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Effects of chlorine and chlorine dynamics during silver-catalyzed epoxidation of butadiene

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Abstract

Silver catalysts that have been modified by Cl addition are more stable with respect to thermal runaway during reaction and exhibit higher activity and selectivity for formation of 3,4-epoxy-1-butene. The Cl effect for activity enhancement is most likely electronic in nature and involves subsurface Cl, although a similar role for surface Cl cannot be excluded. Selectivity enhancement and thermal stability may be due to electronic effects as well, but could also be the result of Ag-site blockage on the surface of the catalyst that lowers the rate of combustion of adsorbed EpB. Unlike alkali promoters used for olefin epoxidation, Cl exists in a very dynamic state. Chlorine is continuously removed from the Ag surface by reaction with EpB and paraffin diluents (that are added to the reaction feedstream). Thus, organic chlorides in the ppm range are also continuously added to the feedstream to replace the Cl lost during reaction. Chlorine is deposited by the dehydrohalogenation of organic halides at the surface of the Ag catalyst. The deposition of surface Cl on the Ag surface is a function of the concentration and reactivity of the organic halide in the feedstream, as well as the concentration of vacant Ag sites. The surface Cl is in equilibrium with subsurface Cl, and the concentration of surface Cl controls the concentration of subsurface Cl. Thus, it is possible to chlorinate a Ag catalyst to levels considerably greater than one monolayer equivalent, based on exposed Ag surface, since the Ag subsurface is capable of “storing” substantial amounts of Cl. The excess Cl can be easily removed by reaction with paraffin reaction diluents, such as n-butane, to give an optimally Cl-modified catalyst. However, silver catalysts can also be overchlorinated by exposure to excessively high levels of organic halide and/or temperature, leading to the formation of bulk AgCl, which is catalytically inactive. Such catalysts cannot be regenerated by Cl removal.

Keywords: Chlorine; Chlorine modifiers; Butadiene epoxidation; Epoxybutene; Organic chlorides; Chlorine deposition; Chlorine removal; Subsurface chlorine; Silver chloride

1. Introduction

The Ag-catalyzed epoxidation of olefins requires the addition of both alkali promoters and Cl moderators to attain high selectivities [1–3]. The addition of Cl moderators to Ag catalysts used for C_2H_4 epoxidation to increase selectivity to ethylene oxide (EO) is well known. Some of the very earliest patents describing the Ag-catalyzed epoxidation of ethylene discuss the beneficial role of Cl moderators for improving the selectivity to EO [4,5]. However, the method in which selectivity enhancement is attained is very poorly understood, even though it has been rigorously studied, primarily using model catalysts [6–12], although some studies have included real catalyst compositions [13–16]. Campbell and co-workers [6–8] have studied Cl-precovered Ag(111) and Ag(110) surfaces using ultrahigh vacuum techniques and then evaluated these surfaces for EO activity and selectivity using a microreactor attached directly to the UHV system. The authors concluded that under reaction conditions of 100 Torr total reactor pressure and temperatures between 165 and 335 °C (approximately 5000 turnovers of C_2H_4 reacted/surface Ag sites), the presence of Cl improves selectivity at the expense of overall activity by formation of surface Ag ensembles that are too small for C_2H_4 combustion, but not too small for EO formation. On the other hand, Lambert and co-workers [9–11] have examined similar Ag single crystal surfaces under similar conditions and

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concluded that the role of Cl, particularly subsurface Cl, could be rationalized by the way it alters the electron density on O_{ads} (oxygen adsorbed on Ag). By competing for Ag metal electrons, the electron density of O_{ads} was lowered, which favored the electrophilic addition of O_{ads} to the C=C of adsorbed C_2H_4 to form EO, rather than the otherwise more electron-rich O_{ads} undergoing nucleophilic reaction with one of the C–H bonds of adsorbed C_2H_4 (and forming CO_2/H_2O). Very recently, Lambert and co-workers [12] have extended their studies on the effects of halogens on EO catalyst performance to include the effects of F, Br, and I. Specifically, Lambert and co-workers report that when unpromoted Ag/α-Al_2O_3 catalysts are modified by F, Cl, Br, and I by pulsing aliquots of $CH_2{=}CHF$, CH_2Cl_2, C_2H_5Br, and CH_3I-containing gas mixtures to the feed stream, respectively, the selectivities to EO are improved for each reaction condition. Because the selectivity enhancement was greatest for the Cl-modified, Ag catalyst, the authors argue that these results support their conclusion that halogen promotion is electronic, rather than geometric in nature, since the electron affinity for Cl is greater than for the other halogens. In all cases, activities were lowered as the Ag/α-Al_2O_3 catalyst was dosed with the organic halide-containing gas stream.

Other supported Ag catalysts have also been studied to determine the role of Cl moderators under continuous flow conditions. The use of real catalysts has introduced added variables in determining the role(s) of Cl in olefin epoxidation, including different methods of adding Cl to the Ag catalyst and the recognition that Cl is continuously removed from the Ag surface during extended reaction by components in the reaction gas streams. Force and Bell [13] used infrared spectroscopy to examine a Ag/SiO_2 catalyst wafer in a recirculation loop reactor under reaction conditions. Chlorine was added to the Ag catalyst by circulating a gas mixture containing 8.2% 1,2-dichloroethane (DCE) before the reaction of C_2H_4 and O_2 to form EO. The authors concluded that surface Cl (on Ag) resulted in lower concentrations of both adsorbed ethylene and oxygen, which led to the more selective formation of EO, which was favored at lower surface concentrations of $(C_2H_4)_{ads}$ and O_{ads}. Combustion to CO_2 and H_2O, the authors argued, was favored at higher surface concentrations of both adsorbates. Thus, the Cl functioned by diluting the Ag surface to favor lower surface coverages of adsorbates. Ostrovskii and co-workers [14] examined the effects of S, Se, and Cl on Ag catalysts by incorporation of the moderators by coprecipitation during catalyst preparation and concluded that for levels less than 10% surface coverage, Cl increased both the activity and the selectivity for EO formation. At higher initial levels of Cl, activity declined to levels less than for the unmodified Ag catalyst, while selectivity remained at higher levels. The authors claimed that Cl weakened the strength of the Ag–O bond, making it more active for EO formation. Higher levels of Cl gave an overall effect of surface poisoning of Ag sites by Cl coverage. Petrov et al. [15] have also used a recirculation reactor to study the role of Cl during C_2H_4 epoxidation. Chlorine was added to the catalyst during reaction by pulsing doses of DCE to the recirculation loop. The authors noted that at high concentrations of DCE (about 300 ppm), the Ag catalyst was completely poisoned by high coverages of Cl on Ag. At DCE levels of approximately 1–30 ppm in the feedstream, stable behavior was observed. The authors concluded that Cl increased the selectivity for EO formation by inhibiting the dissociative adsorption of O_2 on Ag. Because molecular oxygen was believed to be the oxygen species responsible for EO formation, while atomic oxygen led to CO_2 and H_2O formation, the selectivity to EO was enhanced. However, it should be noted that experimental data from other researchers [1,2] strongly supported the view that atomic oxygen, not molecular oxygen, was responsible for EO formation, thus bringing into question the conclusions of Petrov et al. Berty [16] has discussed results obtained from an internal recycle reactor for C_2H_4 epoxidation, whereby Cl was added to the catalyst during reaction by the addition of ppm levels of DCE. Like Petrov et al., excessive levels of DCE caused catalyst deactivation. However, using appropriate levels of DCE in the $C_2H_4 + O_2$ feedstream, which also contained some C_2H_6 as an impurity in the C_2H_4, the selectivity to EO was improved, while overall activity declined somewhat. The levels of C_2H_6 in the C_2H_4 feedstream could build up to levels as high as 5–10% during extended periods of recycle. Further, by using more sensitive GC detectors, he determined that some of the DCE was not accounted for during reaction, but smaller levels of vinyl chloride (VCl) and ethyl chloride (EtCl) were observed and built up during reaction. Under some reaction conditions, experimental data showed that more Cl was leaving the catalysts as organic chlorides than the DCE which was being fed, indicating that the Ag catalyst could effectively store Cl. Further analysis led Berty to the conclusion that (1) Cl was deposited on Ag by the dehydrochlorination of DCE to form vinyl chloride and formally HCl, (2) Cl was removed from Ag by the oxychlorination of C_2H_6 to form EtCl and H_2O, and (3) VCl and EtCl could also function as chlorinating agents, but neither was as active as DCE. Similar observations have been made by others, mostly in the patent literature [17,18]. Moskovits et al. [19], however, examined the interaction of DCE with vapor-deposited Ag films using surface-enhanced Raman spectroscopy and concluded that DCE undergoes decomposition on clean Ag surfaces to form C_2H_4 and Cl_2 at temperatures as low as 55 K, results clearly at odds with the interaction of DCE on conventional catalysts under reaction conditions.

