

Rhenium promotion of Ag and Cu–Ag bimetallic catalysts for ethylene epoxidation

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Abstract

Rhenium remains the least understood promoter of silver catalysts for the epoxidation of ethylene. While a large number of patents can be found claiming the use of rhenium to yield ethylene oxide selectivities over 80%, very little is present in the open literature to explain these results. In this work we report initial studies of rhenium promoted Ag and Cu–Ag bimetallic catalysts under chlorine-free operating conditions. Rhenium addition improves the selectivity of both the monometallic and bimetallic catalysts, while decreasing activity in each case. Optimization of preparation procedures shows maximum ethylene oxide selectivities are obtained with rhenium loadings of 25 ppm for the monometallic catalysts and between 50 and 100 ppm for Cu–Ag bimetallic catalysts. The reaction kinetics for rhenium-promoted Ag and unpromoted Ag catalysts suggest that the catalysts containing rhenium present a more uniform distribution of sites for oxygen adsorption than do unpromoted catalysts, thus enhancing the ethylene oxide selectivity.

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1. Introduction

Since the original patent by Lefort [1], improvement of supported catalysts for ethylene epoxidation has been an active area of research and development. Numerous papers and patents have reported ways of increasing ethylene oxide (EO) selectivity; these include the use of different silver precursors, use of different preparation techniques, and the use of promoters. Typical industrial catalysts comprise an α - Al_2O_3 support impregnated with 10–30 wt.% silver oxalate, which is then reduced to silver metal through calcination and reduction steps. It has been found that promoters added during catalyst preparation, such as Cs and Re, as well as co-feed of organic chlorides to maintain Cl on the catalyst during operation, increase the selectivity further [2–5]. Both Cs and Cl have been the targets of model catalyst studies in order to understand their effects on key reaction steps and to explain their role in promotion. In previous studies from our laboratory, Cs was found to have relatively small effects on catalyst activity at levels up to 80 ppm, but to produce

progressive increases in selectivity within this range [6]. We have proposed that the principal role of Cs is to influence the transition states for ring closure (to ethylene oxide), versus isomerization (to acetaldehyde), of a common oxametallacycle intermediate via long range ion–dipole interactions [4]. In contrast to Cs, addition of small amounts of Cl decreases activity dramatically but produces a large increase in selectivity [6]. This behavior has been explained by earlier workers in terms of the poisoning of combustion sites [7] and tuning of the electronic state of surface oxygen [8]. It is also consistent with the dipole mechanism proposed for Cs promotion, as Cl has been shown to locate in the subsurface region of silver [9,10], altering the surface electric field in the same direction as cationic species on top of the surface.

Very little information is available to explain the effect of Re on silver catalysts for ethylene epoxidation. In the patent literature, Lauritzen has claimed that Re has a promotional effect if Cl is present, but provides no data without Cl [11]. Patent examples have shown apparent interactions between Re and other promoting metals including cesium [11], molybdenum [11], potassium [12], as well as many others. These patents teach optimized preparation techniques, but few studies shed light on the mechanism of Re promotion. In this work we report

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initial studies of Re promotion of monolith-supported Ag and Cu–Ag bimetallic catalysts under chlorine-free operating conditions. Performance variations as a function of preparation techniques and catalyst composition provide insights into possible locations and roles of Re promoters for these catalysts.

2. Experimental methods

Ag and Cu–Ag bimetallic catalysts were prepared using the methods outlined by Jankowiak and Barteau [13]. Foam monoliths composed of 99.5% α -Al₂O₃, obtained from Vesuvius Hi-Tech Ceramics, were used as the catalyst support. The monoliths were 18 mm \times 10 mm cylinders (diameter \times length) and had 45 pores per linear inch. The monoliths were impregnated using silver nitrate (AgNO₃) as the silver precursor. Re was added via a standard solution of 1000 μ g/ml Re in 5% HNO₃. Two different impregnation methods were used for catalyst preparation. The first method, a co-impregnation method, involved the addition of both the AgNO₃/distilled water and the Re solution to the catalyst in one step. These catalysts were then dried at 353 K, calcined at 673 K in an open air furnace and reduced at 573 K under the flow of 20% H₂ in He. In the second method, a sequential impregnation method, the monolith was first immersed in AgNO₃/distilled water. The catalyst was dried and calcined under the conditions listed above before the Re solution was applied to the catalyst. After the catalyst was dried, it was exposed to the reduction conditions listed earlier.

