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Journal of Catalysis 236 (2005) 379–386

JOURNAL OF CATALYSIS

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Ethylene epoxidation over silver and copper–silver bimetallic catalysts: II. Cs and Cl promotion

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Received 1 July 2005; revised 8 October 2005; accepted 11 October 2005

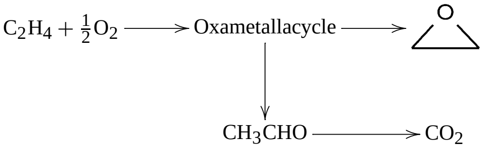
Abstract

Copper–silver bimetallic catalysts offer improved selectivity relative to silver in the direct epoxidation of ethylene, as predicted by density functional theory calculations. The performance advantages of bimetallics over silver have been shown previously for unpromoted, monolith-supported catalysts. Here we demonstrate that the higher activity and selectivity of Cu–Ag bimetallic catalysts prepared by sequential impregnation are maintained when conventional promoters, such as cesium and/or chlorine, are used. Selectivities to ethylene oxide obtained for promoted bimetallic catalysts were up to 15 points higher than those obtained for promoted silver catalysts at comparable conversions.

Keywords: Ethylene epoxidation; Silver catalysts; Bimetallic catalyst; Alkali promotion; Chlorine promotion

1. Introduction

Unpromoted copper–silver bimetallic catalysts prepared by sequential impregnation exhibit increased activity and selectivity relative to unpromoted silver catalysts for the epoxidation of ethylene to ethylene oxide (EO) [1,2]. The design basis for these bimetallic catalysts was provided by density functional theory (DFT) calculations for the simplified reaction network illustrated in Scheme 1. The key feature of the reaction mechanism is the surface oxametallacycle intermediate. Reactions of this intermediate control selectivity, because it can react via competing channels to either the desired product, EO, or the gateway product to combustion, acetaldehyde [3]. The basic structure of the reaction network in Scheme 1 is central to DFT- and kinetics-based models of the reaction selectivity proposed by us [1–4] and others [5–9]. DFT calculations predicted that incorporating 25% Cu atoms into the silver surface should enhance selectivity by favoring the transition state for ring closure of the oxametallacycle relative to that for isomerization to acetaldehyde. The validity of this prediction has been shown by catalytic reaction studies of monolith-supported silver and Cu–Ag bimetallic catalysts prepared to embody the DFT-based design [1,2].



Scheme 1. Simplified reaction network for ethylene epoxidation [3]. (Depictions and structural details of the oxametallacycle can be found in [1,3–5].)

Commercial catalysts for ethylene epoxidation are typically promoted by alkali-metal salts incorporated during catalyst preparation [10]. Among these alkali-metal salts, cesium has been reported to be especially effective [11,12]. Although promotion using cesium additives can increase the selectivity to EO by as much as 10% [13,14], the role of cesium continues to be debated. It has been suggested that the presence of cesium neutralizes acid sites on the support that are active for the isomerization of EO to form acetaldehyde [15], or that cesium reduces the binding strength of EO to the surface [16,17], thereby minimizing further reaction to form carbon dioxide. In addition, it has been suggested that cesium plays a role in binding and dispersing the silver particles on the support [15], as well as increasing the adsorption probability of oxygen on

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doi:10.1016/j.jcat.2005.10.017

silver [18]. We have recently suggested that the presence of cesium promotes selectivity to EO via cesium-induced long-range dipole–dipole electrostatic effects [6]. Because the transition states for the two competing reactions of the oxametallacycle intermediate in Scheme 1 have different dipole moments, the selectivity can be shifted by manipulating the surface field with ionic promoters [6]. It should be noted that the catalyst activity is sensitive to alkali metal loading, and in fact it is possible to suppress all activity by adding larger amounts of alkalis [12]. From an industrial standpoint, alkali metals are added to increase selectivity at the expense of some activity.

Adding chlorine to the catalyst also has been shown to increase the selectivity to EO [19–24]. Chlorine is continuously added to the reactor feed at ppm levels in the form of chlorinated hydrocarbons, such as dichloroethane ($C_2H_4Cl_2$) and vinyl chloride (C_2H_3Cl). Reactions of these hydrocarbons deposit chlorine atoms on the catalyst surface. A continuous feed of chlorine is used to offset the slow removal of surface chlorine under reaction conditions. It is generally found that the presence of chlorine significantly increases the selectivity to EO while at the same time decreasing the rates of EO and carbon dioxide formation. Therefore, chlorine works as a poison to inhibit the rate of carbon dioxide formation to a greater extent than EO formation. How chlorine functions as a promoter is not well understood and has been attributed to both geometric/ensemble effects [19,21,22] and electronic effects [20,25,26]. These effects have been postulated to affect both the adsorption and reaction of oxygen [27,28], as well as the adsorption strength of ethylene and EO, thus changing the relative populations of surface species during reaction [29,30]. Because Cl diffuses below the surface [27,28] even at low coverage [31], it may also alter the field at the surface in the same direction as do adsorbed cations, such as Cs. Thus it may improve selectivity in a fashion analogous to Cs, creating a surface field that disfavors the transition state for oxametallacycle rearrangement to acetaldehyde relative to ring closure to EO.

The purpose of the present work is to investigate whether the superior selectivity of Cu–Ag bimetallic catalysts is maintained when these catalysts are promoted with the typical alkali and halide promoters used in commercial epoxidation catalysts, and whether the selectivity enhancement by these promoters is comparable for Ag and Cu–Ag bimetallics. Although it is not the objective of this work to probe mechanisms of promotion, to the extent that the effects between different promoters are synergistic, one may suggest that different promoters work in different ways, as one would expect to see diminishing returns from promoter addition if all promoters served to tune a single surface property that influenced selectivity.

