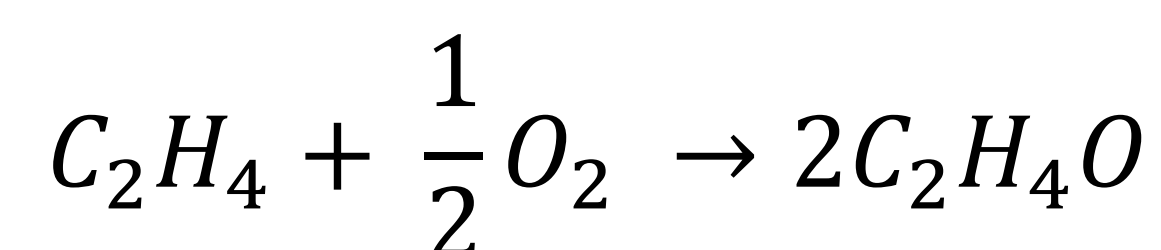


An Investigation of Highly Selective CO₂ Resistant Catalysts for Ethylene Oxide Production.

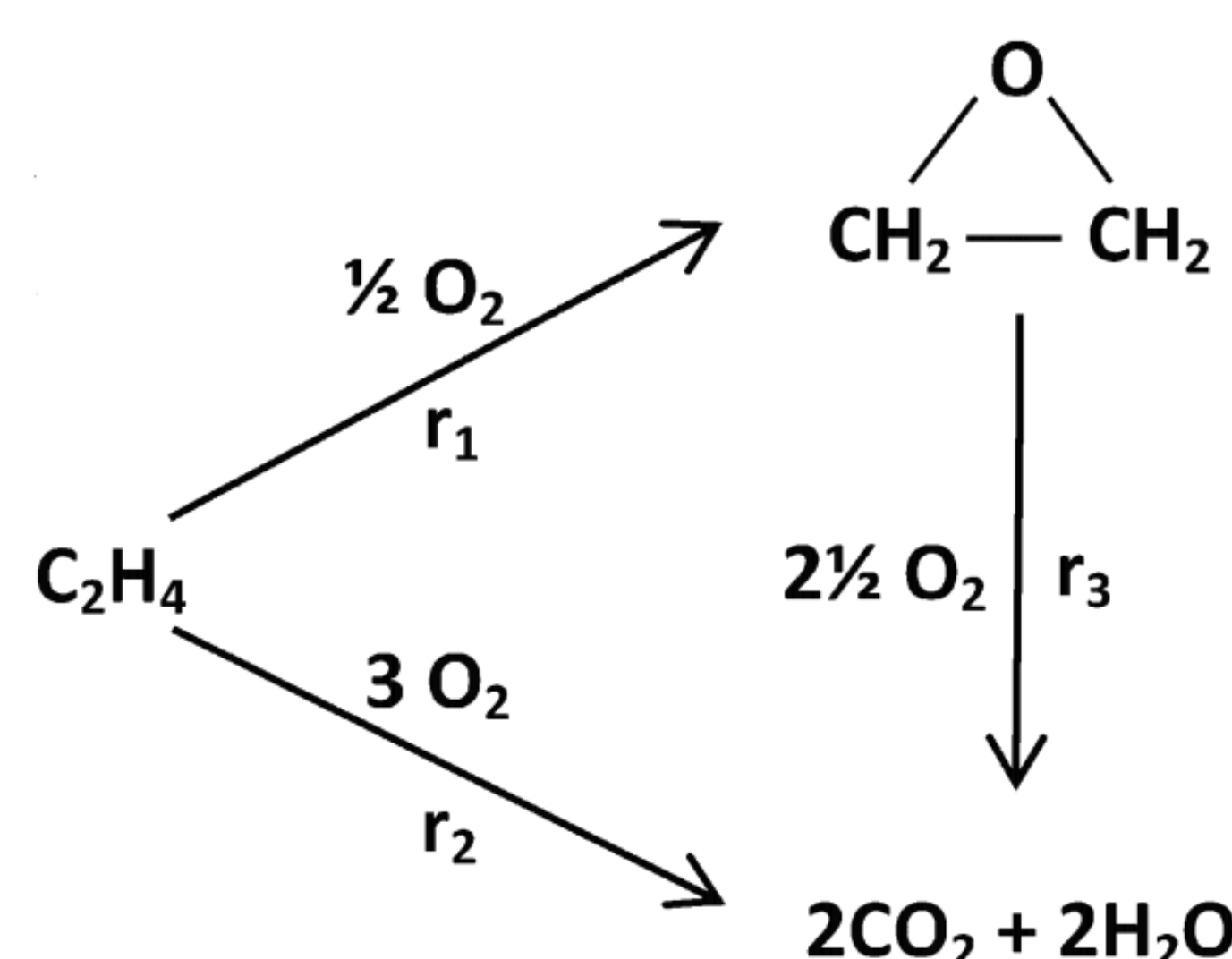
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Introduction

