

Investigation of Ag and Promoted Ag Catalysts for Ethylene Epoxidation using High-Throughput Experimentation

Joseph C Dellamorte*, Jochen Lauterbach and Mark A Barteau
University of Delaware, Newark, Delaware 19716 (USA)
*dellamor@udel.edu

Introduction

The direct gas phase epoxidation of ethylene over Ag has been widely studied to create more active and selective catalysts. Research in this area has included both computational and experimental studies leading to many patents and papers which have shown improvements of ethylene oxide selectivity with the addition of different promoters. Recent results from Linic, Jankowiak and Barteau have proposed an oxametallacycle mechanism as a predictive tool for bimetallic catalysts for this process [1]. To facilitate these studies and allow for new materials discovery and mechanistic investigations of ethylene epoxidation, a modified high-throughput catalytic reactor system was fabricated for monolith catalysts with independent temperature control.

Materials and Methods

The details of the preparation and the testing of these catalysts have been described previously [2-3]. All Ag catalysts were prepared by impregnation of α -Al₂O₃ monoliths (Vesuvius Hi-Tech Ceramics) with a AgNO₃ precursor. Impregnation involved immersion of the monoliths in a mixture of AgNO₃ 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 which was varied for the catalysts produced. Catalysts were reduced in situ under a 50 sccm flow of 10% H₂/He before being placed under reaction conditions.

An eight-well HTE system based on a powder reactor design described by Hendershot et al [4] was fabricated for the investigation of monolith catalysts less than 22mm in diameter. By using separate thermocouples and radiant heaters, the temperature of each monolith can be 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 was analyzed using FTIR spectroscopic imaging, univariate, and multivariate calibrations to predict the concentrations of CO₂, ethylene, and EO. Specifically, the ethylene and EO concentrations can be determined within 380 and 80 ppm respectively.

Results and Discussion

Using the HTE system described above, several Ag catalysts were tested to investigate the effects of calcination temperature, calcination time, reduction temperature, and reduction time on ethylene conversion and EO selectivity. The reduction temperature and time do not significantly affect the catalyst performance in the range of 250-350°C and 6-18 hours, respectively. However, calcination temperature and time do play a significant role. Catalysts calcined at temperatures less than 300°C showed no activity. This was attributed to lack of proper conversion of AgNO₃ to Ag, which is reported to occur at 350°C [5]. Catalyst calcination at 400°C resulted in the optimum yield to EO. Calcination time, as shown in Figure 1, can create dramatic changes in the ethylene conversion with little change in the EO

selectivity. In particular Ag catalysts calcined for 3 hours exhibited the greatest activity. At the same time, the activation energy for ethylene conversion was highest for the catalysts calcined for 3 hours. This result indicates that calcination longer than 3 hours sinters the Ag catalyst, decreasing the active surface area and decreasing the activity.

Significance

The use of HTE for ethylene epoxidation presents an opportunity for materials discovery as well as estimation of kinetic parameters for Ag and promoted Ag catalysts. These results can be further refined using UHV experiments and modeling to rationally design catalysts for increased activity and selectivity.

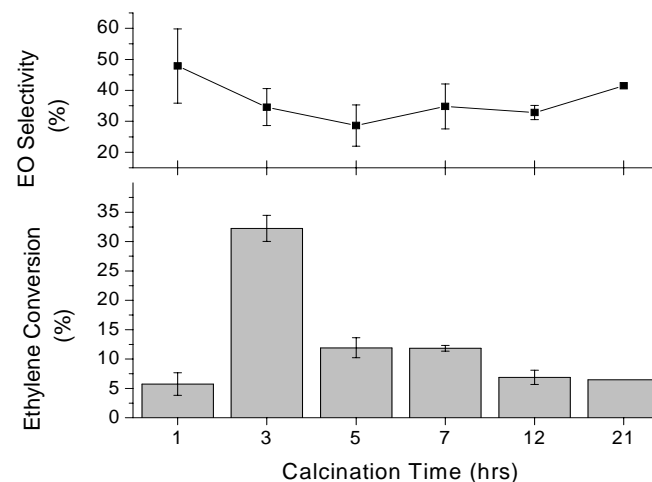


Figure 1. Ethylene conversion and EO selectivity of Ag catalysts calcined for various amounts of time at 400°C. All results are presented for catalysts run at 267°C under a flow of 6 v/v% ethylene and 10 v/v% oxygen with a balance of nitrogen.

References

1. Linic, S., Jankowiak, J., and Barteau M.A. *J. Catal.* 224, 489 (2004).
2. Jankowiak, J. and Barteau, M.A. *J. Catal.* 236, 366 (2005).
3. Dellamorte, J.C., Lauterbach, J.A., and Barteau, M.A. *Catal. Today* In Press.
4. Hendershot, R.J., Lasko, S.S., Fellmann, M.-F., Oskardottir, G., Delgass, W.N., Snively, C.M., Lauterbach, J. *Appl. Catal. A: General* 254, 107 (2003).
5. Dever, J.P., George, K.F., Hoffman, W.C., and Soo, H. in "Ethylene Oxide (Kirk Othmer Encyclopedia of Chemical Technology)" John Wiley and Sons, Inc., 2004