Using these methods, catalysts with 10–11 wt.% Ag and nominal Re loadings of 25, 50, 100 and 200 ppm were prepared and then tested. During impregnation, all the Re was assumed to adsorb on the catalyst for purposes of estimating loading. After impregnation, the catalyst was reduced under a flow of 35 sccm of 20% H₂ in He at 573 K. Finally, the catalyst was placed under reaction conditions (100 sccm feed of 10% ethylene, 10% oxygen, and 80% nitrogen at 540 K) and allowed to reach steady-state (typically 36–48 h) before temperature and/or reactant partial pressures were altered. After reaching steady-state, the temperature of each catalyst was changed as necessary to give 1.8% ethylene conversion. This allowed for comparison of the EO selectivities at fixed conversion of all catalysts. Reactor effluents were analyzed and quantified using an HP6890 gas chromatograph with a flame ionization detector (FID) and thermal conductivity detector (TCD).

Catalysts containing additional components such as Cs and Cu were also prepared and tested. Details are provided below for each. In cases where more than two impregnations were carried out, the first two impregnations were performed as described previously and the catalyst was dried and reduced under the conditions listed above after each subsequent impregnation. For ease of comparison, these catalysts will be labeled with the reverse order in which the impregnation took place. For example, a catalyst produced by the sequential impregnation of Ag, followed by Re, followed by Cu, is labeled Cu–Re–Ag. All components added by co-impregnation are included within parentheses. For example, a co-impregnated

catalyst of Ag and Cs which was sequentially impregnated with Re is denoted Re–(Cs–Ag).

3. Results and discussion

Previous studies have shown that optimum preparation procedures of Cu–Ag bimetallic catalysts for ethylene epoxidation involve the addition of Cu sequentially to Ag [13,14]. Following this direction, Re–Ag catalysts were first prepared by the sequential impregnation method in order to examine the influence of Re content on ethylene conversion and EO selectivity. For steady-state operation at 540 K with an equimolar feed of ethylene and oxygen (10 mol% each), the ethylene conversion of Re–Ag catalysts passed through a maximum at 25 ppm Re, as shown in Fig. 1. Ethylene conversion and EO selectivity versus Re loading for Re–Ag on α -alumina monolith with \sim 11 wt.% Ag. Selectivity and conversion data without individual temperatures indicated were obtained at 540 K. Selectivity results labeled by temperature were obtained at 1.8% ethylene conversion.

The EO selectivities, determined concurrently, followed a similar trend, exhibiting a maximum between 25 and 50 ppm. Comparing catalyst performance at constant temperature can be problematic, since the yield depends on both the ethylene conversion and EO selectivity. In order to compare catalysts more easily, after reaching steady-state at 540 K the ethylene conversion associated with the Re–Ag catalysts (and all other catalysts that will be discussed) was tuned to 1.8% by adjusting the temperature, thus allowing the selectivities to be compared at constant conversion. These results, also in Fig. 1, show a clear maximum of 42% EO selectivity at 25 ppm Re loading. After passing through a maximum at 25 ppm, the activity and selectivity decreased dramatically as Re loading was increased. The catalysts became almost completely inactive and non-selective at Re loadings of 200 ppm. This performance decrease at higher Re loadings was similar to

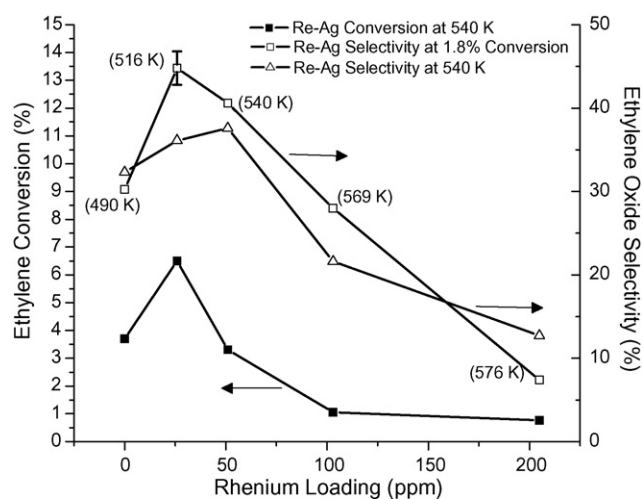


Fig. 1. Ethylene conversion and EO selectivity vs. Re loading for Re–Ag on α -alumina monolith with \sim 11 wt.% Ag. Selectivity and conversion data without individual temperatures indicated were obtained at 540 K. Selectivity results labeled by temperature were obtained at 1.8% ethylene conversion.

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