2. Experimental methods

The preparation of monolith-supported silver and Cu–Ag bimetallic catalysts and the reactor setup have been described previously [2]. Cesium-promoted silver monolith catalysts were prepared by coimpregnation of cesium and silver onto the catalyst support. Cesium was added to the aqueous silver nitrate precursor via an aqueous solution of Cs_2CO_3. After the deposition of the cesium and silver salts, the catalyst was exposed to the same calcination and reduction steps outlined previously. For the bimetallic catalysts, copper was deposited onto the reduced Cs–Ag/Al_2O_3 catalysts by secondary wet impregnation and reduction as described previously [2]. For all samples, the reported cesium weight loadings assumed that all of the cesium present in the precursor solution was adsorbed onto the surface of the catalyst.

Chlorine was introduced to the catalysts by cofeeding vinyl chloride (C_2H_3Cl) at a concentration of 1 ppm by volume of feed. The vinyl chloride source consisted of a 50-ppm (by volume) mixture in a balance of nitrogen, the concentration of which was certified by the manufacturer (Keen). The flow was introduced through the use of an electronic mass flow controller as described for the C_2H_4, O_2, and N_2 flows [2].

Catalysts were synthesized containing copper concentrations of 0–1.0% (mol Cu/mol Cu + Ag). Catalysts corresponding to batch A of our previous study [2] were used in the present work. All experiments were conducted with a total feed rate of 100 sccm (at STP), giving a contact time on the order of 0.5 s. Catalysts were tested over a wide range of feed conditions, ranging from 6:1 ethylene to oxygen to 6:1 oxygen to ethylene. All catalysts operated under Cl-free conditions were lined out for an initial 24-h period of operation under consistent feed and temperature conditions. During this period, the feed contained 10 mol% each of oxygen and ethylene, and the reactor temperature was maintained at 540 K. Once a catalyst had been lined out, composition and temperature variation experiments were carried out to probe the kinetics and selectivity of the reaction. After each change of temperature or composition, the reactor was operated at steady state for a minimum of 1 h before results were recorded. In the case of catalysts operated with Cl-containing feeds, an initial 48-h line-out period was needed to reach steady-state, as we discuss below.

3. Results

3.1. Cesium-promoted catalysts

Fig. 1 shows ethylene conversion data for a series of Cs_2CO_3-promoted silver and Cu–Ag bimetallic catalysts at Cs loadings up to 132 ppm by weight of reduced catalyst for a feed consisting of 10% ethylene and 10% oxygen at 540 K and 1.34 atm. As mentioned above, the addition of cesium can have a significant effect on catalyst activity, with the suppression of all activity occurring at very high loadings. This is evident from the data in Fig. 1, which show that catalyst activity declined rapidly for cesium loadings above ca. 70 ppm. Fig. 2 shows the selectivity to EO for these catalysts after lining out for 24 h. The selectivity of both Ag and Cu–Ag bimetallic catalysts increased for cesium loadings of up to 70 ppm, with no additional performance enhancement observed for higher loadings. The correspondence of the optimal Cs loadings for both Ag and Cu–Ag bimetallic catalysts is illustrated more clearly by comparing the selectivities at constant (1.8%) ethylene conversion, shown in Fig. 3. The data reveal an optimum cesium loading around 70 ppm. At this loading, EO selectivity was in-

Table 1
Ethylene conversion data obtained for promoted and unpromoted silver and Cu–Ag bimetallic catalysts for ethylene and oxygen feed pressures of 0.13–0.8 atm, collected at constant temperature. The temperatures used to conduct the measurements were selected to give a conversion of approximately 1.8% for a feed stream consisting of 0.13 atm of ethylene and oxygen. These temperatures are listed in parentheses below each catalyst

$P_{C_2H_4}$	P_{O_2}	Ag (490 K)	0.2% Cu–Ag (481 K)	Cs–Ag (494 K)	Cs–Cu–Ag (479 K)	Cl–Ag (540 K)	Cl–Cu–Ag (508 K)	Cl–Cs–Ag (540 K)	Cl–Cs–Cu–Ag (507 K)
0.13	0.13	1.81	1.80	1.84	1.80	1.67	1.80	1.68	1.80
0.27	0.13	0.90	0.78	0.98	0.96	0.94	0.99	1.49	1.55
0.54	0.13	0.38	0.30	0.50	0.48	0.38	0.45	0.98	0.93
0.8	0.13	0.22	0.18	0.32	0.30	0.25	0.23	0.82	0.63
0.13	0.27	2.18	2.46	2.22	2.24	2.11	2.34	2.19	2.36
0.13	0.54	2.97	3.26	2.90	2.78	2.77	2.82	2.90	3.09
0.13	0.8	3.58	3.72	3.17	3.26	3.01	3.45	3.58	3.73
0.27	0.27	1.30	1.21	1.22	1.17	1.09	1.17	1.76	1.62
0.54	0.27	0.55	0.51	0.66	0.62	0.74	0.69	1.56	1.66
0.27	0.54	1.62	1.65	1.63	1.56	1.49	1.75	2.34	2.37
0.54	0.54	0.88	0.85	0.90	0.83	1.19	1.05	1.62	1.49

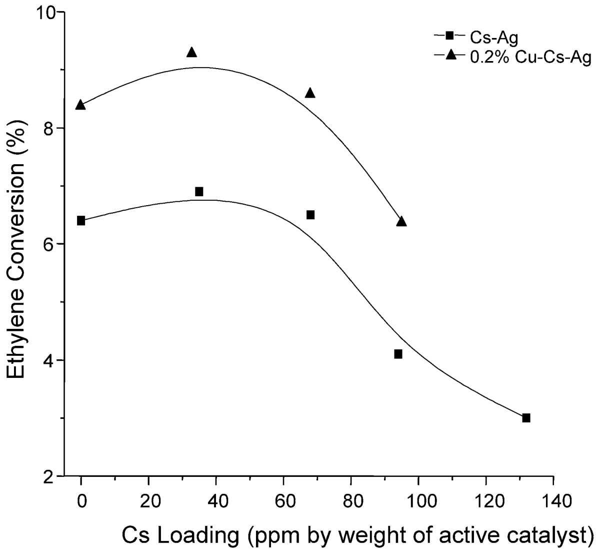

Fig. 1. Ethylene conversion for a series of Cs-promoted silver and 0.2% Cu–Ag bimetallic catalysts as a function of cesium loading. Conversions are reported for a feed stream containing 10% ethylene and 10% oxygen at 540 K.