- Ethylene oxide (EO) is manufactured through the direct oxidation of ethylene over a silver (Ag) surface.



- The primary reaction (r1) is mildly exothermic but is accompanied by total oxidation (r2) and consecutive oxidation (r3) to produce CO₂ and H₂O.



r₁: Partial Oxidation, Δh = -106.7 kJ/Mol

r₂: Total Oxidation, Δh = -1323 kJ/Mol

r₃: Consecutive Oxidation, Δh = -1216 kJ/Mol

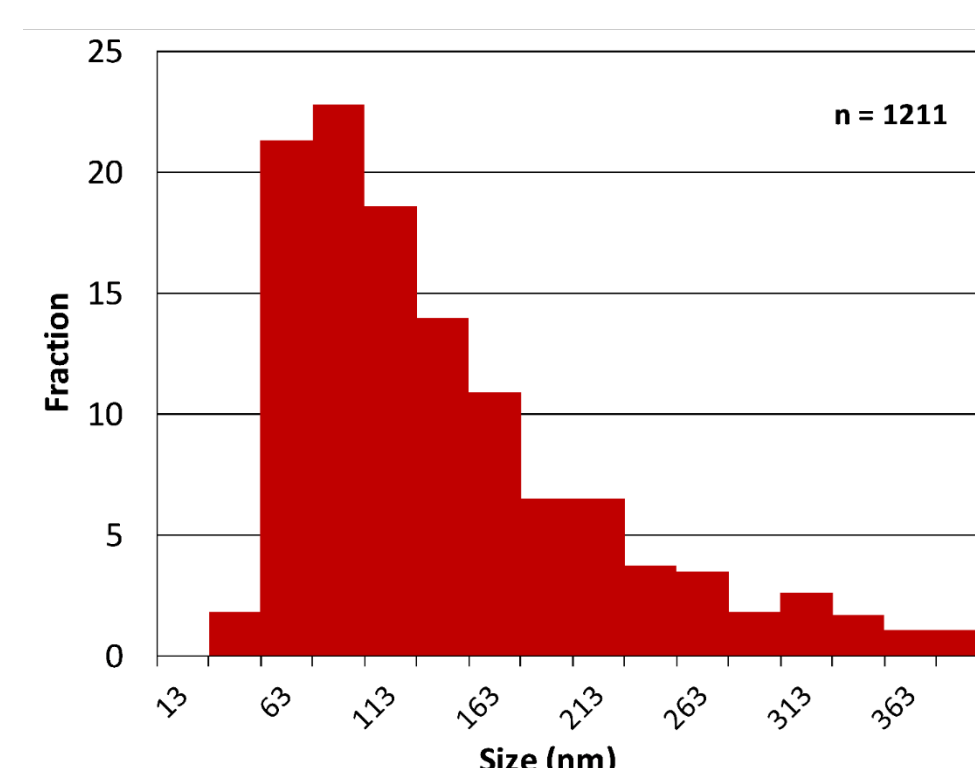
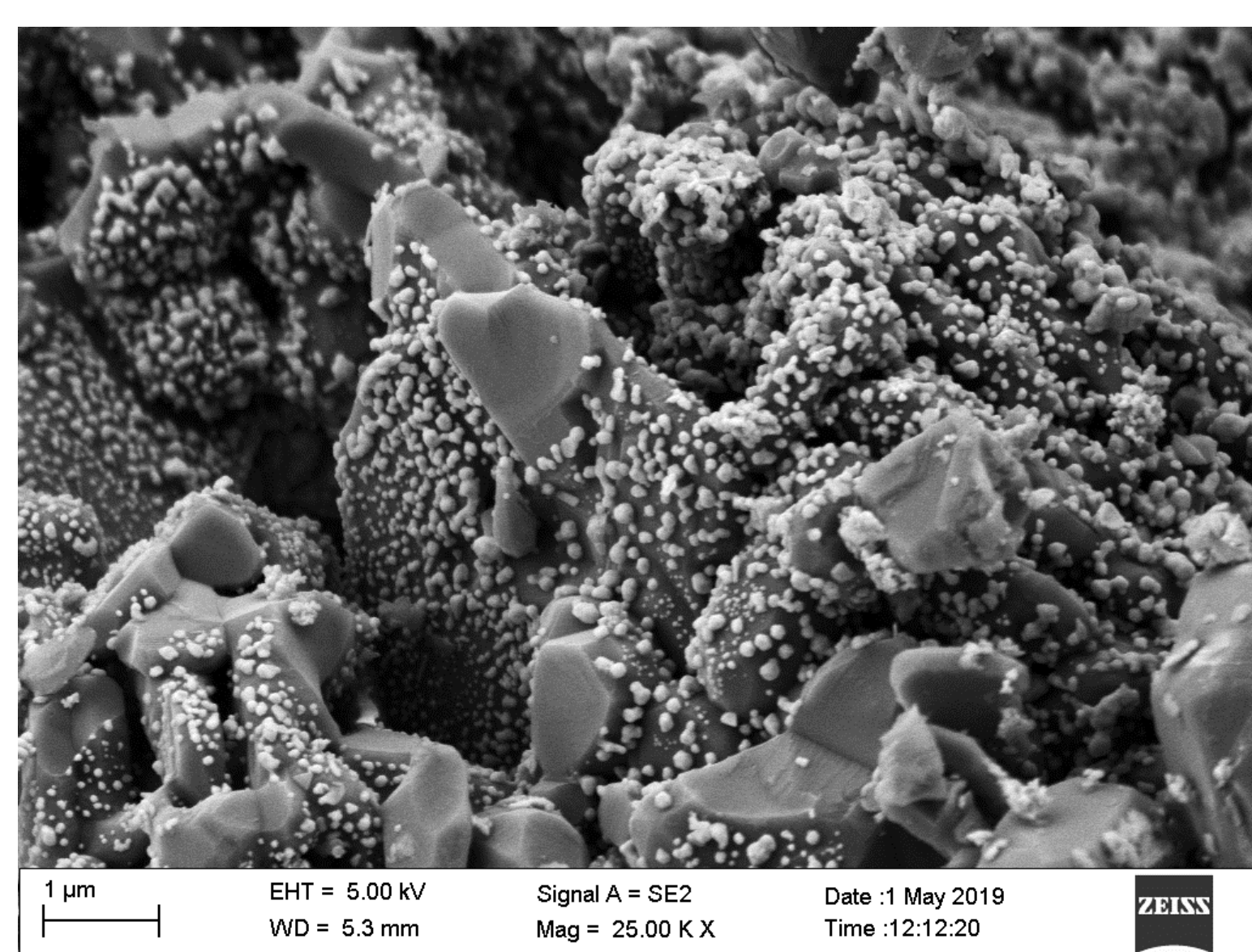
- Promoters, and co-promoters, are added to improve EO selectivity by limiting r2 and r3.
- Process economics require a recycle stream containing CO₂ resulting in lower catalytic activity. Greater activity loss is observed for promoted samples.

Project Description

- State of the art catalysts containing Silver (Ag), Cesium (Cs), Rhenium (Re), Molybdenum (Mo), and Sulphur (S) are prepared through incipient wetness.
- Samples are evaluated for kinetic dependencies on CO₂ and O₂.
- Temperature programmed desorption is proposed as a prescreening technique for CO₂ resistance.

