

## Performance of Bimetallic Catalysts for Ethylene Epoxidation: Model vs. Experiment

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### Introduction

The direct gas phase epoxidation of ethylene over Ag has been widely studied in an attempt to create more active and selective catalysts. Computational and experimental studies have led to many patents and scientific publications which have shown improvements of ethylene oxide (EO) selectivity with the empirical discovery of many different catalyst promoters. To accelerate the discovery process, a rational catalyst design methodology has been applied to this chemistry to predict improved catalyst formulations based on microkinetic modeling and density functional theory. Using this methodology, a Cu-Ag bimetallic catalyst was predicted and later validated to improve the selectivity toward EO [1]. Several other bimetallic combinations have been modeled [2], but remained without validation. To facilitate the investigation of these bimetallics, as well as to allow for new material discovery and mechanistic investigations of ethylene epoxidation, a high-throughput catalytic reactor system was fabricated for the testing of monolith catalysts.

### Materials and Methods

The details of the preparation and the testing of these catalysts have been described previously [1]. All Ag catalysts were prepared through impregnation of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> monoliths (Vesuvius Hi-Tech Ceramics) with a AgNO<sub>3</sub> precursor. Impregnation proceeded through the immersion of the monoliths in a mixture of AgNO<sub>3</sub> and distilled water. This solution was then evaporated off at 90°C before the monolith was placed in a muffle furnace with a heating rate of 2K/min and a dwell time of 2 or 12 hours. Promoting materials were added sequentially the catalyst after calcination. Finally, catalysts were reduced in situ under a 50 sccm flow of 10% H<sub>2</sub>/He before being placed under reaction conditions.

An eight well HTE system was fabricated for the investigation of supported catalysts less than 22mm in diameter. Using separate thermocouples and radiant heaters, the temperature of each catalyst bed is measured and controlled independently with a steady state temperature distribution within  $\pm 0.5^\circ\text{C}$  of a setpoint. The effluent from these reactors is analyzed using FTIR spectroscopic imaging, univariate, and multivariate calibrations to predict the concentrations of CO<sub>2</sub>, ethylene, and EO. Specifically, the ethylene and EO concentrations are determined within 380 and 80 ppm respectively.

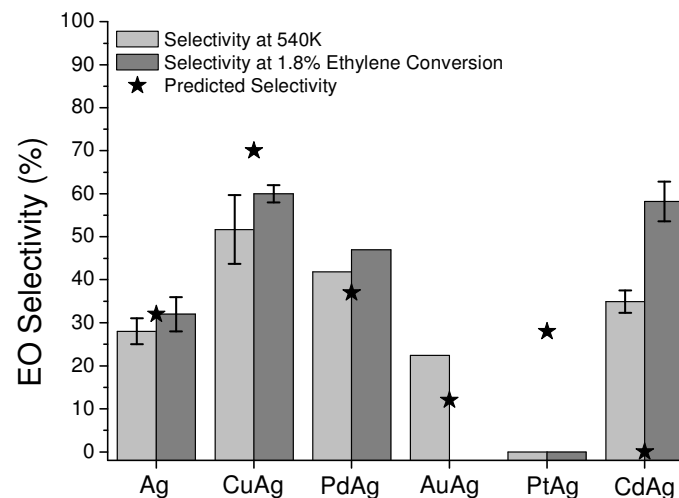
### Results and Discussion

The HTE system has been used to study the effect of preparation conditions and promoters on Ag catalysts. In particular, high throughput reactor studies were performed to investigate the effect of Pt, Au, Pd, and Cd addition to Ag catalysts. Comparisons between the reactor studies and modeling results (Figure 1) show that, as predicted, Pd improved the EO selectivity modestly, while Au diminished it. Cd-Ag and Pt-Ag catalysts differed significantly from the model however. Model predictions indicated that Cd-Ag catalysts would be completely unselective toward EO. Instead, 58% EO selectivity was achieved at 1.8% ethylene conversion,

which is almost twice that of an unpromoted Ag catalyst at 31%. Pt-Ag catalysts on the other hand were predicted to leave the EO selectivity unchanged compared to Ag, however 0% EO selectivity was seen. In order to understand the differences between the modeled and experimentally tested catalysts, characterization using SEM/EDS was undertaken. Bimetallic formation for the Au-Ag and Pt-Ag catalysts was not observed. Instead Au and Pt particles on the Ag particles led to deactivation of the catalyst due to a reduction in surface area. The Cd-Ag catalysts showed a redistribution of the Ag into a bimodal distribution of  $\sim 40\mu\text{m}$  and  $1\mu\text{m}$  particles. These results indicate that characterization may play a crucial role in understanding the correspondence (or lack thereof) between modeling and experimental results, particularly in future studies to identify improvements needed in the model to predict the observed Cd-Ag performance.

### Significance

Rational catalyst design presents a unique opportunity for material discovery as well as optimization of promoted Ag catalysts. The results indicate the integration of microkinetic modeling and HTE would improve the optimization of catalyst performance.



**Figure 1.** Comparison between the predicted EO selectivity through microkinetic modeling (stars) with the measured EO selectivity both at constant conversion (dark gray) and constant temperature (light gray).

### References

1. Linic, S., Jankowiak, J., and Barteau M.A. *J. Catal.* 224, 489 (2004).
2. Mhadeshwar, A., Barteau, M.A. in "Mechanisms of Homogeneous and Heterogeneous Epoxidation Catalysis," Oyama, S.T. (ed.), Elsevier, Amsterdam, 2008, p. 255-270.