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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.

Keywords: Ethylene epoxidation; Silver catalyst; Rhenium promotion; Copper promotion

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-Al_2O_3, obtained from Vesuvius Hi-Tech Ceramics, were used as the catalyst support. The monoliths were 18 mm × 10 mm cylinders (diameter × length) and had 45 pores per linear inch. The monoliths were impregnated using silver nitrate ($AgNO_3$) as the silver precursor. Re was added via a standard solution of 1000 μg/ml Re in 5% HNO_3. Two different impregnation methods were used for catalyst preparation. The first method, a co-impregnation method, involved the addition of both the $AgNO_3$/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% H_2 in He. In the second method, a sequential impregnation method, the monolith was first immersed in $AgNO_3$/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% H_2 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 ~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

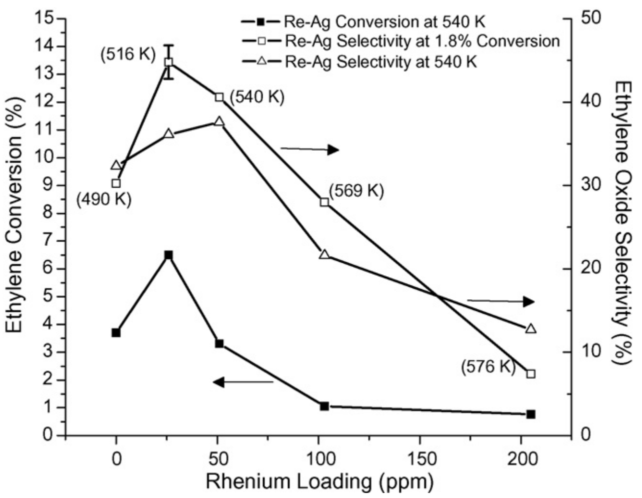


Fig. 1. Ethylene conversion and EO selectivity vs. Re loading for Re–Ag on α-alumina monolith with ~11 wt.% Ag. Selectivity and conversion data without individual temperatures indicated were obtained at 540 K. Selectivity results labeled by temperature were obtained at 1.8% ethylene conversion.

Table 1
EO selectivity vs. order of Re- and/or Cu-impregnation for Re–Ag and Re–Cu–Ag catalysts at 1.8% ethylene conversion

Ag loading (wt.%)	Re loading (ppm)	Cu loading (ppm)	Order of impregnation	EO selectivity at 1.8% conversion (%)	Temperature (K)
11	0	0	Ag	30.25	490
11	25	0	Re–Ag	18.40	571
11	25	0	Re–Ag	44.70	516
11	25	270	Cu–Re–Ag	49.30	513
11	25	270	Re–Cu–Ag	38.20	524

previous results for Cs-promoted catalysts [6]; however, Re-containing catalysts were more sensitive to changes in composition.

The effects of impregnation order were examined for catalysts containing the optimal Re loading of 25 ppm. These results are shown in Table 1. The catalyst prepared by Ag and Re co-impregnation was less active, giving rise to 1.8% conversion at 571 K, than its counterpart prepared by sequential impregnation, with 1.8% conversion at 516 K. Both catalysts were less active than an unpromoted Ag catalyst, which achieved 1.8% conversion at 490 K.

Similar to the activity results, the co-impregnated catalyst with Re and Ag was less selective than the unpromoted Ag and sequentially promoted Re–Ag catalysts as well. The sequentially prepared Re–Ag catalysts, however, produced higher selectivities than unpromoted Ag catalysts, and these catalysts were chosen for further investigation.

Some insight into the functioning of Re-promoted catalysts was obtained from consideration of the effect that ethylene partial pressure had on the variation of the oxygen reaction order for promoted and unpromoted catalysts. Oxygen reaction orders, shown in Table 2, were measured at several constant partial pressures of ethylene for both a Ag and 25 ppm Re–Ag catalyst. The oxygen reaction orders for the unpromoted Ag catalyst increased from 0.34 to 0.85 as the partial pressure of ethylene was increased. The Re–Ag catalyst exhibited different behavior. The oxygen reaction order remained at approximately 0.7 for all partial pressures of ethylene examined. Only a slight increase was seen at high partial pressures of ethylene. This suggests that the Re-promoted catalysts present a more uniform distribution of sites for oxygen adsorption than the unpromoted catalyst, as these catalysts exhibit less sensitivity in the kinetics with variations in oxygen coverage. The Re on the surface of the catalyst is most likely present as Re_2O_7 [5]. Such oxidic species would be expected to bind at sites on the Ag surface with the highest oxygen affinities, i.e. step and defect sites, consequently making the surface more uniform. Atkins et al. determined that the EO selectivity on the Ag (1 1 1) terraces is 57% versus 33% for Ag step or defect sites [15], based on TPD results. Thus, Re-containing catalysts may produce higher selectivities via rhenium oxides blocking less selective Ag sites. While such an effect cannot explain the initial increase in conversion at 540 K with the addition of small amounts of Re in Fig. 1, it is consistent with activity trends measured at lower temperatures in constant conversion experiments. It is also consistent with the higher selectivities and smaller variation of oxygen reaction orders on the Re-promoted catalyst.

