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RESEARCH NOTE

Comparison of Cu and Ag Catalysts for Epoxidation of Higher Olefins

John R. Monnier and Gary W. Hartley

Eastman Chemical Company, Research Laboratories, P.O. Box 1972, Kingsport, Tennessee 37662-5150

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Catalyst performance of both promoted and unpromoted Ag/Al_2O_3 catalysts for the epoxidation of butadiene is summarized and compared to temperature programmed reaction data for the reaction of butadiene with submonolayer coverages of oxygen on Cu(111) that has been presented in the literature (6). The role of the alkali promoter salts used for the supported silver catalysts is compared to the role of Cs metal deposited on the Cu(111) surface with respect to changing catalyst performance. The comparison indicates that, unlike the previously published data, silver catalysts, and in particular, promoted silver catalysts, are far superior to their copper counterparts. For the Cu(111) case, reaction of adsorbed butadiene with adsorbed oxygen is especially selective for the formation of 3,4-epoxy-1-butene. However, this reaction is best described as a Cu-mediated, substoichiometric reaction between adsorbed butadiene and adsorbed oxygen. Unlike Ag catalysts, activity of the Cu(111) surface is highly dependent upon maintaining the surface as Cu°, not the thermodynamically more favored Cu_2O state. © 2001 Academic Press

Key Words: **silver; copper; butadiene; epoxidation; epoxybutene; catalyst; olefin epoxidation; cuprous oxide.**

1. INTRODUCTION

There has been renewed interest in epoxidation of higher olefins (1–8). Very recently, Cowell, Lambert, *et al.* (6, 7) have reported results for the reaction of butadiene and O_2 and styrene and O_2 on Cu(111) surfaces at ultrahigh vacuum conditions. The authors have concluded that under their reaction conditions Cu(111) surfaces were not only "ultra selective" for the epoxidation reactions of butadiene to form 3,4-epoxy-1-butene and styrene to form styrene epoxide, but were superior to Ag catalysts for the epoxidation of higher olefins. We, too, have been actively involved in the epoxidation of higher olefins, such as butadiene (1, 2) and styrene (3), using promoted Ag catalysts, which has, in fact, culminated in the commercialization of the epoxidation of butadiene to selectively produce 3,4-epoxy-1-butene (EpB) in high yields (8). We would therefore like to offer our comments regarding the comparison of both unpromoted and alkali-promoted Ag catalysts with the results for Cu presented by Cowell for the epoxidation of butadiene.

2. EXPERIMENTAL

The promoted Ag catalysts were prepared using the methodology described earlier (1–3). Essentially, the appropriate amounts of $AgNO_3$ and promoter salt (either CsCl, RbCl, TlCl, or KCl) were coimpregnated onto SA-5562, an extruded α-Al_2O_3 support in the shape of 1/4-inch-diameter rings, which was supplied by Norton Corporation. The surface area of the SA-5562 support was 0.7–0.8 m^2/g, with a total pore volume of 0.55 cc/g, and median pore diameter of 7 μm. The salt-impregnated support rings were dried and then calcined at 250°C for 2 h in flowing air. The active catalyst was then prepared by reduction in a flowing H_2/He stream (4–20% H_2) for 2 h at a maximum temperature of 350°C. Silver weight loadings and promoter loadings were determined by atomic absorption spectroscopy. Promoter loadings were varied over predetermined ranges, while Ag weight loadings were maintained between 12 and 14% by weight, relative to the finished catalyst. Using automatic particle counting/measuring software with scanning electron micrographs, average Ag particle diameters were typically determined to be between 0.2 and 0.3 μm.

The supported Cu/SiO_2 catalyst was prepared from a SiO_2-supported $CuCO_3$ catalyst supplied by Strem Chemicals. The $CuCO_3$ was reduced to metallic Cu by reduction in a flowing stream of 10% H_2/90% He at 300°C for 2 hrs. The Cu weight loading was determined by atomic absorption spectroscopy to be 4.1% by weight. X-ray line broadening of the Cu(111) reflection gave an average diameter of Cu crystallites between 7 and 12 nm.