In addition to the Cl moderator studies for C_2H_4 epoxidation, Monnier and co-workers [20,21] have discussed the use of Cl moderators for the Ag-catalyzed epoxidation of butadiene to 3,4-epoxy-1-butene (EpB). The authors found that ppm levels of various organic chlorides must be added to the C_4H_6 and O_2-inclusive feedstream to maintain long-term stability with respect to thermal runaway under reaction conditions, even though the catalysts were often promoted with CsCl, and, thus, contained several hundred ppm of Cl from the preparative step. The need to replace the preexistent high levels of Cl after different periods of time on-line indicated that Cl was continuously being lost from the Ag catalyst. The rate of Cl loss from Ag was strongly linked to the choice of inert hydrocarbon diluent used in the reactor feedstream. The rate of Cl loss from Ag by paraffins followed the order $n\text{-}C_4H_{10} > n\text{-}C_3H_8 > C_2H_6 \gg CH_4$. Further, the selective reaction product, EpB, also appeared to be capable of removing Cl from the Ag surface, since there was evidence of Cl loss, even when N_2 was used as the gas-phase reaction diluent. The rate of Cl removal by the paraffin diluents followed the expected order based on the reactivity of secondary versus primary C–H bonds [22–24]. Because $n\text{-}C_4H_{10}$ contains twice as many secondary C–H bonds than $n\text{-}C_3H_8$, the $n\text{-}C_4H_{10}$ is statistically favored over $n\text{-}C_3H_8$. To maintain adequate Cl coverage on Ag, it was essential to use higher levels of organic chlorides in the feedstream when $n\text{-}C_4H_{10}$ was used as the diluent, rather than CH_4. The reactivity of the organic chlorides used as moderators also followed expected trends:

$$\begin{aligned}&\text{DCE} > \text{2-chlorobutane (2-CB)} > \text{2-chloropropane (2-CP)}\\&\quad > \text{EtCl} > \text{VCl} > CHCl_3 > CH_2Cl_2.\end{aligned}$$

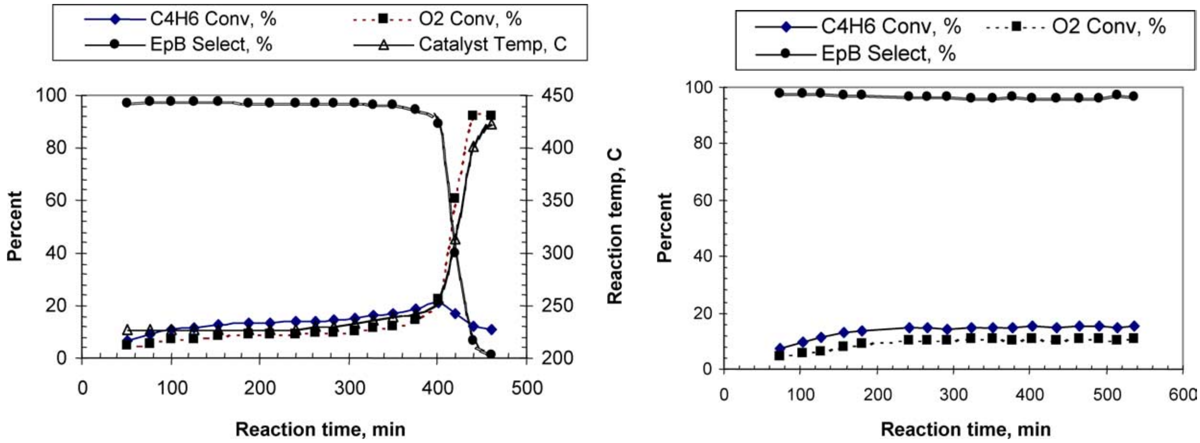
Since Cl deposition occurred by dehydrochlorination, organic chlorides that contained acidic C–H groups vicinal to the C–Cl bond were also more active toward dehydrochlorination. This explains why DCE was more reactive than EtCl; because Cl is strongly electronegative, geminal C–H groups (on $-CH_2Cl$) are relatively more acidic than in the case of the CH_3– group for EtCl. Mochida et al. [25] studied the catalytic dehydrochlorination of 1,1,2-trichloroethane and found that the formation of 1,1-dichloroethylene is highly favored over the formation of 1,2-dichloroethylene, because the C–H group on the $CHCl_2$ end of 1,1,2-trichloroethane is more acidic than either of the C–H groups on the CH_2Cl portion.

The above results indicate the degree of uncertainty surrounding, not only the role(s) of Cl moderators for olefin epoxidation, but also how much surface Cl even exists under steady-state reaction conditions. The continuous removal of Cl from Ag during reaction and different reactivity trends of gas-phase organic chlorides make it very difficult to even infer the concentration of surface Cl. Further, the apparent existence of subsurface Cl adds another level of uncertainty. It also appears that, while the model studies are very informative, longer periods of reaction time are required to reach some steady-state concentration of Cl on the Ag surface. This may explain why there are different results and interpretations for the model studies; insufficient exposure time to meaningful reaction conditions makes it difficult to determine the effects of Cl on Ag surfaces. Because of the importance of having critical amounts of Cl on the Ag surface to prevent thermal runaway during butadiene epoxidation [20,21], we have carefully investigated the factors that influence both the amounts and the roles of Cl that control the performance of catalysts used for butadiene epoxidation. In this paper, we present results showing the dynamic nature of Cl on Ag catalysts used for butadiene epoxidation. We show the effects of temperature and reactivities of different organic chlorides and paraffinic diluents on Cl concentrations. We also present data showing that Cl increases both selectivity to EpB and activity for C_4H_6 conversion. Because of the dynamic nature of Cl on Ag, we are unable to determine how Cl affects both activity and selectivity, although references to relevant EO catalysts are made.

2. Experimental

The preparation of the CsCl-promoted, Ag/α-Al_2O_3 catalysts has been summarized in earlier reports [20,21]. Some of the catalysts were supported on Norton SA-5552 fused α-Al_2O_3 rings, while others were supported on Norton SA-5562 rings. The SA-5552 rings were 0.25 inch in diameter with a surface area of 0.43 m^2/g, a total pore volume of 0.37 cc/g, and a median pore diameter of 7 µm. The Ag weight loadings for the 5552-supported catalysts were either 12 or 15%. Chemisorption of a similarly prepared unpromoted Ag/SA-5552 catalyst by O_2 at 170 °C, according to the method of Vannice et al. [26] gave a surface concentration of 1.5×10^{18} Ag sites/g catalyst for the 15% Ag loading, corresponding to an average Ag crystallite size of 0.62 µm. The catalysts that were supported on SA-5562-fused α-Al_2O_3 rings also contained either 12% Ag or 15% Ag loadings. The SA-5562 rings had a surface area of 0.7–0.8 m^2/g with a total pore volume of 0.55 cm^3/g and a median pore diameter of 7 µm.

Most of the features of the microreactor used in this study have been presented in earlier publications [27,28]. The only difference is that a Cl-sensitive detector, Model 4420 Electrolytic Conductivity Detector, OI Corporation, was attached to the exit of a second Poraplot Q capillary column mounted in the HP 6890 gas chromatograph that was used for GC analyses. One of the Poraplot Q columns was hooked to a TC detector to measure reaction products during C_4H_6 epoxidation experiments, while the second column was hooked to the Electrolytic Conductivity Detector. By turning a six-port Valco switching valve, the contents of the in-line sample loop could be directed to either of the GC columns. The Electrolytic Conductive Detector works by reductive hydrogenolysis of organic halides which are eluted in a normal manner from the GC column. Before the eluted peak enters this halogen-sensitive detector, it is mixed with approximately 100 SCCM of H_2. The organic halide component undergoes catalytic, reductive hydrogenolysis while flowing through a capillary nickel tube maintained at 800 °C. Organic halides are converted to a mixture of CH_4, other small hydrocarbons such as C_2H_6, and HCl gas and are swept from the Ni reduction tube via Teflon tubing to a thin liquid film, direct current (DC) detector, employing n-propanol as the



(a) (b)

Fig. 1. (a) No organic halide cofeed. (b) 4 ppm DCE added after 270 min on-line. Reaction temperature was stable at 228 °C throughout run. Catalyst is 12 wt% Ag/SA-5552 alumina rings, promoted with 1.12 mg CsCl/g catalyst + 0.16 mg $CsNO_3$/g catalyst to give final nominal promoter compositions of 990 ppm Cs/g catalyst and 235 ppm Cl/g catalyst. Feed composition is 17% O_2, 17% C_4H_6, balance N_2 at GHSV = 2200 h^{-1}. Catalyst was brought on-line at 200 °C and heated to 228 °C over a 2-h time interval. Reaction times in the figures below refer to reaction at 228 °C.

solvent. Because only strongly ionic components are dissociated in a weakly ionizing solvent such as n-propanol, the only component that generates a DC current is dissociated HCl, existing as H^+ and Cl^- species. The detector is essentially insensitive to all other reaction components, including O_2, CO_2, H_2O, EpB, C_4H_6, and paraffin diluents. The level of organic halide sensitivity is sub-ppm and all organic halides have the same response factor per Cl. Thus, 2-CB, EtCl, and VCl all have the same response factor which is 50% of that for DCE. This detector, coupled with the Poraplot Q column, permitted resolution and quantification of all volatile organic halide components that exited the reactor.