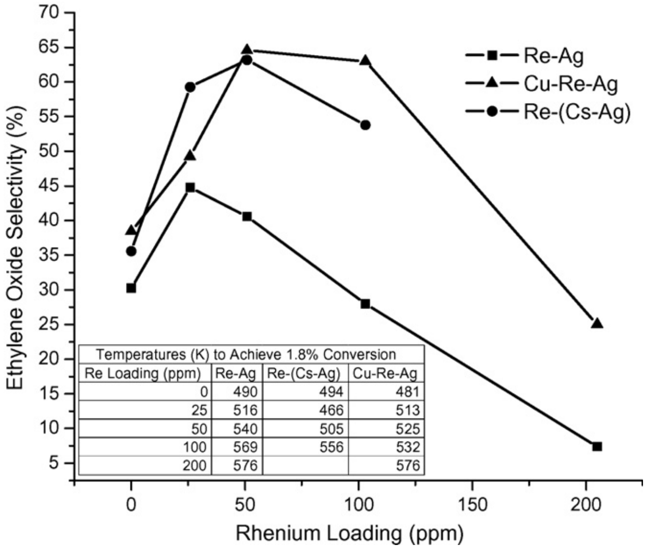
Table 2
Oxygen reaction orders based on ethylene conversion measured at constant partial pressures of ethylene listed

Ethylene partial pressure (atm)	Oxygen reaction order
Ag	
$P_{C_2H_4} = 0.13$	0.34
$P_{C_2H_4} = 0.27$	0.46
$P_{C_2H_4} = 0.54$	0.85
Re–Ag	
$P_{C_2H_4} = 0.13$	0.65
$P_{C_2H_4} = 0.27$	0.73
$P_{C_2H_4} = 0.54$	0.79

Most patents which focus on the promotion of Ag catalysts with Re claim the use of co-promoters to further enhance EO selectivity [11,12,16]. As mentioned earlier, these promoters include alkali metals, other transition metals, and Cl. The use of an organic chloride is outside the scope of the present study, but the incorporation of Cs and Cu in Re-promoted catalysts was examined to investigate the synergies, if any, between these components.

Similar to the approach for the Re–Ag catalysts, preparation procedures for the Re–Cs–Ag and Re–Cu–Ag catalysts were first optimized. Jankowiak and Barteau [6], Minahan et al. [2], and Atkins et al. [15] have reported Cs–Ag catalyst preparation via a co-impregnation technique. Since incorporation of Cs at this stage should not interfere with the sequential addition of Re, Re–(Cs–Ag) catalysts were prepared by co-impregnation of Cs and Ag followed by the sequential impregnation of Re. The strategy for preparation of Re–Cu–Ag catalysts was less obvious from prior work. As stated earlier, Cu must be impregnated sequentially with Ag [13,14], which may conflict with the sequential addition of Re. Therefore, in order to determine how the sequence of Cu, Re and Ag impregnation should progress, the following catalysts were prepared by sequential impregnation: (1) Ag followed by 25 ppm Re and then 270 ppm Cu and (2) Ag followed by 270 ppm Cu and then 25 ppm Re. The results in Table 1 show that the catalyst for which Cu was added last exhibited similar activity and improved selectivity relative to the Cu-free, Re-promoted Ag catalyst. The catalyst with Re added last showed no promotional effect from the Cu, and gave poorer performance than a Cu-free catalyst. The lack of promotion by Cu in this case may be attributed to masking of the Cu by Re when not impregnated on the silver surface in the correct order, since Cu–O bond energies are greater than that of Ag–O, though further investigation will be needed to understand this phenomenon.

Using the optimized impregnation sequence, the co-promoted catalysts were analyzed by varying the Re loadings from 0 to 200 ppm for the (Cs–Ag) and Cu–Ag catalysts. Fig. 2 shows that the Re–(Cs–Ag) catalysts exhibited higher activity at small Re loadings requiring temperatures 50 and 35 K less



Temperatures (K) to Achieve 1.8% Conversion			
Re Loading (ppm)	Re-Ag	Re-(Cs-Ag)	Cu-Re-Ag
0	490	494	481
25	516	466	513
50	540	505	525
100	569	556	532
200	576		576

Fig. 2. EO selectivity vs. Re loading for Re–Ag, Re–(Cs–Ag) and Cu–Re–Ag catalysts. All EO selectivities are reported at 1.8% ethylene conversion at the temperatures listed in the inset table.

than the Re–Ag catalysts for 1.8% ethylene conversion. However, the activity enhancement was dampened at higher Re loadings, with only a 10 K difference in operating temperature for 100 ppm Re loading. The maximum in EO selectivity was not as narrow for the Cs-containing Re–Ag catalysts, spanning loadings between 25 and 100 ppm Re. In any event, Cs improves the performance of Re-promoted Ag catalysts, as it does for unpromoted Ag and Cu–Ag bimetallic catalysts [6].

Unlike Cs, the addition of Cu to Re–Ag catalysts had a more pronounced effect on selectivity than on activity. Operating temperatures to achieve 1.8% ethylene conversions were similar for Cu–Re–Ag and Re–Ag catalysts at comparable Re loadings. However, a definite shift of the EO selectivity maximum from 25 ppm for Re–Ag to between 50 and 100 ppm for the Cu–Re–Ag was observed. We have previously shown that Cu–Ag bimetallic catalysts are more active and selective than Ag alone. Re addition improves the selectivity of both the monometallic and bimetallic catalysts, while decreasing activity in each case. This observation is consistent with the proposal that rhenium oxides may block low selectivity, high binding energy sites for oxygen adsorption on Ag.

4. Conclusions

Re remains the least understood promoter of Ag epoxidation catalysts. This work has shown that Re can promote the epoxidation of ethylene without the presence of Cl, although a sequential impregnation method must be employed instead of the co-impregnation technique often cited in the patent literature. Re only promotes EO selectivity at very small loadings, with a large decrease in catalyst activity seen as loadings are increased above 50 ppm. The selectivity trends were attributed to step and defect site blocking, shifting oxygen adsorption and reaction to more uniform Ag terraces, suggested to be more selective toward EO. The addition of Cs and Cu to the Re–Ag system showed that the catalyst activity and selectivity can be modified by the action of co-promoters with Re. However, further investigations will be required to understand the how these promoters interact.

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