Butadiene epoxidation was carried out in tubular Pyrex reactors containing catalyst charges of 3.0–3.2 g in the mid-section of the tube. The catalyst bed dimensions were approximately 10 mm diameter × 25 mm in height. Catalyst samples were ground and sieved to give particle diameters between 0.8 and 2.0 mm. The reactor was tightly clad with a 2.5-cm-o.d. aluminum jacket to help ensure a

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more isothermal catalyst bed. A thermocouple embedded in the catalyst bed was used to monitor and maintain catalyst temperature. Before reaction, each catalyst sample was loaded into the reactor and heated in flowing air *in situ* at 250°C for 2 h. The temperature of the sample was then lowered to 200°C and the reaction was started by supplying a reaction feed composition to the catalyst. Feed composition was 9% C_4H_6, 18% O_2, 73% n-C_4H_{10} as diluent plus 2 ppm 2-chlorobutane, which was added as a reaction moderator. The overall flow rate was 300 ml (STP)/min, which gave a $GHSV = 5400\ h^{-1}$. Catalyst performance was monitored every 2 h throughout the entire run by automatic in-line gas sampling injection into a Poraplot Q gas chromatographic column installed in a Hewlett-Packard 5890 Series Gas Chromatograph. Data collection and interpretation were carried using a Hewlett-Packard 3396 Series II computing integrator.

3. RESULTS AND DISCUSSION

Cowell *et al.* (6), using temperature-programmed reaction methods and X-ray photoelectron spectroscopy (XPS), have examined the reaction of adsorbed butadiene on fractional, oxygen-precovered Cu(111), i.e., oxygen coverages (θ_O) between 0 and 0.5 monolayers (ML) on Cu(111), and concluded that epoxybutene was selectively produced as the only reaction product at reaction/desorption temperatures of 230 and 350°K. Epoxybutene yield was highest for $\theta_O = 0.04$, and yield to epoxybutene was zero at $\theta_O = 0.50$. The surface composition of the Cu (111) surface at $\theta_O = 0.50$ was equivalent to a disordered Cu_2O phase. Unlike the claims of Cowell, we have previously evaluated Cu supported on silica for the epoxidation of butadiene at conditions of continuous operation and found that the catalyst was totally inactive for the epoxidation reaction at the same reaction conditions that were used for the promoted Ag catalysts. The surface of the catalyst under butadiene epoxidation conditions was found to correspond to Cu_2O, as determined by low-angle X-ray diffraction and XPS. Further, we observed that when reduced Cu/SiO_2 catalysts were exposed to gas streams containing only epoxybutene and helium, the only reaction product observed was butadiene. Only after the Cu° surface had been oxidized to Cu_2O was unreacted epoxybutene detected in the reactor effluent. This observation is corroborated by considering the thermodynamics of the interaction of EpB with metallic Cu surfaces. The free energies of reaction data (9, 10) in Table 1 reveal that the oxidation of metallic Cu by EpB is a very thermodynamically favored reaction, indicating that Cu° should not be capable of functioning as an epoxidation catalyst, especially in typical reactor situations where readsorption of epoxide product on Cu° surfaces can and does occur, i.e., in a tubular reactor. In fact, the conditions used by Cowell are essentially the only way that EpB could be formed and detected, since readsorption of products in the ultrahigh-vacuum system used to conduct the temperature-programmed reaction experiments is highly unlikely. By comparison, the analogous reaction of metallic Ag with EpB is thermodynamically very unfavorable, consistent with the acknowledged high activity of Ag-based catalysts for olefin and, in this case, butadiene epoxidation.

TABLE 1

Comparison of the Free Energies of Reaction of EpB with Metallic Cu and Ag. EpB is Denoted as C_4H_6O and Butadiene as C_4H_6

Reaction	$\triangle G_{rxn}$ (25°C) (kcal/mol)	$\triangle G_{rxn}$(200°C) (kcal/mol)
$C_4H_6O \rightarrow C_4H_6 + 1/2\ O_2$	+17.7	+12.8
$Cu^\circ + 1/2\ O_2 \rightarrow Cu_2O$	−34.8	−31.5
$Ag^\circ + 1/2\ O_2 \rightarrow Ag_2O$	−2.5	0
$C_4H_6O + Cu^\circ \rightarrow C_4H_6 + Cu_2O$	−17.1	−18.7
$C_4H_6O + Ag^\circ \rightarrow C_4H_6 + Ag_2O$	+15.2	+12.8

Cowell (6) has, in fact, also acknowledged the importance of maintaining the Cu surface in a zero-valent state to maintain reactivity and states that for the Cu(111) surface, the role of the Cs promoter is to act as reducing agent with Cu_2O to form Cu° with subsequent oxidation of Cs° to Cs^{+1}. Vapor deposition of 0.07 ML of Cs metal on the Cu(111) surface resulted in greater tolerance of adsorbed oxygen on the Cu(111) surface toward reactivity with adsorbed butadiene. Thus, while epoxybutene formation was maximized for $\theta_O = 0.04$ ML for the clean Cu(111) surface, the deposition of 0.07 ML Cs on Cu(111) resulted in maximum conversion of butadiene to $\theta_O = 0.07$ ML. Selectivity to epoxybutene was quantitative for both cases. However, in conventional catalyst systems, the alkali promoters are added as alkali salts, i.e., as CsCl, CsOH, or $CsNO_3$. These promoters are incapable of functioning as reducing agents for either Cu_2O or Ag_2O. Even for the case of Cowell, Cs metal would not function as a true catalyst promoter, since it can function only as a one-time, one-electron reducing agent. Once oxidized to Cs^+, it cannot be reduced to Cs° under any type of oxidation reaction condition.