The second reactor system used was a larger scale, tubular reactor 4 feet in length, i.d. of 1.60 inches, operated in a downflow mode. The flow rate used in this reactor was typically 3 SLM; for a catalyst volume of 420 ml, the catalyst bed was 12 inches in length, to give a GHSV = 1200 h^{-1}. A three-junction C/A thermocouple was embedded in the catalyst bed; the top, middle, and bottom T/C junctions were 1, 6, and 11 inches, respectively, from the top of the catalyst charge. On-line GC analysis was made using a 100 SCCM slip stream of the total reactor flow.

Cs and Ag loadings for the different catalysts were made using atomic absorption-inductively coupled plasma (AA-ICP). X-ray fluorescence was tried for Cl analysis for the catalysts that were promoted with CsCl. The lack of sensitivity and scatter in the data made this method unreliable, so the Cl loadings for the CsCl promoted catalysts is assumed to be equivalent to the molar loadings that were determined for Cs. Surface analyses by XPS were conducted using a Physical Electronics Model 5400 spectrometer employing monochromated Al-K_α radiation. Finally, powder X-ray diffraction measurements were conducted on a Phillips PW-1840 Diffractometer using Cu-K_α radiation ($\lambda = 0.15405$ nm).

3. Results

The data in Fig. 1 illustrate the need for continuous addition of ppm levels of organic chloride (RCl) to the C_4H_6 and O_2-inclusive feedstream during steady-state operation. The curves in Fig. 1a illustrate that severe catalyst instability leading to a thermal runaway to temperatures in excess of 400 °C occurs when RCl is not present in the feedstream, even though this catalyst contained approximately 235 ppm Cl added as CsCl during catalyst preparation. Fig. 1b shows that addition of 4 ppm DCE after 270 min of reaction time (fresh sample) prevents thermal runaway and permits active and selective catalyst performance over the same time interval. The thermal runaway under reaction conditions is most likely due to the loss of selectivity to EpB by insufficient surface Cl, resulting in combustion to form CO_2 and H_2O; the much higher heat of reaction (550 kcal/mol for CO_2 and H_2O formation) versus 25 kcal/mol for EpB formation [3] results in rates of heat release that far exceeds rates of heat removal. Since N_2 was used as the inert diluent during the reaction, some species other than a paraffin diluent caused the Cl loss from the catalyst. The XPS results summarized in Table 1 for a catalyst sample after reaction strongly imply that EpB is the primary cause for Cl loss. This sample had exhibited stable performance over an 8- to 12-h period of time before a thermal runaway in the bottom portion of the reactor occurred. Surface analysis indicated that the thermal excursion is linked to the loss of Cl from the Ag surface; over 50% of the surface Cl had been removed during reaction. Note that the Cs/Ag atomic ratios were relatively constant throughout the reaction and were similar to the fresh catalyst. The somewhat higher Cs/Ag ratio for the sample from the bottom of the reactor may be due to the concurrent loss of Cl from the same Ag surface, thus enriching the Cs concentration. Regardless, the thermal in-

$$n\text{-}C_4H_{10} + \text{Ag-Cl} \rightarrow \text{Ag} + \text{2-CB}$$
$$\text{DCE} + \text{Ag} \rightarrow CH_2{=}CHCl + \text{Ag-Cl}$$
$$C_2H_6 + \text{Ag-Cl} \rightarrow \text{Ag} + CH_3CH_2Cl$$

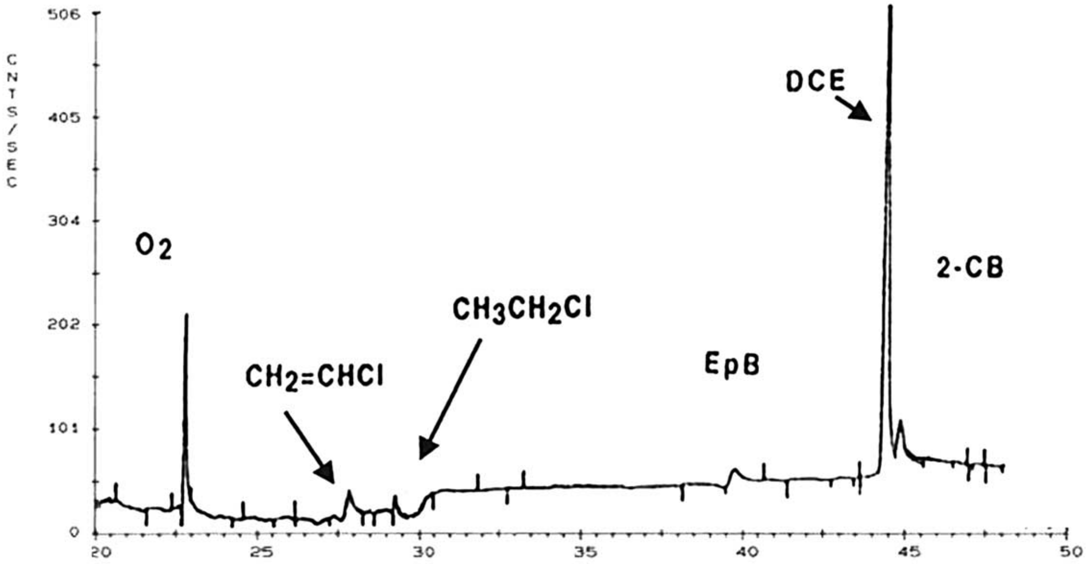


Fig. 2. Gas chromatogram of reactor effluent using Electrolytic Conductor Detector. The catalyst was CsCl-promoted, 12% Ag/SA-5562 (700 ppm Cs). Feed is 9% C_4H_6, 18% O_2, 20% n-C_4H_{10}, 53% C_2H_6 + 5 ppm DCE at GHSV = 20,000 h^{-1}. Reaction temperature = 210 °C. DCE = 1,2-dichloroethane and 2-CB = 2-chlorobutane.

Table 1
XPS surface analysis of a used catalyst after thermal runaway

Reaction condition	Reaction temp (°C)	T/C position, from top of bed	Cl/Ag atomic surface ratio	Cs/Ag atomic surface ratio
Before reaction			0.13	0.29
Controlled	227	1 in.	0.11	0.27
Controlled	228	6 in.	0.10	0.29
Exothermic	260–300	11 in.	0.045	0.36

Catalyst was CsCl-promoted, 15% Ag/SA-5552, Cs loading = 560 ppm Cs. Catalyst bed was approximately 12 inches in height and 1.60 inches in diameter. The feed stream was 17% O_2, 17% C_4H_6, balance N_2 at GHSV = 1200 h^{-1}. No RCl was added to the feed stream during reaction.

stability does not appear to be due to changes in the Cs/Ag ratio. These results also suggest that EpB is the likely Cl-stripping agent, since the only gas-phase components that increase in concentration in this downflow mode of operation are CO_2, H_2O, and EpB. Neither CO_2 nor H_2O have been linked to Cl loss from Ag catalysts in the literature. Earlier work by Monnier et al. [27,29] has established that EpB is strongly adsorbed on Ag surfaces; a strongly bound and reactive species such as EpB is a very likely source as the Cl-stripping agent. Efforts to identify any such EpB-linked chloride species have been unsuccessful, even though extensive analyses of liquid reaction condensates by GC-MS obtained by cold trapping have been conducted. Chlorine-containing compounds derived from C_4H_6 have also been ruled out; none has been detected, even though blank experiments have shown that ppm levels of 2-chloro-1,3-butadiene, 3-chloro-1-butene, and 4-chloro-2-butene (expected products if butadiene is capable of removing Cl from the Ag surface) can be easily detected by the Electrolytic Conductivity Detector. The thermal profile of the used catalyst in Table 1 also argues against C_4H_6 as the likely cause of Cl stripping, since the concentration of C_4H_6 actually decreases during downflow operation.

