into propylene epoxidation.

DFT suggests adsorbed O-SO₃ can participate in PO formation. APXPS reveals, however, that O-SO₃ is not present under propylene epoxidation conditions. We found it can be formed via SO₂ dosing, a process that increases PO selectivity with increasing O-SO₃ coverage. The formed O-SO₃ is not, however, stable and requires a continuous sulfur source to maintain the SO_x surface coverage.

By combining APXPS and DFT were we able to solve the nature of electrophilic oxygen thought to be responsible for EO production. Extending this study to propylene epoxidation allowed us to identify the steady-state coverage of electrophilic oxygen as a key factor limiting PO selectivity, and, moreover, develop a strategy to circumvent this limitation.

References

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if "Other", please specify:

I apply for a travel grant

No

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