Catalyst Preparation

- Silver salt is impregnated on α-Al₂O₃
- In a separate step, ppm levels of Cs and Re promoters as well as Mo and S co-promoters are added.
- Samples are calcined in air before evaluation.



Commercial Process

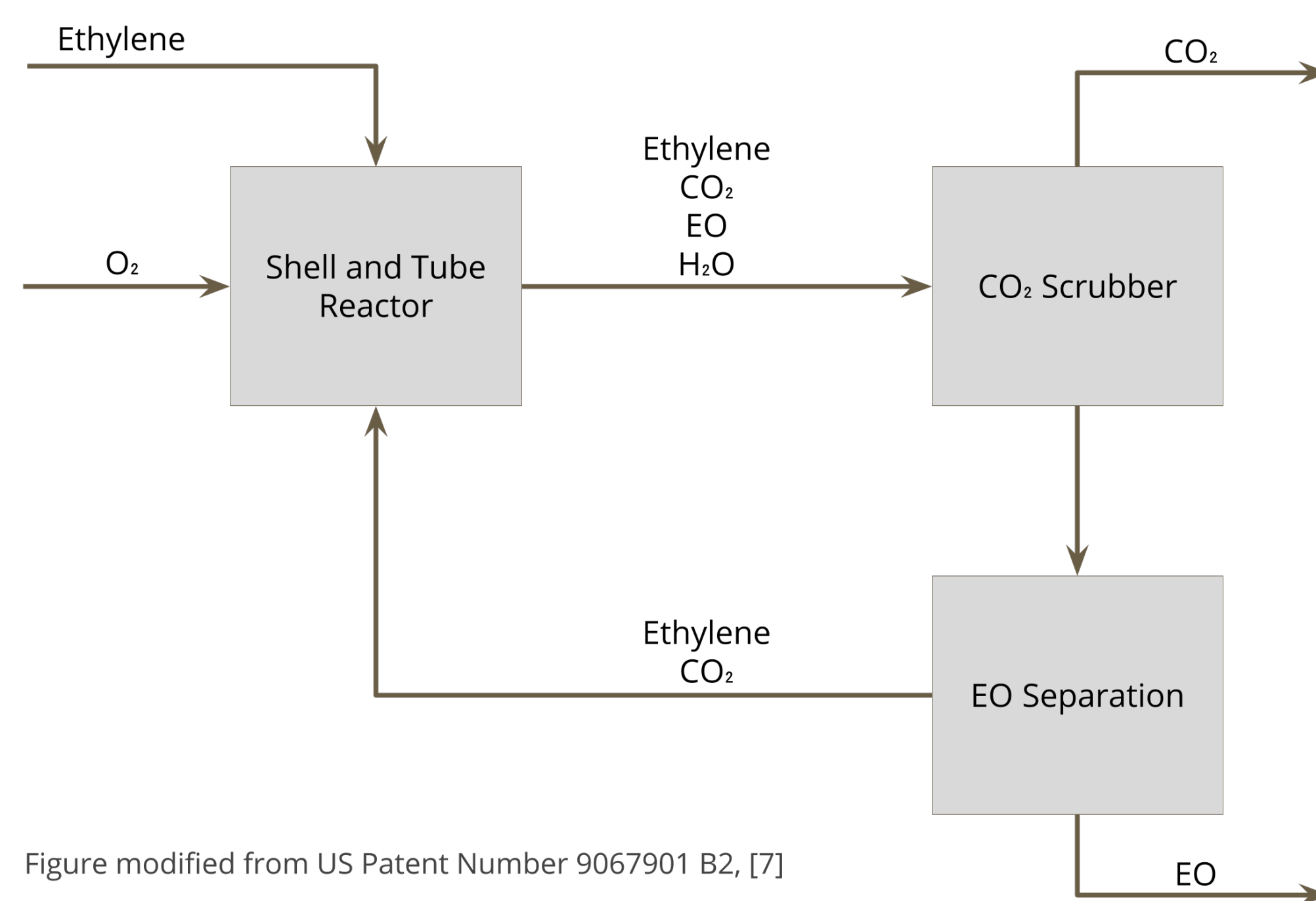
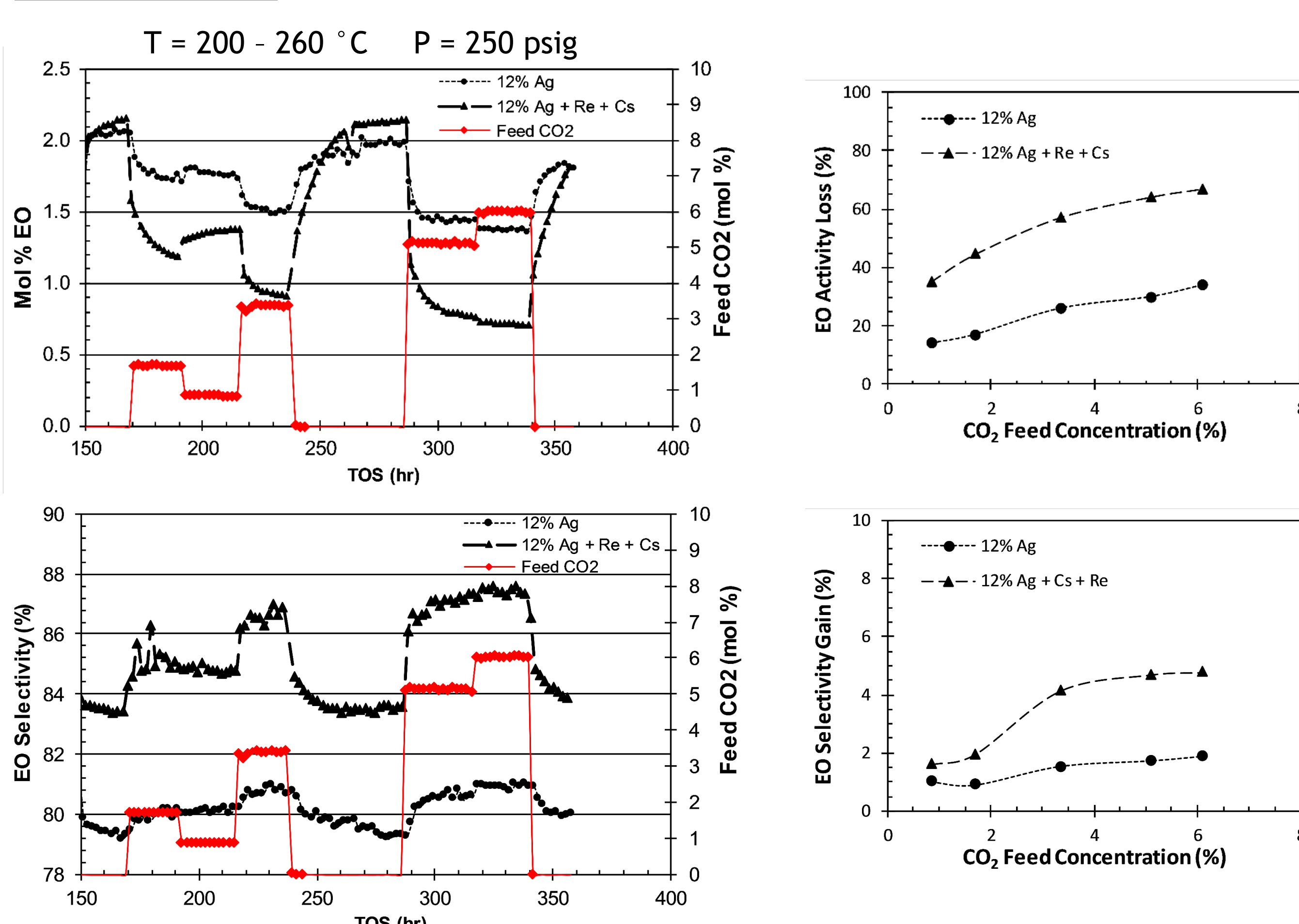


Figure modified from US Patent Number 9067901 B2, [7]