The gas chromatogram shown in Fig. 2 illustrates the sensitivity and selectivity of the Electrolytic Conductivity Detector. The GC trace represents the Cl content of all stable gas-phase organic chloride components in the reaction product stream. Note that even though the organic chlorides constituted only a few ppm of the total gas stream, they were quite easily detected. The peak for 5 ppm DCE was off-scale; the peaks for vinyl chloride (VCl), ethyl chloride (EtCl), and 2-chlorobutane (2-CB) indicate concentrations in the sub-ppm level. Interestingly, even though the concentration of C_2H_6 was almost three times higher than n-C_4H_{10}, the peak for 2-CB was larger than the peak for EtCl, indicating the higher reactivity of n-C_4H_{10} for Cl removal from the Ag surface. The presence of VCl also confirms that dehydrochlorination of DCE is the preferred route for Cl deposition on the Ag surface. Oxygen and EpB, present in molar fractions of approximately 0.18 and 0.03, respectively, gave only small responses with the Electrolytic Conductivity De-

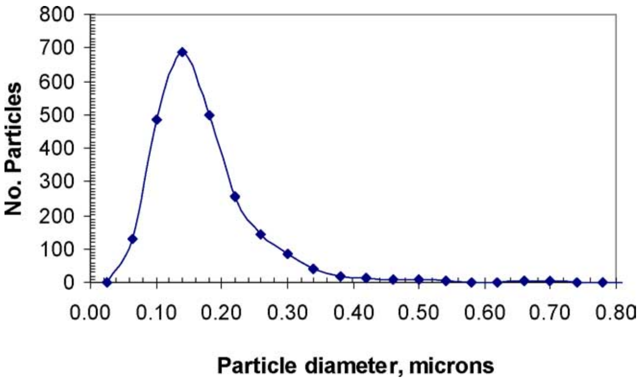


Fig. 3. Ag particle size distribution for 15% Ag/SA-5562 catalyst promoted with $CsNO_3$ (Cs loading = 1250 ppm). Ag particles counted using Visilog software.

tector. Ethane was virtually undetected, while n-C_4H_{10} was represented as the slight baseline shift after the EtCl peak.

In order to more closely examine the Cl dynamics occurring during reaction, a large sample of $CsNO_3$-promoted, 15% Ag/SA-5562 catalyst (1250 ppm Cs) was prepared and used for an extensive series of Cl pretreatments and C_4H_6 epoxidation reactions to examine Cl deposition and Cl loss from the Ag catalyst. Before the Cl experiments were conducted, the catalyst was examined by scanning electron microscopy and the Ag crystallite distribution was determined so that the surface concentration of the Ag sites could be estimated. The Ag particle-size distribution is shown in Fig. 3. From this size distribution and the Ag weight loading, the concentration of Ag surface sites could be determined, assuming either spherical or hemispherical particle shapes (same answer for each geometry), which closely approximated the SEM images. The calculated surface concentration was found to be 3.69×10^{18} Ag sites/g catalyst. The Ag-site concentration does not take into consideration the presence of Cs on the Ag surface, since earlier experiments had indicated that Cl deposition appeared to be independent of Cs previously deposited on the Ag surface.

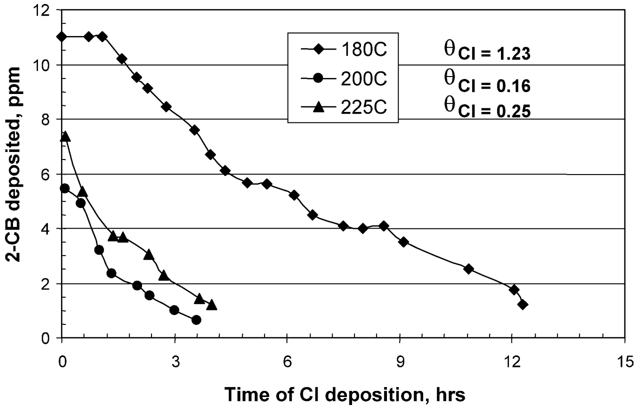


Fig. 4. Chlorine deposition on $CsNO_3$-promoted, 15% Ag/SA-5562 (Cs loading = 1250 ppm) done sequentially at 180, 200, and 225 °C on the same sample of catalyst from a gas stream containing 400 SCCM CH_4, 100 SCCM He, and 11 ppm 2-CB. Catalyst weight was 12.0 g, giving a total Ag surface concentration = 4.42×10^{19}.

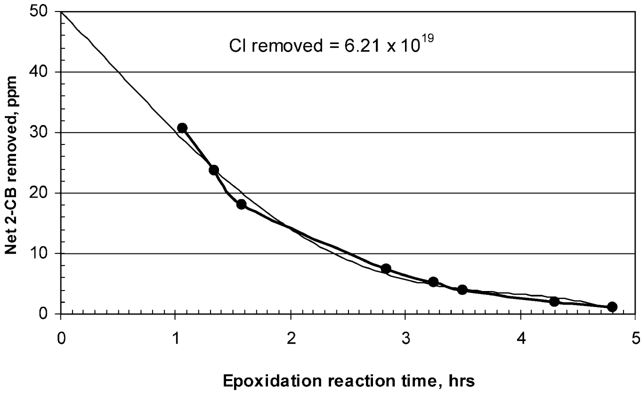


Fig. 5. Chlorine removal from $CsNO_3$-promoted, 15% Ag/SA-5562 (1250 ppm Cs) during C_4H_6 epoxidation reaction conditions. Catalyst prechlorination sequence shown in Fig. 4. Reaction temperature = 200 °C, feed stream = 9% C_4H_6, 18% O_2, 73% n-C_4H_{10} + 2 ppm 2-CB at GHSV = 5500 h^{-1}. Chlorine deposition in Fig. 4 was 7.29×10^{19} Cl. Curve fit for experimental data is shown as lighter line.

The results in Fig. 4 show sequential Cl deposition isotherms at 180, 200, and 225 °C on the same sample of $CsNO_3$-promoted, Ag/SA-5562 catalyst using 2-CB as the chlorinating agent. Chlorine deposition was observed at all three temperatures, but was highest at 180 °C since there was no preexisting Cl on the catalyst surface. The sum of Cl uptakes at the three temperatures is considerably higher than the calculated monolayer coverage of Cl. The integrated Cl uptake curves give a value of 7.24×10^{19} Cl deposited, equivalent to 1.64 Ag monolayers. These results indicate that some of the Cl has gone into the subsurface Ag, consistent with earlier observations [30,31] for Cl penetration into the bulk of Ag(111) surfaces at temperatures as low as room temperature. The deposited Cl is quite labile as shown in Fig. 5 for the same catalyst when it is used for C_4H_6 epoxidation immediately after the Cl deposition experiments had been completed. At a reaction temperature of 200 °C in a typical reaction feedstream, there is substantial removal of Cl from the catalyst, even though the feedstream contains 2 ppm 2-CB. Levels of 2-CB as high as 30 ppm were experimentally observed; curve fitting back to initial time on-line infers 2-CB concentrations as high as 50 ppm, clearly indicating the reactivity of n-C_4H_{10} in removing excess Cl from the Ag catalyst. The integrated Cl uptake curve indicates that 6.2×10^{19} Cl atoms have been removed from the catalyst, equivalent to 1.40 monolayers of Cl. This high level of Cl removal clearly suggests that even subsurface Cl is labile, and is almost certainly in equilibrium with surface Cl under reaction conditions. The activity data for this catalyst are shown later in the discussion.