For supported silver catalysts, Cs^+, Rb^+, or even K^+ alkali salt promoters have been used as promoters for ethylene oxide catalysts, since they have been shown to increase selectivity to ethylene oxide (11–13). Similarly, Cs^+, Rb^+, and Tl^+ salts (2, 3, 14) have been employed as promoters for butadiene and styrene epoxidation because they not only increase selectivity, but also dramatically increase both activity and catalyst lifetime (1–3). As postulated previously (1), the role of the promoters is to decrease the desorption energy of epoxybutene, which is involved in the rate-determining step of epoxybutene formation (15). Thus, in the case of silver-catalyzed formation of epoxybutene, the lower desorption energy of

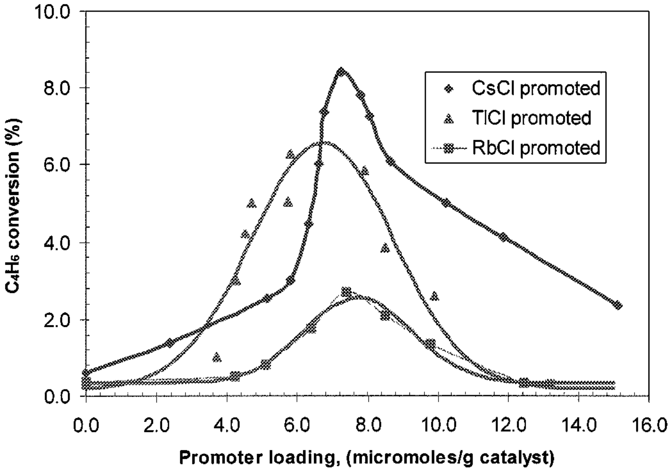

FIG. 1. Effect of promoter loadings on catalytic activities. Promoter loadings are based on micromoles of cation only. At optimum levels of promotion, selectivities to epoxybutene were 90–94% for each of three series of catalysts.

epoxybutene from the Ag surface increases activity (higher turnover frequency), increases selectivity (shorter lifetime of the adsorbed state of EpB lowers the amount of consecutive decomposition/combustion of EpB), and increases lifetime (by reducing the amount of catalyst fouling from condensation reactions of strongly adsorbed EpB). These trends are illustrated in Fig. 1 for three series of promoted Ag catalysts for butadiene epoxidation, where butadiene conversion at steady-state is plotted as a function of promoter loading. In each of the three series of catalysts, at optimum promoter loadings, the selectivities to EpB varied between 90 and 94%, much higher than the selectivity level of 50% for epoxybutene reported for unpromoted Ag catalysts (1). The optimum levels of promoter represent the balance between underpromotion (not all sites are promoted) and overpromotion (surface is poisoned by excess promoter concentration). While not plotted in Fig. 1, activity and selectivity values for catalysts promoted by comparable loadings of $CsNO_3$, $RbNO_3$, and $TlNO_3$ were very similar to those shown for the chloride salts, indicating that the promoter effects are primarily linked to the cation, not the Cl^- anion (2, 3, 14). The promoter loadings in Fig. 1 are expressed as micromoles promoter cation per gram of finished catalyst. Silver loadings in all cases were 12–14% by weight and the catalyst support was fused α-Al_2O_3, typical of the supports used for olefin epoxidation reactions. Potassium chloride at similar loading levels were also evaluated at the same reaction conditions; however, for all KCl loadings there was no enhancement in either activity, selectivity, or catalyst life relative to the unpromoted catalyst.

