Sulfur in Ethylene Epoxidation on Silver


The direct partial oxidation of ethylene to ethylene oxide over silver is one of the most well studied heterogeneously catalyzed partial oxidation reactions. The interest in this reaction stems both from its industrial importance—with nearly $15 \times 10^6$ t/a produced—and because the apparent simplicity of the desired reaction:

makes it an attractive case in which to study selectivity. That is, how can silver favor epoxidation over the thermodynamically favored total combustion reaction? The apparent simplicity of this question belies a complex chemistry that has made a mechanistic understanding consistent with experimental data elusive despite efforts dating back to 1931. The first plausible models dealing with selectivity appeared already in the 1940s. These postulated a special form of oxygen is involved in epoxidation, which became known as electrophilic oxygen. This oxygen species, characterized by an O 1s binding energy (BE) of ~530.5 eV is the only species known to produce epoxide during temperature programmed reaction, yet its structure remained elusive until we were able to show it is the oxygen in adsorbed SO$_4$ (SO$_4$$_{ad}$) that is part of a non-stoichiometric two-dimensional Ag/SO$_4$ phase where the sulfur is formally S(+V).

With the structure and function of electrophilic oxygen solved we have begun performing in situ XPS experiments aimed at uncovering both its role during steady state epoxidation and understanding the mechanism of SO$_x$ management during ethylene epoxidation. These experiments have demonstrated that under mbar pressures—and during surface titrations with ethylene—the epoxide selectivity tracks the coverage of SO$_4$$_{ad}$, as expected for the selective species, see Figure 1a. Furthermore, they have exposed a rich subsurface chemistry involving the exchange of dissolved and surface SO$_x$ species, see Figure 1b and 1c. Here a species with a BE of 163.1 eV has been observed and assigned to sub-surface SO, based on the computed BE of 162.8 eV. The computed phase diagram of sub-surface species (Figure 1c) supports this assignment, showing that at the reaction conditions subsurface SO is the preferred SO$_x$ dissolved species. This subsurface chemistry may play a critical role in mediating the coverage of SO$_4$$_{ad}$ and hence epoxide selectivity.

Figure 1. (a) Amount of detected CO$_2$ and C$_2$H$_4$O (by gas chromatography) vs SO$_4$ on silver powder at 503 K in C$_2$H$_4$:O$_2$ 1:1 (total pressure 0.3 mbar) and selectivity evolution during time on stream. (b) S 2p taken at the same reaction conditions for different kinetic energies (indicated in the figure) of the emitted photoelectrons. (c) Computed phase diagram of the sub-surface SO$_x$ species.
References


† Department Chemie, Ludwig-Maximilians-Universität München, Butenandtstr. 5-13, 81377 Munich (Germany).
§ Chemie Department, Technische Universität München, Lichtenbergstr. 4, 85748 Garching (Germany).
¶ Department of Earth and Environmental Sciences, Ludwig-Maximilians-Universität München, Theresienstrasse 41, 80333 Munich, Germany.
‡ CNR-IOM DEMOCRITOS, c/o SISSA, Via Bonomea 265, 34136 Trieste (Italy).