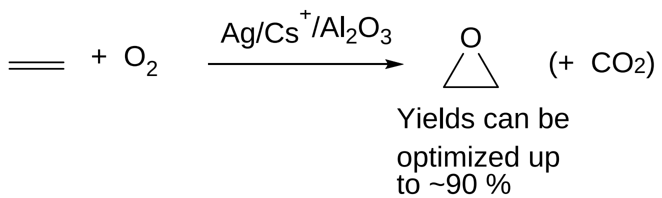
Ethylene oxidation

ETHYLENE OXIDE PRODUCTION

- Ethylene oxide is a raw material that is used industrially for making many consumer products as well as non-consumer chemicals and intermediates.
    - Ethylene oxide is important or critical to the production of various organic chemicals such as ethylene glycol, ethanol amines, simple and complex glycols, polyglycol ethers and other products such as detergents or polymers.
- Ethylene oxide can be produced by reacting
    - oxygen (O_2) and ethylene (C_2H_4) at temperatures of **200 – 300°C** and pressures of **10 – 20 bar**. The catalysts is silver doped by Lewis acids deposited on alumina.

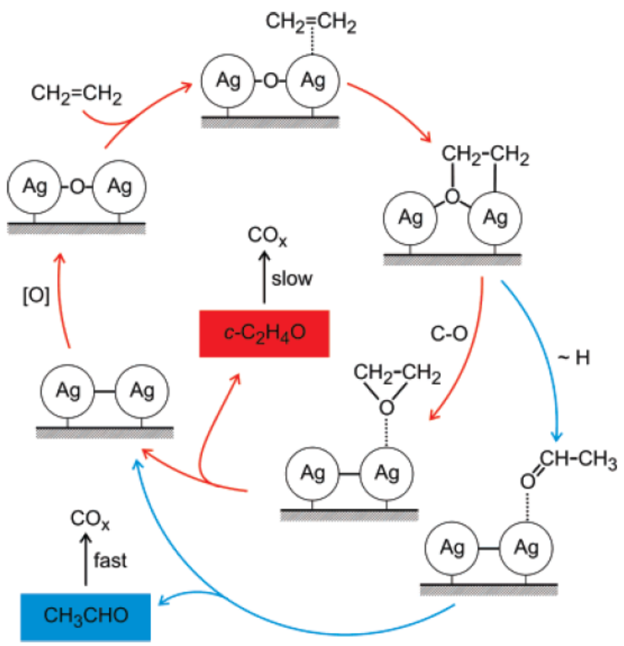


INDUSTRIAL PROCESS

- The main goal in EO production processes is to increase the selectivity and the EO concentration at the outlet of the reactor.
- However, maintaining a high selectivity at moderate to high conversion rates remains challenging in view of the susceptibility of ethylene and EO to be completely oxidized to CO_2 in the presence of oxygen.
- The reference industrial catalysts for this reaction consist of large silver nanoparticles (100–200 nm) supported (circa 15 % wt.) on low-surface-area alumina (high-surface areas lead to stronger adsorption of ethylene oxide and thereby to its combustion).
- Highly optimized by promotion with alkali metals (mainly cesium)[3] and also with other metals, such as rhenium, molybdenum, tungsten, and chromium.
- To minimize the formation of CO_2, chlorine-containing compounds, such as 1,2-dichloroethane (DCE), hydrochloric acid, and ethyl chloride, are also used as promoters. These chlorinated compounds are added continuously to the reactor feed and have a strong influence on the final EO selectivity. Furthermore, it is also customary to add ethane to the reactor feed (around 10 % of the total volume) to facilitate the adsorption/desorption equilibrium of Cl on the Ag surface. Otherwise irreversible poisoning of the Ag active sites by Cl occurs.

Consider a mechanistic study (J. AM. CHEM. SOC. 9 VOL. 129, NO. 49, 2007 15317)

Scheme 1 Schematic Mechanistic Proposal Implied by the Present Gas-Phase Studies for Epoxidation of Ethene on Silver Surfaces



$$C_2H_4 + (1/2)O_2 \rightarrow C_2H_4O \quad \Delta H = -105 \text{ kJ/mol}$$

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \quad \Delta H = -1327 \text{ kJ/mol}$$

$$C_2H_4O + (5/2)O_2 \rightarrow 2CO_2 + 2H_2O \quad \Delta H = -1223 \text{ kJ/mol}$$

The reaction is performed at ~ **200 – 300°C.** Why?