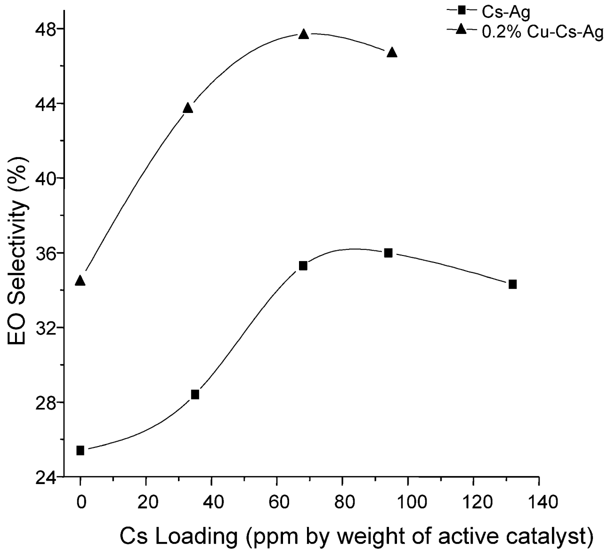

Fig. 2. EO selectivity for a series of Cs-promoted silver and 0.2% Cu–Ag bimetallic catalysts as a function of cesium loading. Selectivity data are reported for a feed stream containing 10% ethylene and 10% oxygen at 540 K.

creased by approximately 9% relative to pure silver, with silver catalysts containing the optimal cesium loading achieving an EO selectivity of approximately 41%. The Cs-promoted Cu–Ag (0.2 mol% Cu) bimetallic catalysts were superior to the Cu-free catalysts at all cesium levels, with a selectivity to EO of ca. 56% for a Cs–Cu–Ag catalyst at optimal cesium loading. As Fig. 3 shows, adding cesium to a Cu–Ag bimetallic catalyst increased the selectivity by approximately 10%. Thus the effects of Cs and Cu on catalyst selectivity are roughly additive.

To further investigate the performance of cesium-promoted silver and Cu–Ag bimetallics, catalysts containing optimized Cs levels (as defined in Fig. 3) were investigated at different feed stoichiometries. The ethylene conversion data for these studies are presented in Table 1. Fig. 4 shows EO selectivity data collected for Ag, Cs–Ag, Cu–Ag, and Cs–Cu–Ag catalysts at constant temperature for ethylene-rich feed stoichiometries ranging from 1:1 to 6:1 ethylene to oxygen at similar ethylene conversions. Feed variations were conducted by maintaining the oxygen feed concentration at 10% (0.13 atm) and increasing the ethylene feed concentration from 10 to 60% (0.13 to 0.8 atm). The data for each catalyst shown in Fig. 4 were collected at constant temperature, with the temperature of each catalyst sample adjusted to give an ethylene conversion of approximately 1.8% for a 1:1 feed stoichiometry (0.13 atm each of ethylene and oxygen). This temperature was then maintained (as given in Table 1) as the ethylene pressure was increased. As Fig. 4 shows, the effects of cesium and copper are largely additive for feed stoichiometries of 1:1 to 4:1 ethylene to oxygen, with a pinching effect occurring at 6:1, where the performance of the Cu–Ag and Cs–Cu–Ag catalysts were effectively the same. The maximum observed selectivities to EO for Cs–Ag and Cs–Cu–Ag catalysts were 54 and 60%, respectively, for a feed stoichiometry of 6:1 ethylene to oxygen.

Also investigated were oxygen-rich feed streams with feed stoichiometries ranging from 1:1 to 6:1 oxygen to ethylene. These data are presented in Fig. 5 at similar ethylene conversions. Feed variations were conducted by maintaining the ethylene feed concentration at 10% and increasing the oxygen feed

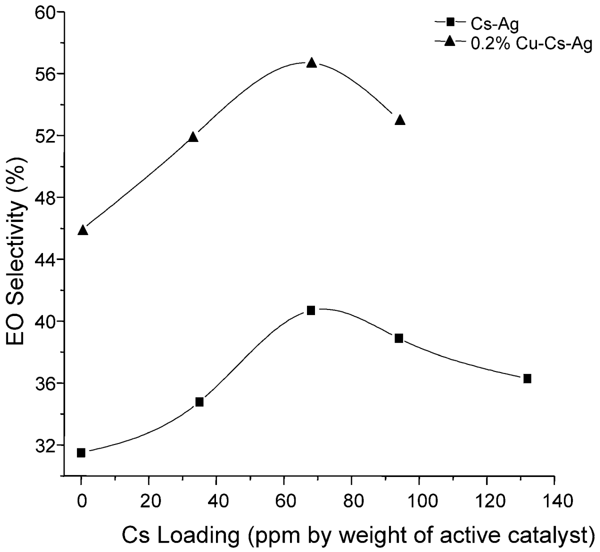

Fig. 3. EO selectivity for a series of Cs-promoted silver and Cu–Ag bimetallic catalysts as a function of cesium loading. Selectivity data are reported for a feed stream containing 10% ethylene and 10% oxygen at differential ethylene conversion (∼1.8%). Data for the Cs-promoted Ag catalysts were obtained at 492 ± 2 K; data for the Cs-promoted Cu–Ag bimetallic were obtained at 480 ± 1 K.