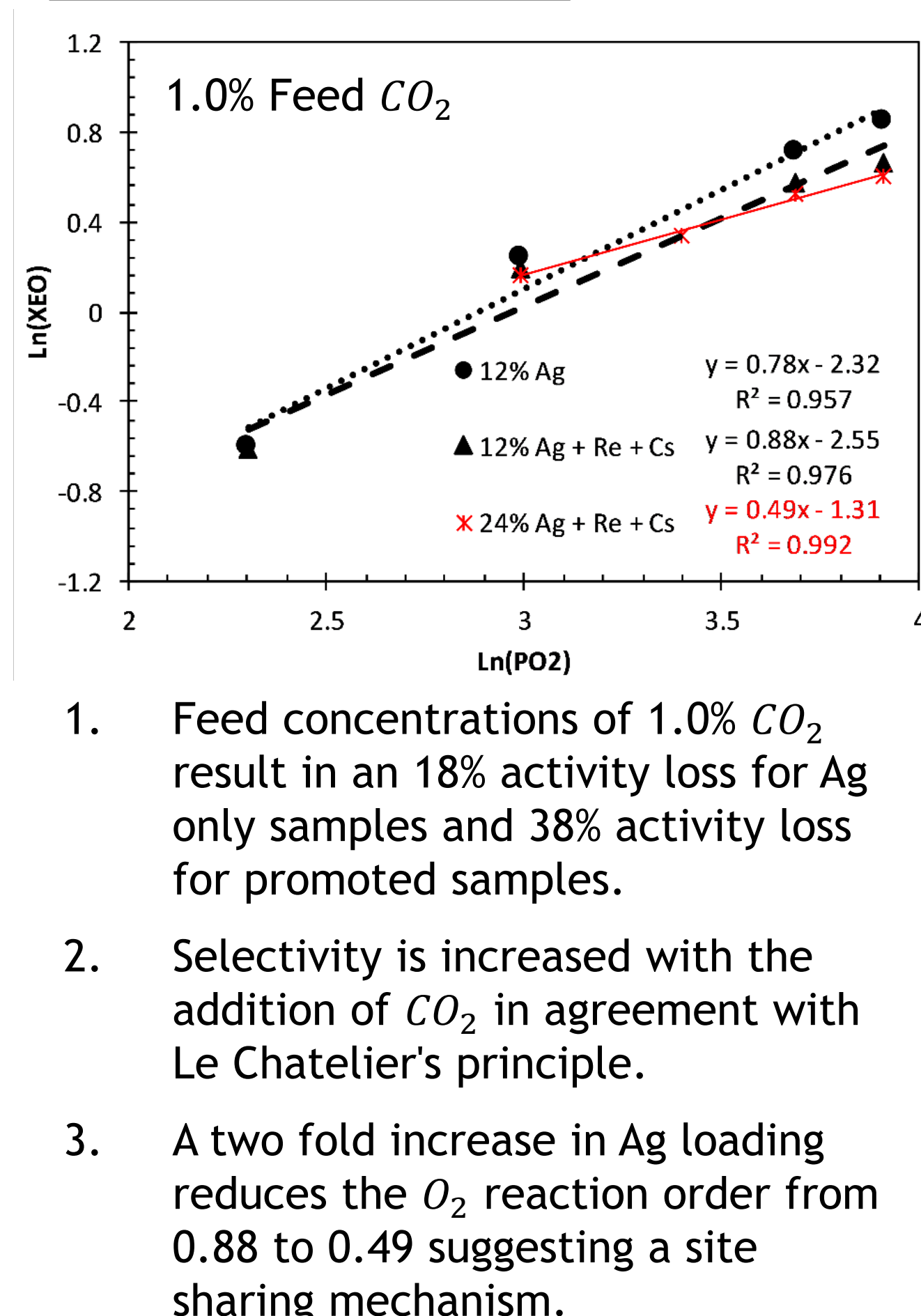
Experimental Setup



CO₂ Effects

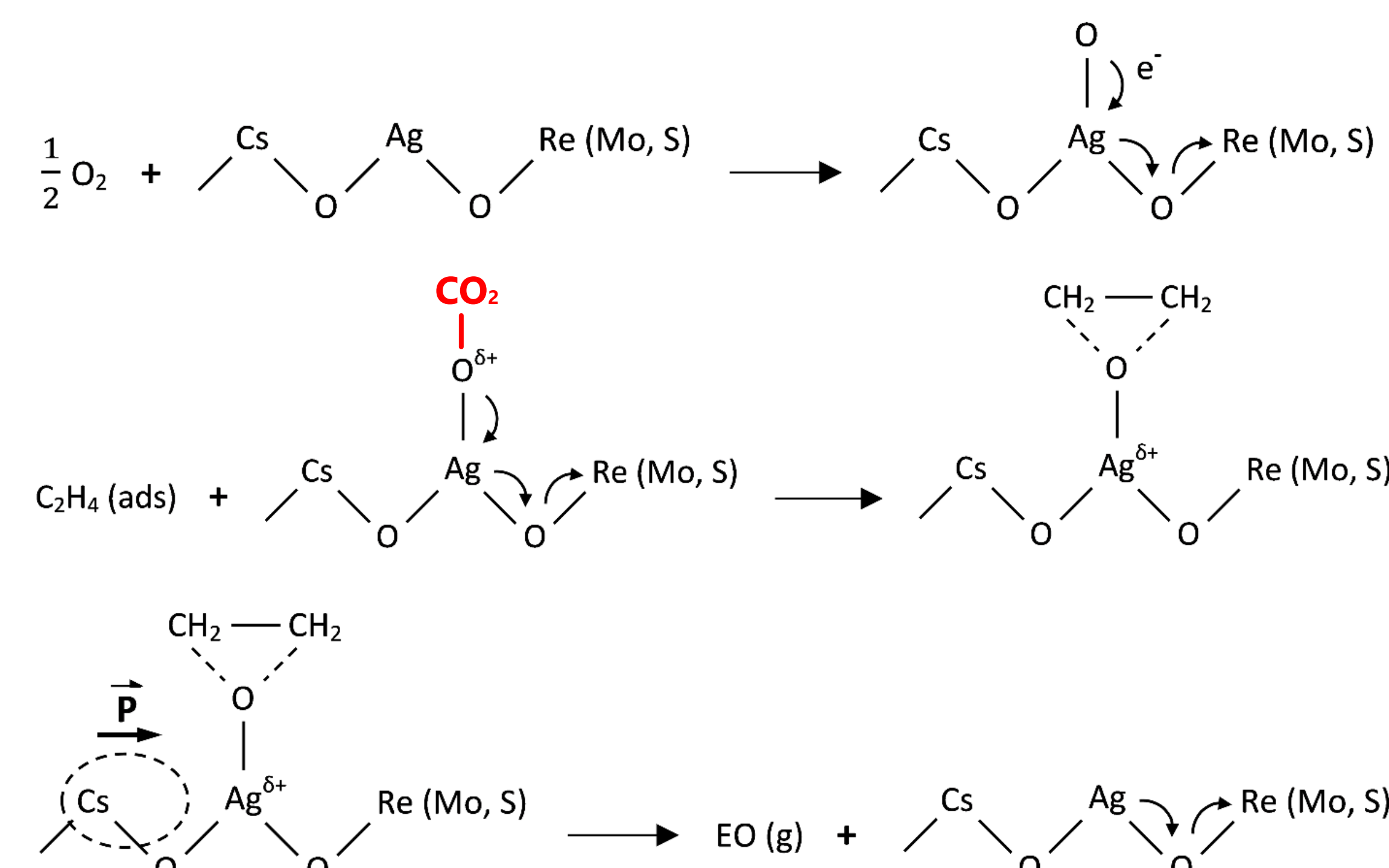


O₂ Dependency

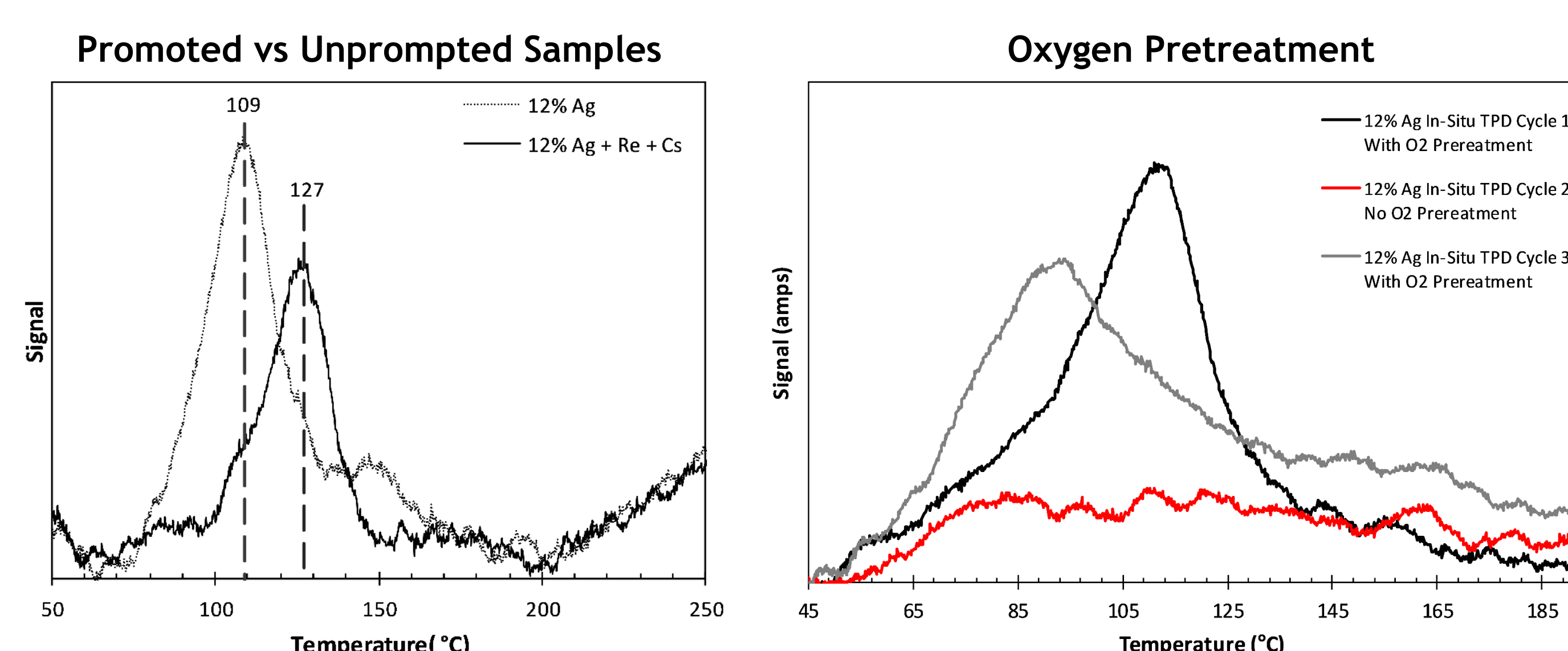


Mechanism

- High Valent Re, and (Mo,S) co-promoters, draw the electron density from Ag sites.
- In the absence of adsorbed carbonate, electron deficient oxygen performs an electrophilic attack on the double bond of gas phase C₂H₄.
- Electron rich Cs reduces the adsorption energy of the EO intermediate limiting the degree of complete combustion.



Atmospheric Temperature Programmed Desorption



- Promoted samples show a measurable shift to higher temperature CO₂ desorption.
- Oxygen pretreatment is required for CO₂ coverage which agrees with the proposed mechanism.
- Peak fitting and CO₂ quantification suggests separate high temperature and low temperature adsorption sites

Conclusion and Future Work

- Promoters result in a measurable effect on adsorption and suggest a stronger Ag-O-CO₂ bond. This concept will be explored with XPS to further define promoter interactions in the presence of CO₂.
- Future experiments will continue to probe the mechanism under atmospheric conditions while in a separate line of work, high pressure adsorption studies will be developed.
- Results will be correlated with reactor evaluation data to prescreen samples for CO₂ resistance.