The data in Fig. 6 compare the reactivities of various organic chlorides for Cl deposition on the $CsNO_3$-promoted, Ag/SA-5562 catalyst. As expected, the dehydrochlorination activities are 2-CB > EtCl > VCl, and are consistent with the reactivities of both the C–Cl bonds and the C–H bonds vicinal to the C–Cl bonds of the organic chlorides. These

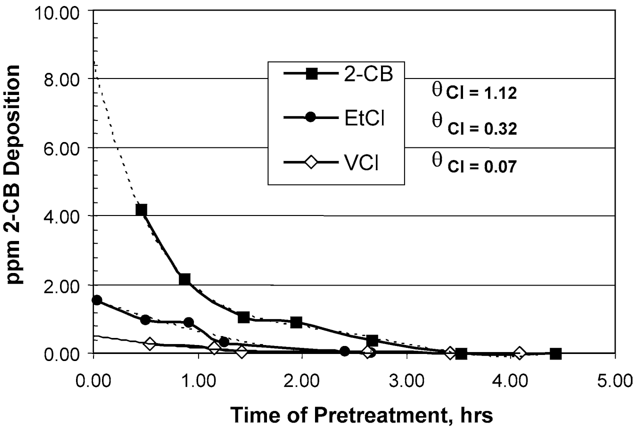
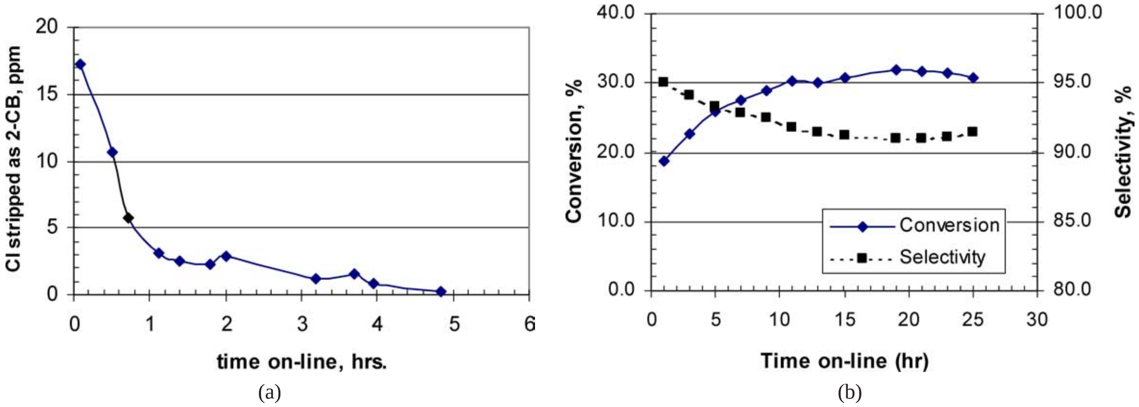


Fig. 6. Chlorine deposition on $Cs(NO)_3$-promoted, 15% Ag/SA-5562 (1250 ppm Cs) at 180 °C. Chlorine sources are 2-CB, EtCl, and VCl; each pretreatment gas stream composed of 400 SCCM CH_4, 100 SCCM He and 10–11 ppm RCl. Fresh catalyst sample (1.00 g) used for each Cl deposition experiment.

results also indicate that higher concentrations of EtCl and VCl are needed in the reaction feedstream to maintain the same Cl coverage on Ag as that for 2 ppm 2-CB, which is normally added to the C_4H_6, O_2, and n-C_4H_{10} feedstream during reaction conditions.

Chlorine addition to Ag can also be made during preparation of the catalyst. If the Ag catalyst is promoted with CsCl addition by coimpregnation with the soluble Ag salt (usually either $AgNO_3$ or an amine-solubilized $Ag_2(C_2O_4)_2$), Cl will be present without the need for a separate Cl deposition step. The results in Fig. 7 show the Cl dynamics for a CsCl-promoted, 12% Ag/SA-5562 catalyst (Cs loading is 700 ppm) when the catalyst is brought on-line under typical reaction conditions. Note that rapid and extensive Cl removal occurs in the first 5 h on-line, even in the presence of 2 ppm 2-CB in the feedstream. The amount of Cl removed in Fig. 7a corresponds to 1.52×10^{19} Cl atoms, which is 44% of the theoretical Cl that was present as CsCl during the preparation step. The nominal Cl content of this catalyst charge was 3.8×10^{19} Cl atoms, which is equivalent to 1.07 monolayers of Cl on the Ag surface. The activity data in Fig. 7b show that loss of Cl in the first 5 h of operation is accompanied by a concurrent increase in activity from approximately 18 to 26% C_4H_6 conversion, suggesting that loss of excess surface Cl from reactive Ag sites may be responsible for the higher activity. Catalytic activity continues to increase until 15 h of reaction time, suggesting that further surface Cl was removed over this time interval. The data in Fig. 7a indicate, however, that the majority of Cl was removed in the first 5 h of reaction time. The fraction of Cl removed from the CsCl-promoted catalyst is less than for the catalyst prechlorinated by 2-CB addition (Fig. 5) over the same time interval. In the latter case, 6.21×10^{19} Cl atoms were removed from the catalyst, corresponding to 85% of the total Cl deposited. This large difference is consistent with the methods of Cl deposition; addition during coimpregnation with the Ag salt should give a more uniform distribution of Cl throughout the Ag crystallite than surface deposition by dehydrochlorination of 2-CB, which should at least initially favor a Cl-rich Ag surface.

This observation is supported by the data in Fig. 8, which show catalytic activities as a function of reaction time for a series of $CsNO_3$-promoted, 15% Ag/SA-5562 catalysts, prechlorinated to different levels. The activity vs reaction time curves show that, in general, the catalysts having higher levels of Cl deposition require longer to reach steady-state activities. The catalysts prechlorinated at $\theta_{Cl} = 0.81$ and 1.04 require approximately 80 h to reach stable activities, while the two catalysts at lower levels of Cl addition exhibit steady-state activities at approximately 40 h on-line. Note that for these reactions, CH_4 was used as the inert feedstream diluent; thus, EpB was the likely Cl removal agent in these reactions. Regardless, catalysts with higher levels of Cl need longer reaction times to remove excess surface Cl from the active Ag sites. As a corollary, the catalysts with lower Cl loadings have higher initial activities, since more of the Ag surface is available for reaction. Interestingly, the two catalysts with θ_{Cl} values of 0.026 and 0.19 appear to have lower steady-state activities than the two catalysts with θ_{Cl} values



(a) (b)

Fig. 7. (a) Cl removed from catalyst during reaction of 9% C_4H_6, 18% O_2, balance n-C_4H_{10} + 2 ppm 2-CB at GHSV = 5500 h^{-1}. (b) C_4H_6 epoxidation for catalyst as a function of reaction time. Chlorine removal and catalyst performance of CsCl-promoted, 12% Ag/SA-5562 catalyst at 200 °C. Cs loading was 700 ppm Cs, corresponding to 5.26 micromoles each of Cs and Cl added during catalyst preparation. Catalyst was given no Cl-pretreatment prior to reaction.

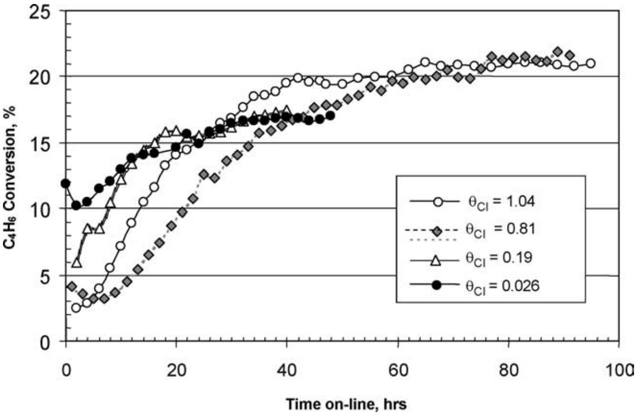


Fig. 8. Evaluation of $CsNO_3$-promoted, 12% Ag/SA-5562 catalysts given different Cl pretreatments. Reaction temperature = 197 °C and feed composition = 9% C_4H_6, 18% O_2, 73% CH_4 + 2 ppm 2-CB at GHSV = 5800 h^{-1}.

of 0.81 and 1.04 (although the catalyst with $\theta_{Cl} = 0.19$ may still be slowly increasing when the reaction was stopped). This would appear to be contradictory to the previous data that suggest similar equilibrium coverages of surface Cl and subsurface Cl should result for all catalysts as long as the reaction feedstream compositions are similar; longer periods of reaction time to reach similar equilibrium coverages should simply be required for catalysts having lower initial levels of surface Cl. That is, the catalyst prechlorinated at a level of $\theta_{Cl} = 0.026$ should ultimately attain the same activity as the catalyst initially prechlorinated at a level of $\theta_{Cl} = 1.04$. Clearly, the catalytic activities for the catalysts having $\theta_{Cl} = 0.81$ and 1.04 are essentially identical, yet are considerably higher than for the other two catalysts. The explanation is likely linked to the concentration of vacant Ag surface sites during C_4H_6 epoxidation conditions. Earlier work [3,27,29] has shown that both EpB and CO_2 are strongly adsorbed on the Ag surface during reaction conditions, resulting in observed reaction orders of approximately −0.5 and −1.0 for CO_2 and EpB concentrations, respectively, under steady-state reaction conditions. This implies a very limited concentration of vacant Ag sites under these conditions, which is where Cl deposition occurs [6–11]. In fact, earlier work of Lambert and co-workers for Cl deposition on CO_2-covered Ag(111) surfaces [32] and EO-covered Ag(111) surfaces [11] showed that Cl deposition was greatly limited by the presence of these two adsorbates. Barteau and co-workers [29,33,34] have shown that EpB is much more strongly adsorbed on Ag than EO; thus, the effect of adsorbed EpB should be even more restrictive than EO for Cl deposition under normal reaction conditions.