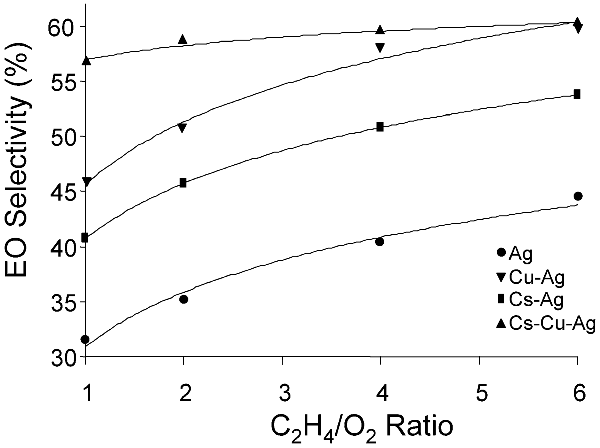

Fig. 4. EO selectivity for Ag, Cs–Ag, Cu–Ag and Cs–Cu–Ag catalysts as a function of feed stoichiometry for ethylene-rich feed conditions. The oxygen partial pressure was fixed at 0.13 atm for all experiments and the ethylene partial pressure was varied. The Cs–Ag and Cs–Cu–Ag catalysts contained 68 ppm of cesium and the Cu–Ag and Cs–Cu–Ag catalysts contained 0.2 mol% copper. The reaction temperature and ethylene conversion for each experiment are specified in Table1.

concentration from 10 to 60%. For oxygen-rich feed streams, the effects of cesium and copper appear to be additive for the entire range of feed stoichiometries investigated. The maximum observed selectivities to EO were 50% for the Cs–Ag catalyst and 63% for the Cs–Cu–Ag catalyst, at a feed stoichiometry of 6:1 oxygen to ethylene.

As for unpromoted silver and Cu–Ag bimetallic catalysts [2], the Cs–Ag and Cs–Cu–Ag catalysts were exposed to feed pressures of 0.13–0.54 atm of ethylene and oxygen. From these results, three-dimensional selectivity contours were generated at constant temperature for each catalyst. These contours

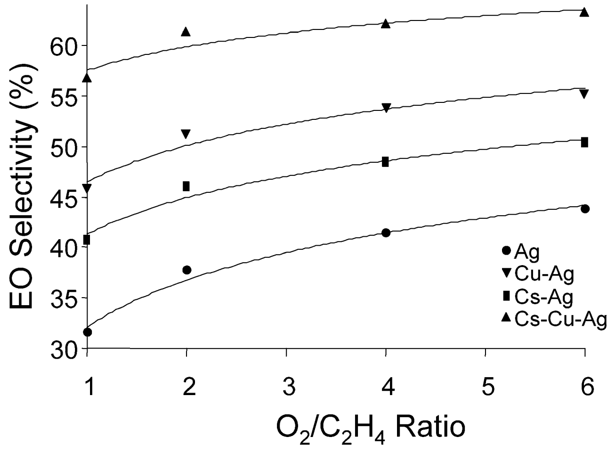

Fig. 5. EO selectivity for Ag, Cs–Ag, Cu–Ag and Cs–Cu–Ag catalysts as a function of feed stoichiometry for oxygen-rich feed conditions. The ethylene partial pressure was fixed at 0.13 atm for all experiments and the oxygen partial pressure was varied. The Cs–Ag and Cs–Cu–Ag catalysts contained 68 ppm of cesium and the Cu–Ag and Cs–Cu–Ag catalysts contained 0.2 mol% copper. The reaction temperature and ethylene conversion for each experiment are specified in Table1.

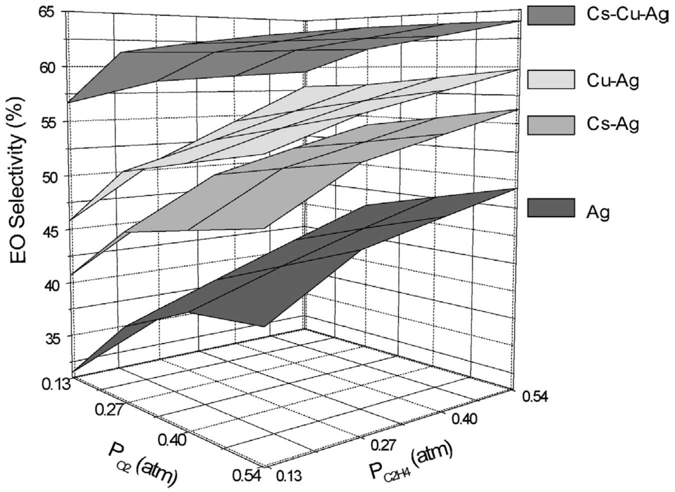

Fig. 6. 3-D contours of EO selectivity for Ag, Cs–Ag, Cu–Ag, and Cs–Cu–Ag catalysts for ethylene and oxygen pressures ranging from 0.13–0.54 atm. The Cs–Ag and Cs–Cu–Ag catalysts contained 68 ppm of cesium and the Cu–Ag and Cs–Cu–Ag catalysts contained 0.2 mol% copper. The reaction temperature for each catalyst is specified in Table1.

are shown in Fig. 6, along with contours generated for silver and Cu–Ag at similar ethylene conversions. The operating temperature for each catalyst was chosen to produce an ethylene conversion of ∼1.8% for a feed containing 10% each of ethylene and oxygen. The individual temperatures for each catalyst are listed in Table 1. Each catalyst was maintained at the specified temperature as the feed composition was varied, to produce the selectivity contours shown in Fig. 6. It is evident from this figure that the Cs–Cu–Ag catalyst outperforms both the Cs–Ag and Cu–Ag catalysts over the entire range of feed compositions explored, with maximum observed selectivities to EO of 56% for the Cs–Ag catalyst and 64% for the Cs–Cu–Ag catalyst.

