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

Jerome T. Jankowiak, Mark A. Barteau [*]

Center for Catalytic Science and Technology (CCST), Department of Chemical Engineering, University of Delaware, Newark, DE 19716, USA

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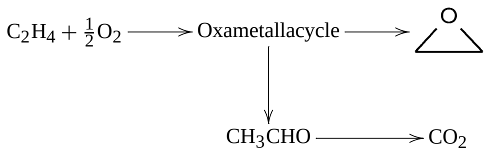
Abstract

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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[*] Corresponding author. Fax: +1 302 831 8201.
E-mail address: barteau@che.udel.edu (M.A. Barteau).

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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-