The importance of adequate Cl concentrations on Ag catalysts during reaction is further emphasized in the data of Fig. 9. Catalyst activity curves at 210 °C (catalysts were run at 200 °C for 30 h to remove excess Cl from the catalysts before the temperature was raised to 210 °C) as a function of reaction time are shown for a series of catalysts, each prechlorinated to a different level before being evaluated under similar conditions using different organic chlorides as Cl sources. The activities for the samples prechlorinated at $\theta_{Cl} = 1.64$ and 1.03 are virtually identical, consistent with earlier data. The catalyst given no Cl pretreatment before reaction is much less active than the other catalysts, also consistent with earlier data and further suggesting that the scarcity of vacant Ag sites under reaction conditions limits the deposition of Cl by 2-CB. The slow increase in activity for this catalyst does suggest, however, that Cl deposition does slowly occur, resulting in higher activity. Most interesting is the activity trend of the catalyst prechlorinated at $\theta_{Cl} = 0.62$ that uses VCl as the chlorinating agent. The activity of this catalyst shows a steady decline in the presence of 3 ppm VCl in the feedstream. Only when the VCl level is increased to 10 ppm does the activity stabilize. Raising the VCl level in the feedstream further to 20 ppm results in a modest increase in catalytic activity. This activity trend is consistent with the reactivity of VCl relative to other organic chlorides, namely 2-CB and EtCl, in Fig. 9. Failure to increase the levels of less reactive organic chlorides in C_4H_6 epoxidation feedstreams results in slow, gradual loss of catalytic activity.

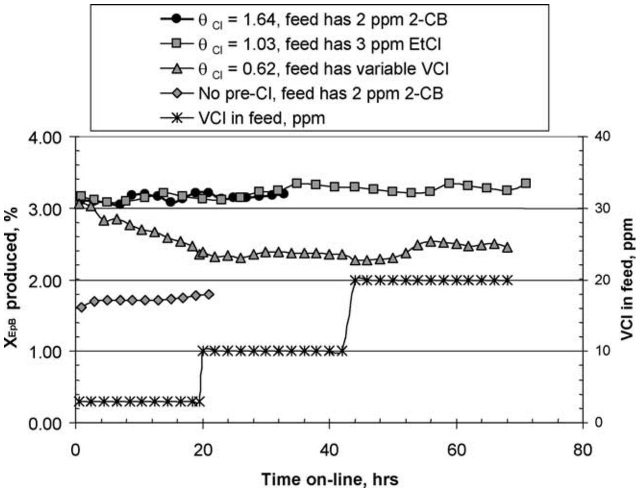
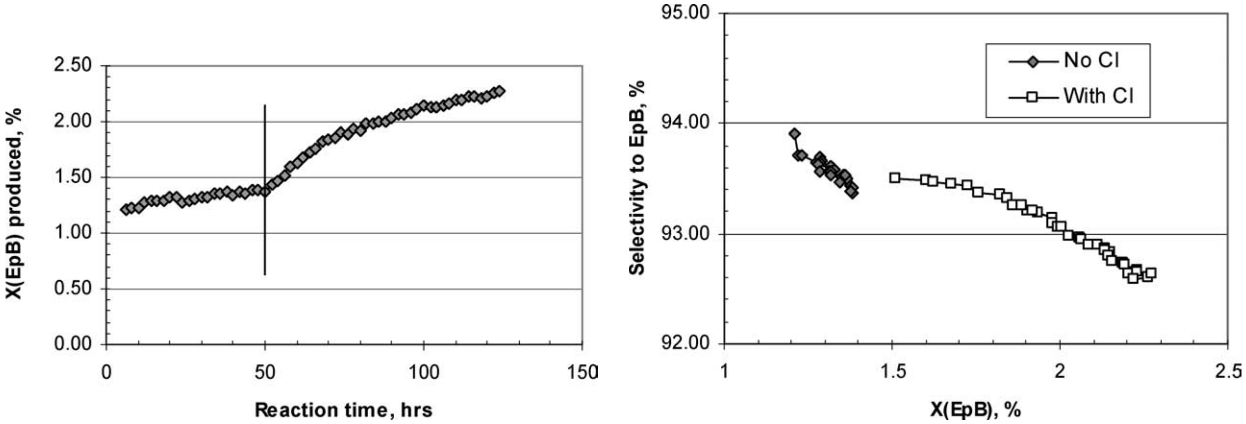


Fig. 9. Performance of $CsNO_3$-promoted, 15% Ag/SA-5562 catalyst after different prechlorination conditions. Each catalyst was evaluated for 30 h at 200 °C, before the temperature was raised to 210 °C. Data shown is for reaction temperature = 210 °C in a feed composition of 9% C_4H_6, 18% O_2, 73% n-C_4H_{10} + RCl as noted. Total GHSV = 5800 h^{-1}.

While it is apparent from the data in Figs. 8 and 9 that some Cl is required for maximum activity, it is not obvious whether the Cl responsible for higher activity is present on the surface or the subsurface of the Ag catalyst. The data in Figs. 7, 8, and 9 strongly indicate that removal of at least some of the surface Cl is linked with catalyst activation, so if surface Cl also increases activity, then opposing effects of surface Cl exist. That is, while activation is apparently linked with removal of Cl to expose more Ag sites (site-blockage effect), the presence of Cl, either on the surface or subsurface, also contributes to higher activity (electronic effect). The simplest interpretation is that once enough surface Cl is stripped from the Ag surface so that site blocking is no



(a) (b)

Fig. 10. (a) Catalyst activity before and after 2-CB added to feed. (b) Selectivity versus EpB concentration. Catalyst is $CsNO_3$-promoted, 15% Ag/SA-5562. Catalyst was given no pretreatment before exposure to feed stream of 9% C_4H_6, 18% O_2, 73% n-C_4H_{10} at GHSV = 5800 h^{-1}. After 50 h on-line, 2.2 ppm 2-CB was added to the feedstream. Reaction temperature = 210 °C.

longer the dominant negative effect on activity, the subsurface Cl can exert its full positive effect on activity. The data in Fig. 9 that indicate loss of activity when insufficient levels of VCl are added to the feedstream support subsurface Cl being responsible for maximum activity, since the 20-h time period over which activity declined is more consistent with the slow loss of subsurface Cl from the Ag catalyst; removal of surface Cl should require shorter time periods. However, participation by some of the surface Cl to increase activity by an electronic effect cannot be excluded; it is simply less likely and opposite to the negative effect of site blockage.

Thus far, only the effect of Cl on activity has been established. In order to determine the effect of Cl on selectivity to EpB, we must remember that nonselective combustion occurs in a consecutive reaction pathway from EpB; there is no apparent parallel pathway for the direct combustion of C_4H_6 to CO_2 and H_2O [3,29]. In very recent work [28] we show that a plot of C_4H_6 conversion versus selectivity to EpB intersects the y axis very near 100% selectivity at 0% conversion, indicating that essentially all combustion occurs consecutively from EpB, or its precursor, and that there is no parallel pathway from C_4H_6 for the formation of CO_2/H_2O. Thus, the only way to examine the effect of Cl on selectivity is to look at selectivity trends as function of EpB concentrations. Because Cl is directly linked to activity for EpB formation and higher EpB concentrations favor EpB combustion, the relationship of Cl to selectivity is not obvious. The results in Fig. 10, however, show conclusively that Cl also increases selectivity toward EpB formation. The activity curve in Fig. 10a for a $CsNO_3$-promoted, 15% Ag/SA-5562 catalyst given (1) no Cl pretreatment before reaction and (2) no 2-CB in the feedstream during the first 50 h on-line shows a slow marked improvement in activity when 2.2 ppm is added to the reaction feedstream. More relevant to selectivity are the concurrent data in Fig. 10b, which show that Cl gives a noticeable and persistent improvement in selectivity to EpB. There are two distinct correlations of EpB concentration versus EpB selectivity; the selectivities for EpB formation are lower when there is no Cl present on the Ag catalyst, compared to when 2.2 ppm of 2-CB has been added to the feedstream. It is interesting to note, however, that the magnitude of selectivity enhancement to EpB by Cl modification is much less than that observed by Lambert and co-workers [9–12] for EO selectivity enhancement on Cl-modified, Ag surfaces, possibly a further result of the differences in kinetics for EpB and EO formation.