3.2. Chlorine promotion

The effect of chlorine promotion on silver and Cu–Ag bimetallic catalysts was also studied. As mentioned above, the presence of chlorine on the catalyst has been shown to enhance the selectivity to EO at the expense of activity. This property is illustrated in Figs. 7 and 8, which show transient activity and selectivity trends for silver catalysts lined out with and without the presence of chlorine cofeed. These data were collected at 540 K for a feed stream consisting of 10% ethylene and 10% oxygen at a pressure of 1.34 atm. As shown in Fig. 7, the activity of the catalyst was significantly reduced with chlorine cofeed, with a ca. 75% reduction in the relative activity at similar conditions (1.7% conversion with chlorine cofeed vs. 6.4% conversion without chlorine cofeed after lining out the catalyst for 24–48 h on stream). A similar reduction in activity was observed for all catalyst samples with chlorine promotion. The conversion decreased dramatically in the first 24 h, most likely due to the uptake of chlorine by the surface and/or subsurface of the silver catalyst, with stable activity observed thereafter. Fig. 8 shows the transient selectivity trends for silver catalysts with and without chlorine cofeed. The results indicate that the presence of chlorine significantly increased the selectivity to EO, with a selectivity increase of ca. 21 percentage points at similar reactor conditions (47% selectivity with chlorine cofeed vs. 26% without chlorine cofeed). The selectivity increased significantly in the first 24 h and reached a stable value at ca. 30 h. At a similar ethylene conversion of 1.7–1.8%, the selectivity enhancement achieved by the chlorine cofeed was approximately 15 percentage points (47% selectivity with chlorine cofeed vs. 32% without chlorine cofeed). Similar trends were observed for a 0.2% Cu–Ag bimetallic catalyst, for which a decrease in the relative activity of approximately 60% was observed at similar reactor conditions (540 K, 10% ethylene and 10% oxygen at 1.34 atm). In addition, the selectivity to EO increased by approximately 22 percentage points at similar reactor conditions (57% selectivity with chlorine cofeed vs. 35% without chlorine co-feed). At an ethylene conversion of approximately 1.8%, the selectivity to EO increased by 18 percentage points (64% selectivity with chlorine cofeed vs. 46% without chlorine cofeed), indicating that the effects of chlorine and copper are additive with respect to EO selectivity enhancement.

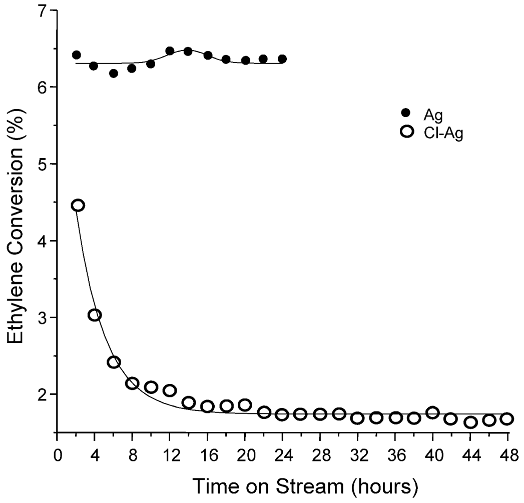

Fig. 7. Ethylene conversion as a function of time on stream for a silver and a Cl-promoted silver catalyst. The conversion data were collected for a feed stream containing 10% ethylene and 10% oxygen at 540 K. The chlorine feed concentration was 1 ppm by volume.

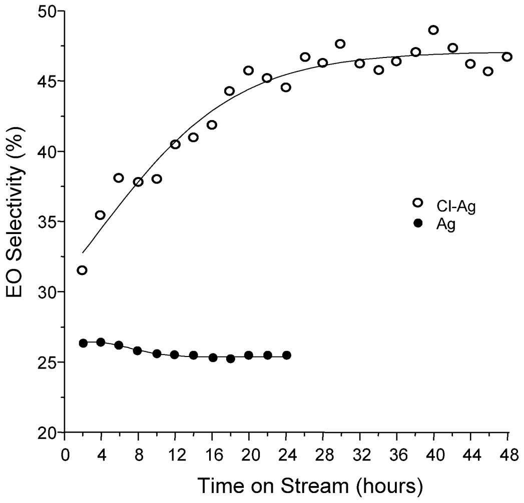

Fig. 8. EO selectivity as a function of time on stream for a silver and a Cl-promoted silver catalyst. The selectivity data were collected for a feed stream containing 10% ethylene and 10% oxygen at 540 K. The chlorine feed concentration was 1 ppm by volume.

Chlorine-promoted catalysts were exposed to a wide range of feed conditions. The chlorine-promoted samples were lined out for 48 h before any feed variations. Table 1 presents the ethylene conversion data for these studies. Fig. 9 shows EO selectivity data collected for Ag, Cl–Ag, Cu–Ag, and Cl–Cu–Ag catalysts collected at constant temperature for ethylene-rich feeds ranging from 1:1 to 6:1 ethylene to oxygen at similar ethylene conversions. The bimetallic samples contained 0.2 mol%

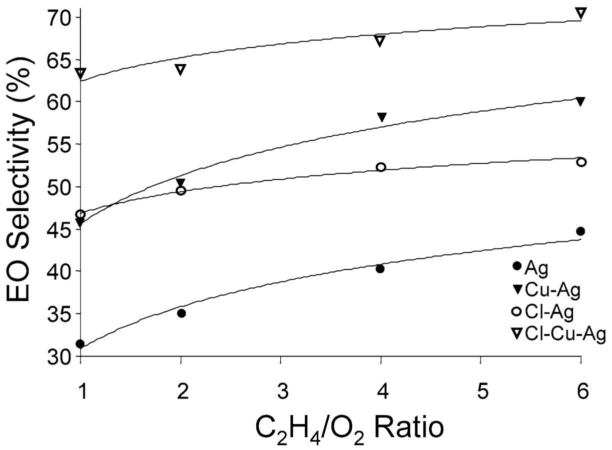

Fig. 9. EO selectivity for Ag, Cl–Ag, Cu–Ag and Cl–Cu–Ag catalysts as a function of feed stoichiometry for ethylene-rich feed conditions. The oxygen partial pressure was fixed at 0.13 atm for all experiments and the ethylene partial pressure was varied. The Cu–Ag and Cl–Cu–Ag catalysts contained 0.2 mol% copper. The chlorine feed concentration was 1 ppm by volume. The reaction temperature and ethylene conversion for each experiment are specified in Table 1.