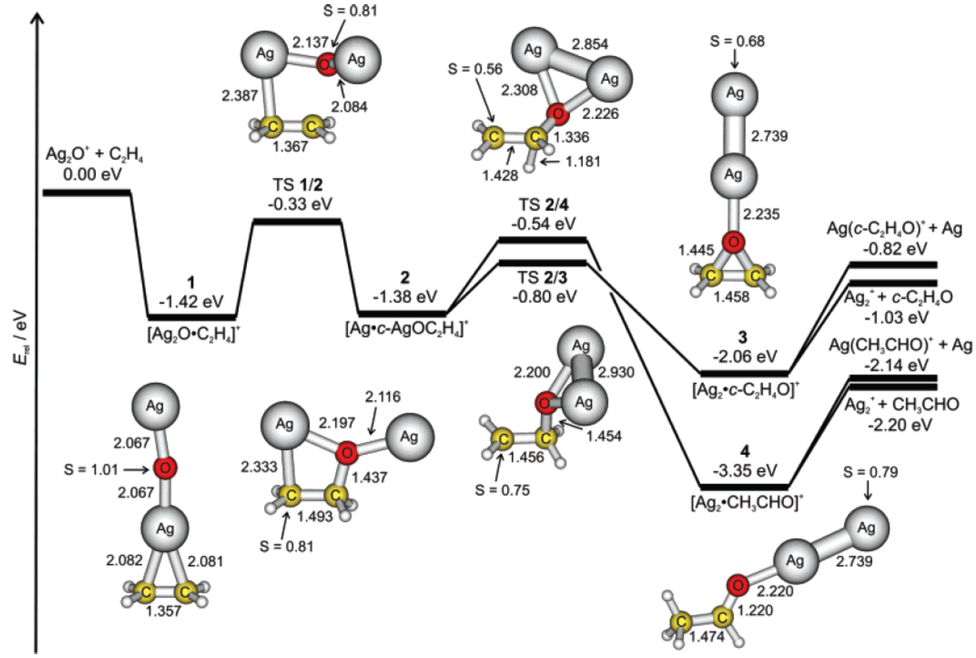
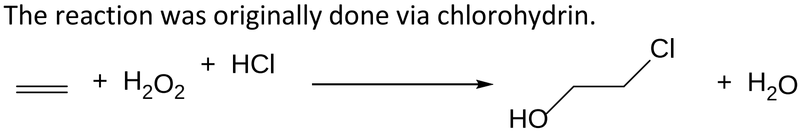
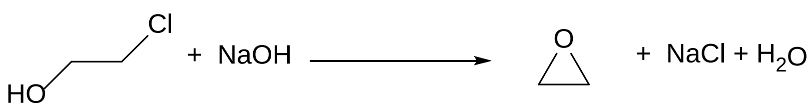


Figure 4. Potential-energy surface for O-atom transfer from Ag_2O^+ to ethene, affording either ethylene oxide or acetaldehyde (relative energies in eV). Selected bond lengths are given in Å, and also shown are the computed spin densities for those atoms at which most of it is located.

Discuss:

1. The reaction was originally done via chlorohydrin.





   Discuss, why the catalysis at silver prevailed although silver is much more expensive that the reactants for the chlorohydrin process.

Direct ethylene oxidation:

2. Shall the reaction be done in a batch or in a continuous manner? Why? What would be advantages/disadvantages of the two approaches?
3. How would you describe a possible reactor?
4. The reaction is done at 1 – 2 MPa. Why should larger pressure be advantageous for this reaction?
5. The reaction is done at rather large "space velocity" during which conversion decreases, but selectivity increases. Why?

6. What are the problems with catalysts?
7. Why would it be useful to study small systems such as Ag_2O^+ reacting with ethylene? What could it tells us in comparison with studying the heterogeneous reaction?
   Discuss advantages and disadvantages of homogeneous and heterogeneous catalysis.