The results to this point would suggest that it is not possible to overchlorinate Ag catalysts, and that given enough reaction time under typical reaction conditions, the Cl levels in both the surface and the subsurface regions should adjust to the proper concentrations. The glancing angle X-ray diffraction (XRD) spectrum in Fig. 11 shows this is not the case. The XRD was made using a whole catalyst ring taken from the top of a long tubular reactor that was unintentionally exposed to concentrations of DCE as high as 1–2% for several hours of operation. By orienting the catalyst ring properly at an angle of 10–20° from the X-ray beam, it was possible to preferentially obtain the crystalline structures of the surface region of the catalyst. The crystalline phases present in Fig. 11 indicate that bulk AgCl is the most prevalent component, while metallic Ag is present as a minority component. Similar XRD measurements for catalyst rings located at lower points in the catalyst bed gave no indication of bulk AgCl; the only difference between the two samples was that the sample from the top of the catalyst bed had full exposure to the high concentrations of DCE, showing conclusively that exposure to high levels of organic chloride under normal reaction conditions can lead to bulk AgCl formation. When a sample of the material in Fig. 11 was loaded into a microreactor and tested for catalytic activity (using n-C_4H_{10} as the inert diluent), no detectable conversion of C_4H_6 was observed, even after 24 h on-line. Thus, exposure to levels of organic chlorides at excessively high concentrations in the feedstream leads to irreversible

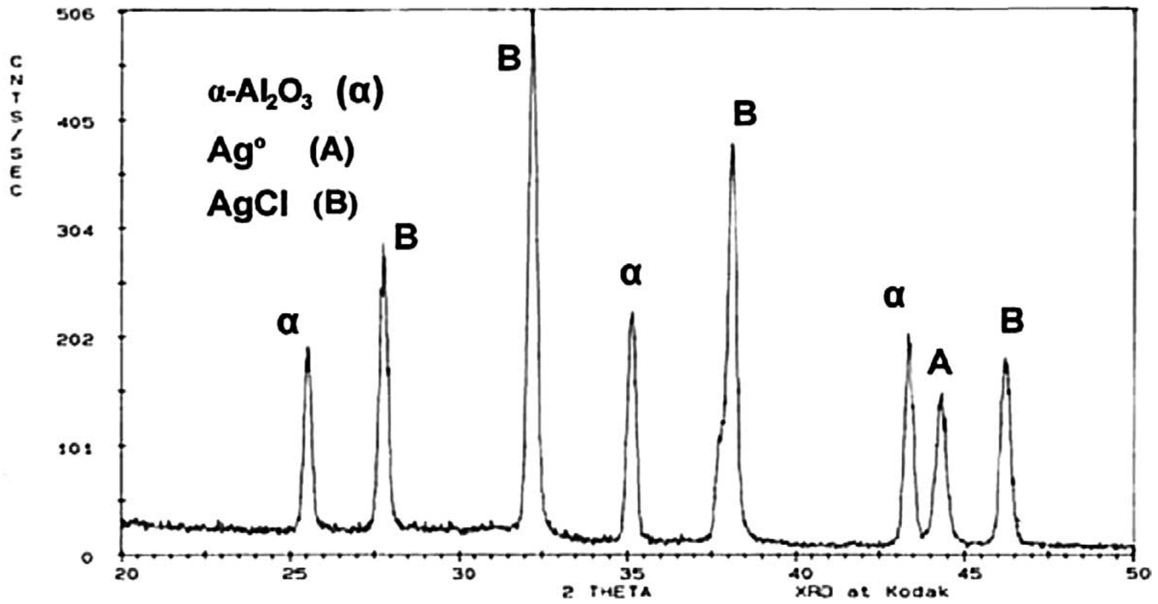


Fig. 11. Glancing X-ray diffraction pattern of EpB catalyst ring over-chlorinated by high levels of DCE. This sample was taken from the top portion of a long tubular reactor.

deactivation of the promoted Ag catalyst; it is not possible to regain activity after formation of crystalline AgCl.

4. Discussion

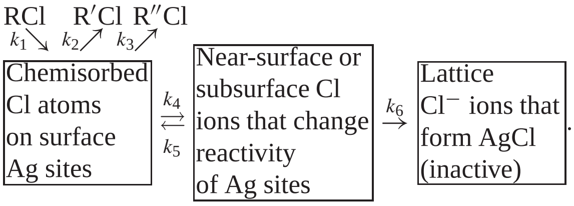
Some of the key points that can be drawn from the above data include the following observations:

(1) Some surface Cl must be present to maintain stability with respect to thermal runaway.
(2) Critical concentrations of Cl in/on the Ag catalyst are required to maintain optimum activity and selectivity.
(3) Under reaction conditions, Cl is continuously removed from the surface of the Ag catalyst by inert hydrocarbon diluents and EpB.
(4) Cl is deposited on the Ag surface by dehydrochlorination of organic chlorides.
(5) Reactivities of organic chlorides are a function of their structures.
(6) Cl can also be deposited by addition of Cl during catalyst preparation.
(7) Cl in excess of one monolayer equivalent (based on Ag-site concentration) can be easily deposited on Ag catalysts.
(8) Cl deposited during preparation is indistinguishable from Cl deposited by dehydrochlorination, except it is more evenly distributed throughout the Ag crystallite.
(9) Cl concentrations in excess of one monolayer equivalent can be rapidly lost during initial periods of reaction time. During this period of time catalytic activity increases.
(10) Catalytic activity versus time on-line suggests that subsurface Cl controls maximum activity for C_4H_6 epoxidation, although participation by some of the surface Cl to enhance activity cannot be excluded.
(11) Excessively high concentrations of Cl lead to irreversible deactivation by formation of a bulk AgCl phase.
(12) Cl can reversibly diffuse into the subsurface of the Ag catalyst and also diffuse back to the surface of the catalyst.
(13) The concentration of surface Cl controls the direction of Cl flux to/from the subsurface region.

Further, if the surface becomes too depleted in Cl by either excess Cl-stripping agents or too low reactivity and/or concentration of organic chloride, then diffusion of Cl back from the subsurface to the surface occurs, ultimately leading to lower catalytic activity and selectivity (i.e., use of VCl as Cl deposition agent). Time on-line data show that activities of Cl-moderated catalysts typically increase during the initial run times and are consistent with removal of excess surface Cl to expose more of the reactive Ag surface. However, since population of the subsurface region takes place by Cl deposition on the surface of the catalyst before diffusion into the subsurface, there must always be some Cl on the surface of the catalyst. Thus, opposing effects occur during reaction. High levels of surface Cl lower activity, presumably by site-blocking reactive Ag sites, while some Cl must be present on the surface of the catalyst to maintain a critical concentration of subsurface Cl, which improves activity and selectivity. The former effect appears to be physical in nature, i.e., site blockage by surface Cl, while the latter effect appears to be electronic in nature. The enhancement of catalyst performance for EpB formation by an electronic promotion due to subsurface Cl is consistent with the conclusions of Lambert and co-workers [9–12] as well as van