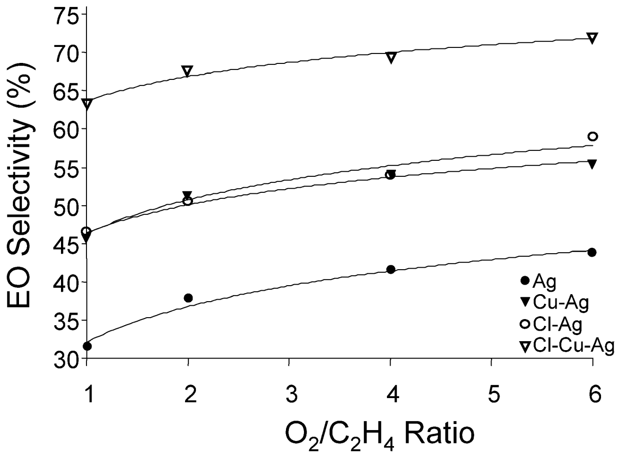

Fig. 10. EO selectivity for Ag, Cl–Ag, Cu–Ag and Cl–Cu–Ag catalysts from batch A as a function of feed stoichiometry for oxygen-rich feed conditions. The ethylene partial pressure was fixed at 0.13 atm for all experiments and the oxygen partial pressure was varied. The Cu–Ag and Cl–Cu–Ag catalysts contained 0.2 mol% copper. The chlorine feed concentration was 1 ppm by volume.

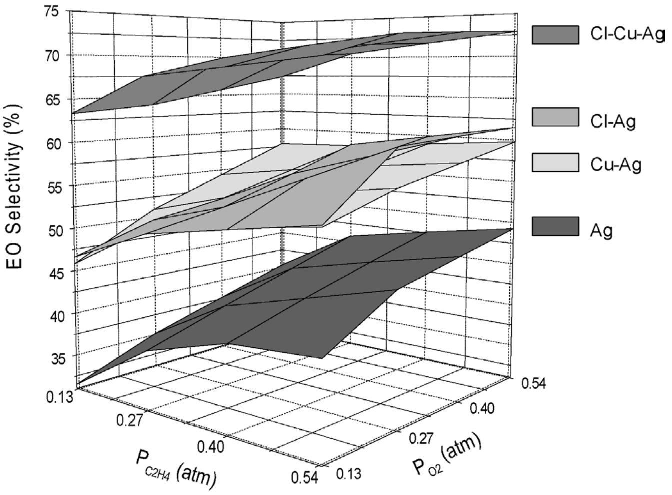

Fig. 11. 3-D contours of EO selectivity for Ag, Cl–Ag, Cu–Ag, and Cl–Cu–Ag catalysts for ethylene and oxygen pressures ranging from 0.13–0.54 atm. The Cu–Ag and Cl–Cu–Ag catalysts contained 0.2 mol% copper. The chlorine feed concentration was 1 ppm by volume. The reaction temperature for each catalyst is specified in Table 1.

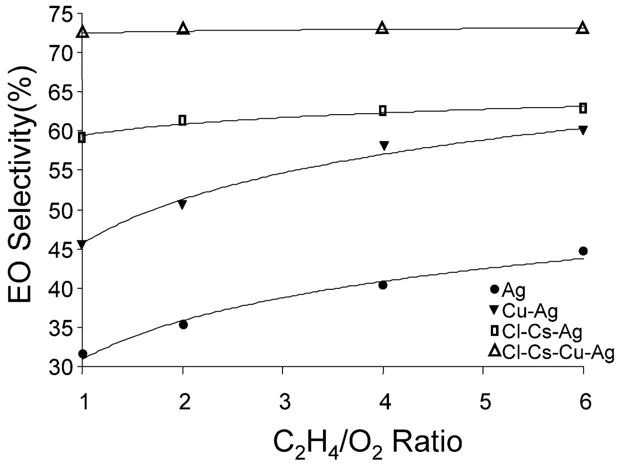

Fig. 12. EO selectivity for Ag, Cu–Ag, Cl–Cs–Ag and Cl–Cs–Cu–Ag catalysts as a function of feed stoichiometry for ethylene-rich feed conditions. The Cu–Ag and Cl–Cs–Cu–Ag catalysts contained 0.2 mol% copper. The Cs-promoted catalysts contained approximately 65 ppm of cesium. The chlorine feed concentration was 1 ppm by volume. The reaction temperature and ethylene conversion for each experiment are specified in Table 1.

copper, whereas the chlorine-promoted catalysts were exposed to a vinyl chloride feed concentration of 1 ppm. The maximum observed selectivities to EO for Cl–Ag and Cl–Cu–Ag catalysts were 53 and 71%, respectively, at a feed stoichiometry of 6:1 ethylene to oxygen. Fig. 10 shows EO selectivity data collected for oxygen-rich feed streams ranging from 1:1 to 6:1 oxygen to ethylene at similar ethylene conversions. As was observed for ethylene-rich conditions, the effects of chlorine and copper were largely additive over the entire range of feed stoichiometries investigated. The maximum observed selectivities to EO for Cl–Ag and Cl–Cu–Ag catalysts were 59 and 72%, respectively, at a feed stoichiometry of 6:1 oxygen to ethylene.