Interestingly, for the three catalyst series in Fig. 1, maximum activities were observed at approximately the same molar loadings, suggesting a specific and common type of interaction with the Ag surface. Random deposition of the promoter salts would not be expected to show such well-defined "volcano" plots, with each activity maximum occurring at the same molar level of promotion. Further, if promoters functioned by physically blocking or neutralizing acidic sites on the support or even the Ag surface, then potassium salt promoters should also show some type of promoter effect. The fact that KCl did not exhibit a promoter effect similar to those in Fig. 1 further corroborates the explanation that a specific interaction between the Ag surface and Cs^+, Rb^+, or Tl^+ governs the promoter effect, specifically the desorption of epoxybutene from the Ag surface. Selected physical and electronic properties of different promoter cations discussed above are summarized in Table 2. The Cs^+, Rb^+, and Tl^+ salts that have shown positive promoter effects for epoxybutene formation have cations that are large and highly polarizable (16). In fact, the ionic radii and the values of the Pauling polarizabilities of Cs^+, Rb^+, and Tl^+ are the largest of any of the naturally occurring elements. Thus, the successful promoters are large and highly polarizable ions under reaction conditions. As stated above, catalysts promoted by K^+ salts are not active for epoxybutene formation, suggesting that size alone is not the critical factor in determining promoter efficiency. Polarizability, or the measure of an ion's ability to deform its electronic core to external electric fields, may be a more important factor in determining promoter efficiency than size alone, particularly in a push–pull type of electronic effect that could be envisioned to assist in desorption of epoxybutene from surface Ag sites.

It is clear that the type of promoter effect during butadiene epoxidation with promoted Ag catalysts is clearly different from that proposed by Cowell (6) during the substoichiometric reaction of butadiene and oxygen adsorbed on Cu(111). Any attempt to extrapolate the mechanism of promoter action from the Cs–Cu(111) system to the Cs–Ag system should be avoided. The Cs–Cu(111) effect is presumably due to the chemical redox reaction between Cs° and Cu^{1+} to form Cs^{1+} and Cu° and is limited to a single reaction event, while the promoter effect for Cs (or Rb or Tl) and Ag is a true promoter effect that is more consistent with catalytic principles.

TABLE 2

Properties of Promoter Cations for Butadiene Epoxidation. Also Included is the Ionic Radius of Ag^{+1} Cation

Cation (+1)	Ionic radius (Å)	Charge/Surface	Polarizability
Lithium	0.78	0.130	0.03
Sodium	0.98	0.085	0.03
Potassium	1.33	0.045	1.10
Rubidium	1.49	0.035	1.90
Cesium	1.65	0.030	2.90
Thallium	1.44	0.040	4.30
Silver	1.26	—	—

Further, we feel caution must be taken when comparing the intrinsic epoxidation activities of Cu and Ag surfaces. In the case of Cu, we are limited to the substoichiometric reaction between submonolayer coverages of adsorbed oxygen (approximately 8% monolayer coverage of oxygen on Cu) and adsorbed butadiene. This is not a catalytic reaction, rather it is a chemical reaction that occurs over a very narrow range of reaction conditions. At these conditions this reaction is extremely selective for the formation of epoxybutene. The high selectivity of the reaction of adsorbed butadiene on the partially oxygen-covered Cu(111) surface is apparent when compared to the results of Madix and coworkers (17, 18), who also used temperature-programmed methods to study the reaction of saturation coverages of co-adsorbed butadiene and oxygen on Ag(110) surfaces. At temperatures between 400 and 500 K, a variety of reaction products, including 2,5-dihydrofuran, furan, carbon dioxide, and water was formed; epoxybutene was not detected as a reaction product. A key difference however, is that while it is nonselective under these conditions, Ag(110) is a catalyst, since it is not deactivated by formation of Ag_2O and is thus capable of more than one turnover. The results of Madix are also consistent with the results for butadiene epoxidation reported by Monnier (1, 2) for unpromoted Ag/Al_2O_3. In the absence of promoters, epoxybutene is strongly bound and undergoes many side reactions, including formation of furan, 2,5-dihydrofuran, acrolein, crotonaldehyde, carbon dioxide, water, and small amounts of epoxybutene. The use of promoters imparts higher activity, higher selectivity, and longer catalyst life. Typical on-line performance parameters for the silver-based epoxybutene catalysts reported by Monnier (1, 2) give TOF $> 1\ s^{-1}$, even after several months of operation. Selectivity values vary between 87 and 95%, depending upon residence times in the tubular reactor.

4. CONCLUSIONS

In summary, it is important to distinguish between stoichiometric (and even substoichiometric reactions) and catalytic reactions occurring at solid surfaces. First, for a reaction to be considered catalytic, the solid substrate should be capable of at least one additional turnover at conditions typically used to evaluate catalytic reactions, i.e., reactants added simultaneously and not sequentially under very controlled conditions. If the solid substrate must be regenerated after a single turnover, then the reaction is not catalytic. Second, the catalytic reaction product must also be stable in the presence of the catalyst. In the case of metallic Cu surfaces, thermodynamic analysis reveals that the oxidation of metallic Cu by EpB is a very thermodynamically favored reaction, indicating that Cu° is not capable of functioning as an epoxidation catalyst, especially in typical reactor situations where readsorption of epoxide product on Cu° surfaces can and does occur. Using these two criteria, silver is clearly superior to copper for epoxidation of butadiene and other olefins.

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