The Cl–Ag and Cl–Cu–Ag catalysts were tested at feed pressures ranging of 0.13–0.54 atm of ethylene and oxygen. From these results, three-dimensional selectivity contours were generated at constant temperature for these catalysts. These contours are shown in Fig. 11, along with contours generated for silver and Cu–Ag bimetallic catalysts at similar ethylene conversions. It is evident that the Cl–Cu–Ag catalyst outperformed both the Cl–Ag and Cu–Ag catalysts over the entire range of feed compositions explored, with maximum observed selectivities to EO for the Cl–Ag and Cl–Cu–Ag catalysts of 62 and 73%, respectively.

3.3. *Cesium and chlorine copromotion*

The effects of cesium and chlorine copromotion on EO selectivity for silver and 0.2% Cu–Ag bimetallic catalysts were also examined. These catalysts were exposed to a similar protocol as for the catalysts discussed previously with respect to variations in feed pressure and stoichiometry. The samples were lined out for 48 h before any feed variation. Table 1 presents the ethylene conversion data for these studies. Fig. 12 shows EO selectivity data collected for Ag, Cu–Ag, Cl–Cs–Ag, and Cl–Cs–Cu–Ag catalysts from batch A collected at constant temperature for ethylene-rich feed stoichiometries ranging from 1:1 to 6:1 ethylene to oxygen at similar ethylene conversions. The cesium-promoted samples contained approximately 65 ppm of cesium added to the catalyst as Cs_2CO_3, while the chlorine-promoted samples were exposed to a vinyl chloride feed concentration of 1 ppm. The bimetallic catalysts contained 0.2 mol% copper. The results shown in Fig. 12 indicate that the effects of cesium and chlorine on the selectivity to EO are additive for the range of feed stoichiometries investigated. A maximum selectivity to EO of 63% was observed for a feed stoichiometry of 6:1 ethylene to oxygen, as compared to selectivities of 53 and 54% observed for Cl–Ag and Cs–Ag catalysts at similar feed conditions and ethylene conversions. The effects of copper, chlorine and cesium also appear to be additive, with a maximum selectivity to EO of 73% observed for a Cl–Cs–

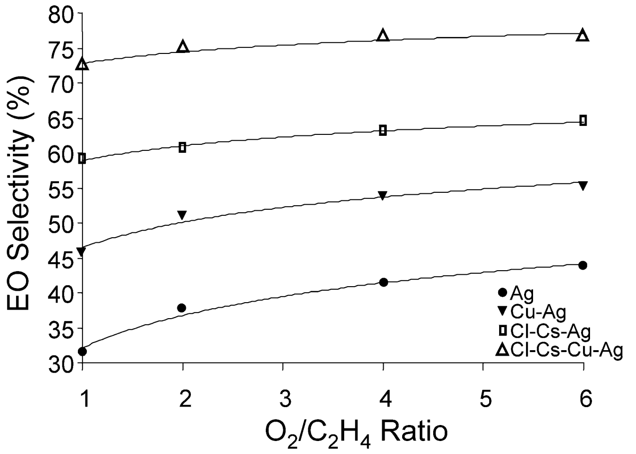

Fig. 13. EO selectivity for Ag, Cu–Ag, Cl–Cs–Ag and Cl–Cs–Cu–Ag catalysts as a function of feed stoichiometry for oxygen-rich feed conditions. The Cu–Ag and Cl–Cs–Cu–Ag catalysts contained 0.2 mol% copper. The Cs-promoted catalysts contained approximately 65 ppm of cesium and the chlorine feed concentration was 1 ppm by volume. The reaction temperature and ethylene conversion for each experiment are specified in Table 1.

Cu–Ag catalyst at 6:1 ethylene to oxygen. Fig. 13 shows EO selectivity data collected for oxygen-rich feed streams ranging from 1:1 to 6:1 oxygen to ethylene at similar ethylene conversions. As was observed for ethylene-rich conditions, the effects of chlorine, cesium and copper on the selectivity to EO were additive over the entire range of feed stoichiometries investigated. The maximum observed selectivity to EO for a Cl–Cs–Ag catalyst was 65% at a feed stoichiometry of 6:1 oxygen to ethylene, compared with selectivities of 55% for Cs–Ag catalyst and 59% for Cl–Ag catalyst at similar feed conditions and ethylene conversions, whereas the maximum observed selectivity to EO for a Cl–Cs–Cu–Ag catalyst was 77% at 6:1 oxygen to ethylene.

As was done previously for silver and Cu–Ag bimetallic catalysts, the Cl–Cs–Ag and Cl–Cs–Cu–Ag catalysts were operated at feed pressures of 0.13–0.54 atm of ethylene and oxygen. From these results, three-dimensional selectivity contours were generated at constant temperature for these catalysts. These contours are shown in Fig. 14, along with contours generated for silver and Cu–Ag at similar ethylene conversions. Clearly, the Cl–Cs–Cu–Ag catalyst outperformed both the Cl–Cs–Ag and Cu–Ag catalysts over the entire range of feed compositions explored, with maximum observed selectivities to EO of 67% for the Cl–Cs–Ag catalyst and 77% for the Cl–Cs–Cu–Ag catalyst.

4. Discussion

The selectivity advantages of Cu–Ag bimetallic catalysts over silver are maintained when these catalysts are promoted with Cs and/or Cl. Indeed, over a wide range of reactant pressures and stoichiometries, adding copper has an additive effect with cesium and chlorine with respect to EO selectivity at comparable conversions. In addition, as shown in Table 1, the bimetallic catalysts are more active and operate at lower temperatures to achieve comparable conversions than their silver counterparts, both with and without alkali and halide promoters. To the extent that lower operating temperature is usually associated with longer lifetime, bimetallic catalysts may offer advantages with respect to this performance measure as well.

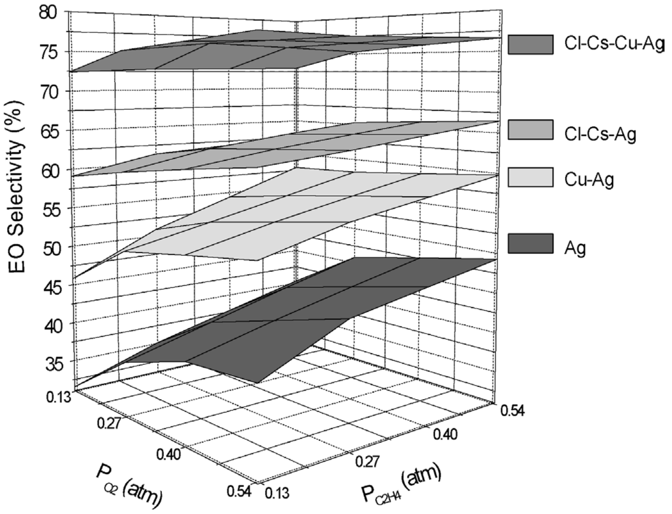

Fig. 14. 3-D contours of EO selectivity for Ag, Cu–Ag, Cl–Cs–Ag and Cl–Cs–Cu–Ag catalysts for ethylene and oxygen pressures ranging from 0.13–0.54 atm. The Cu–Ag and Cl–Cs–Cu–Ag catalysts contained 0.2 mol% copper. The Cs-promoted catalysts contained approximately 65 ppm of cesium and the chlorine feed concentration was 1 ppm by volume. The reaction temperature for each catalyst is specified in Table 1.

We have previously proposed [3] that the selectivity of silver ethylene epoxidation catalysts is controlled by the competing reactions of the oxametallacycle, leading to either EO or acetaldehyde (which rapidly combusts), as shown in Scheme 1. This mechanism provides a framework for understanding the effects of known promoters on catalyst selectivity, as well as for formulating new catalysts, including bimetallics. On the basis of DFT calculations, we have proposed [4] that Cs cations increase selectivity by long-range electrostatic interactions that stabilize the transition state for EO formation (TS1) relative to the transition state for acetaldehyde formation (TS2). (The structures of these two transition states have been described previously [3,4].) The difference in stabilization of the two transition states produced by the electrostatic effect of Cs was attributed to a difference in their respective dipole moments. This electrostatic model suggests that cations above the surface and anions below the surface should have a similar effect on the competing transition states. Thus Cl, which might be expected to counteract the effect of Cs, instead acts in a complementary fashion because it diffuses the subsurface. This model may also explain the role of subsurface oxygen, because this species is also anionic.

In contrast, the role of Cu in Cu–Ag bimetallic surfaces is to alter the chemical and electronic properties of the surface according to our DFT calculations. Cu alters the electronic characteristics of the binding sites available to surface oxametallacycle intermediates (and other adsorbates) and alters the relative energies of the two transition states for the competing reactions of these intermediates. By increasing the relative difference between the barriers for the oxametallacycle ring-closure versus H-shift pathways, Cu addition increases the selectivity to EO.

To perhaps oversimplify the distinction, Cu influences selectivity via through-surface interactions with adsorbates and transition states, whereas Cs influences selectivity via through-space interactions. The observation in the present work that the effects of Cu, Cs, and Cl on epoxidation selectivity are largely additive is consistent with this distinction. If the principal effect of adding all of these promoters was to tune the surface electronic properties to some optimum for selectivity, then one would expect that the maximum selectivities achieved by optimized catalysts using different subsets of these components would be similar. The fact that this is not the case, that promotion of Cu–Ag bimetallic catalysts with alkalis and halides increases selectivity in a nearly additive fashion, suggests that surface alloy components such as copper and ionic promoters such as Cs and Cl act by different mechanisms to increase selectivity. This is not to say each does not have an effect on the electronic properties of sites of the silver surface, but rather that the principal means of impact of ionic promoters is on the surface field.

Finally, it is important to note that the effects on catalyst activity can be quite different for alloy and promoter components that improve selectivity. Higher selectivity is not necessarily associated with lower activity. In the present work we have deliberately carried out experiments under conditions chosen to minimize secondary reactions of the product EO. These include operating at low ethylene conversion and using monolith-supported catalysts to provide uniform, short contact times. For these catalysts and conditions, Cu addition to form a bimetallic increased both activity and selectivity [2]; Cs addition had relatively little effect on activity while increasing selectivity; and Cl addition sharply decreased activity while improving selectivity of both Ag and Cu–Ag bimetallic catalysts. This is also consistent with the network depicted in Scheme 1 and our previous microkinetic analysis of it [32]. The steps that control the *rate* of ethylene epoxidation are those that lead *to* formation of the oxametallacycle; the steps that control the *selectivity* are those that lead *from* the oxametallacycle. The former involve oxygen dissociation and oxygen addition to ethylene. Thus promoter effects on activity are likely dominated by alteration of the oxygen atom binding energy to the catalyst surface, whereas the effects on selectivity involve interaction with the oxametallacycle and the transition states for its conversion to different products. There is no intrinsic connection between the influence of different promoters on activity and selectivity, as demonstrated by both microkinetic models and the results of the present experimental study.

5. Conclusion

Cu–Ag bimetallic catalysts promoted with Cs and/or Cl are more active and more selective for ethylene epoxidation than promoted silver catalysts. The performance advantages of bimetallic catalysts over a wide range of feed compositions are thus maintained when conventional promoters are incorporated. The effects of copper and of ionic promoters on catalyst selectivity are largely additive, consistent with the suggestion from DFT calculations that these components alter the energetics of the competing reaction channels of surface oxametallacycle intermediates by different mechanisms.

Acknowledgments

We gratefully acknowledge the support of the U.S. Department of Energy, Division of Chemical Sciences (grant FG02-84ER13290).

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