Santen and co-workers [2], both of whom claim that subsurface Cl decreases the electron density of oxygen atoms adsorbed on surface Ag sites, leading to the electrophilic addition of adsorbed oxygen to the C=C bond of ethylene, rather than nucleophilic attack at a C–H bond. Theoretical studies by Jørgensen and Hoffmann [35] on Ag(110) surfaces are consistent with the conclusions of Lambert and co-workers and van Santen and co-workers; extended Hückel calculations suggest that adsorbed Cl makes the transfer of adsorbed oxygen to adsorbed C_2H_4 easier, resulting in more facile EO formation. Yet, for C_2H_4 epoxidation, Cl improves only the selectivity to EO, not the activity for C_2H_4 conversion. In light of the results of Jørgensen and Hoffmann, the fact that surface Cl improves only the selectivity, and not the activity, is somewhat surprising in view of the accepted mechanism for ethylene epoxidation. The rate-determining step for ethylene epoxidation is presumed to be the surface reaction of adsorbed ethylene with adsorbed oxygen atoms [1,2]. If in fact Cl makes the transfer of adsorbed oxygen to adsorbed C_2H_4 easier, the rate of EO formation (and C_2H_4 conversion) should increase at optimum levels of Cl. The fact that this is not experimentally observed indicates the complex nature of the effect of Cl on Ag-catalyzed, ethylene epoxidation. In the case of C_4H_6 epoxidation, however, both activity and selectivity are clearly improved by the presence of Cl. However, since the kinetics of EO formation are different from the kinetics for EpB formation, the effects of Cl are apparently manifested quite differently [3]. Earlier work [27,29] has shown that for C_4H_6 epoxidation the kinetically slow step is dissociation of molecular oxygen on vacant Ag sites, where the concentration of vacant Ag sites is controlled by the Cs-assisted desorption of EpB from the Ag surface. Thus, any effect by subsurface Cl that increases the rate of EpB desorption and/or molecular oxygen dissociation will increase the rate of formation of EpB. Selectivity to EpB is controlled by the rate of combustion of EpB to CO_2 and H_2O, since there is no parallel pathway for the direct combustion of C_4H_6. Again, if subsurface Cl increases the rate of EpB desorption from Ag, the selectivity should also be higher, since combustion is a surface process. Alternatively, surface Cl may also block some of the reactive surface Ag sites adjacent to adsorbed EpB that lead to combustion of EpB (Fig. 1).

Finally, the above reactions involving Cl can be summarized by the following reaction scheme where the Cl types present during butadiene epoxidation are divided into three different pools, or types, of Cl:



In this scheme, the only entry point for Cl into the catalyst is via the surface, chemisorbed Cl state, although we know that for CsCl-promoted catalysts, Cl is also introduced into the catalyst during preparation. When either the concentration of surface Cl and/or temperature is high enough, migration of Cl into the subsurface region occurs. Only at very high concentrations of RCl in the gas phase or at high temperatures is AgCl formed. Formation of AgCl is not a reversible state and catalyst activity is permanently lost. Since XRD shows this to be bulk AgCl, formation must come from subsurface Cl.

The above scheme can be summarized as a series of rate expressions:

$$[\mathrm{Ag}]_s + \mathrm{RCl} \xrightarrow{k_1} [\mathrm{Ag–Cl}]_s + \mathrm{R}, \tag{1}$$

$$[\mathrm{Ag–Cl}]_s + \mathrm{R}' \xrightarrow{k_2} \mathrm{R}'\mathrm{Cl} + [\mathrm{Ag}]_s, \tag{2}$$

$$[\mathrm{Ag–Cl}]_s + \mathrm{R}'' \xrightarrow{k_3} \mathrm{R}''\mathrm{Cl} + [\mathrm{Ag}]_s, \tag{3}$$

$$[\mathrm{Ag–Cl}]_s \underset{k_5}{\overset{k_4}{\rightleftarrows}} [\mathrm{Ag–Cl}]_{ss}, \tag{4}$$

$$[\mathrm{Ag–Cl}]_{ss} \xrightarrow{k_6} [\mathrm{Ag–Cl}]_{lat}, \tag{5}$$

where $[\mathrm{Ag}]_s$ denotes vacant surface Ag sites, $[\mathrm{Ag–Cl}]_s$ represents chlorinated surface Ag sites, $[\mathrm{Ag–Cl}]_{ss}$ denotes chlorinated, subsurface Ag sites, and $[\mathrm{Ag–Cl}]_{lat}$ refers to lattice AgCl sites. Under steady-state conditions, we can use the steady-state approximation for chlorinated Ag surface sites, $[\mathrm{Ag–Cl}]_s$, as follows:

$$-\mathrm{d}[\mathrm{Ag–Cl}]_s/\mathrm{d}t = 0, \tag{6}$$

$$\begin{aligned} 0 = {} & k_1[\mathrm{Ag}]_s P_{\mathrm{RCl}} - k_2[\mathrm{Ag–Cl}]_s P_{\mathrm{R}'} - k_3[\mathrm{Ag–Cl}]_s P_{\mathrm{R}''} \\ & - k_4[\mathrm{Ag–Cl}]_s + k_5[\mathrm{Ag–Cl}]_{ss}, \end{aligned} \tag{7}$$

where the Cl deposition reactions of R′Cl and R″Cl have been neglected, due to their necessarily low gas-phase concentrations, relative to RCl. In the case of C_4H_6 epoxidation, R′ and R″ are interpreted to be inert paraffin diluent and EpB which are capable of abstracting surface Cl from the $[\mathrm{Ag–Cl}]_s$ sites.

After rearranging and factoring,

$$[\mathrm{Ag–Cl}]_s = \frac{k_1[\mathrm{Ag}]_s P_{\mathrm{RCl}} + k_5[\mathrm{Ag–Cl}]_{ss}}{k_2 P_{\mathrm{R}'} + k_3 P_{\mathrm{R}''} + k_4}. \tag{8}$$

The concentration of vacant surface Ag sites, $[\mathrm{Ag}]_s$, is given by $L_{\mathrm{Ag}}(1 - \theta_{\mathrm{EpB}} - \theta_{\mathrm{CO_2}} - \theta_{\mathrm{O}})$. L_{Ag} represents the total concentration of Ag surface sites where we have neglected the concentration of $[\mathrm{Ag–Cl}]_s$, which is quite low under steady-state conditions. Substituting into Eq. (8) the final equation is obtained:

$$[\mathrm{Ag–Cl}]_s = \frac{k_1 L_{\mathrm{Ag}}(1 - \theta_{\mathrm{EpB}} - \theta_{\mathrm{CO_2}} - \theta_{\mathrm{O}}) P_{\mathrm{RCl}} + k_5[\mathrm{Ag–Cl}]_{ss}}{k_2 P' + k_3 P'' + k_4}. \tag{9}$$

It can be seen that the $[\mathrm{Ag–Cl}]_s$ concentration is a complex function made up of at least five rate constants, not including the temperature dependencies of the Langmuir coverages of EpB, CO_2, and O atoms.

The numerator of Eq. (9) will approach zero if there is a very low coverage of vacant Ag sites, or if either the partial pressure of RCl (P_{RCl}) or reactivity of RCl (k_1) is too low. The concentration of surface Cl then becomes dependent upon the concentration of subsurface Cl, which leads to rapid depletion of Cl in the subsurface, initially causing lower activity and selectivity, and ultimately loss of thermal stability. The denominator of Eq. (9) shows that the concentrations and reactivities of Cl-stripping agents are very important in determining the surface concentration of Cl on Ag. Finally, further complicating the Cl dynamics in fixed-bed reactors for olefin epoxidation is the realization that reaction temperatures are not isothermal, but vary by several degrees due to thermal gradients. Therefore, it is extremely difficult to define with any accuracy the Cl profile in a tubular reactor. More importantly to this paper, while fundamental studies have proved very helpful in determining the role(s) of Cl in olefin epoxidation, Eq. (9) above illustrates the difficulty in extrapolating fundamental data to the Cl dynamics operative in either microreactors or long tubular, fixed-bed reactors containing Ag catalysts. In fact, full-scale, industrial reactors typically do not use kinetically based models for determining Cl requirements during olefin epoxidation; rather, empirical relationships that include reaction temperatures, gradients in reactor temperatures, feed compositions, changes in feed compositions along the catalyst bed, pressure drops, and total organic chloride(s) concentrations are used for long-term operation of such reactors. Chipman and co-workers [36] recently describe in great detail such a complex empirical relationship, referred to as the Q factor, which describes the quantity of organic chloride (Q) to add to a gas-phase feed composition for optimum performance during epoxidation of C_2H_4 to produce EO. The effective use of the Q factor also required the incorporation of a complex computer program to input all reaction variables, including those described in the above discussion.

5. Conclusions

Silver catalysts that have been modified by Cl addition are more stable with respect to thermal runaway during reaction and exhibit higher activity and selectivity for EpB formation. The Cl effect for activity enhancement is most likely electronic in nature and involves subsurface Cl, although a similar role by surface Cl cannot be excluded. Selectivity enhancement and thermal stability may be also be due to electronic effects, but are more likely the result of Ag-site blockage on the surface of the catalyst that lowers the rate of combustion of adsorbed EpB which in turn controls heat release to maintain thermal control. Unlike alkali promoters used for olefin epoxidation, Cl exists in a very dynamic state. Chlorine is continuously removed from the Ag surface by reaction with EpB and paraffin diluents (that are added to the reaction feedstream). Thus, organic chlorides in the ppm range are also continuously added to the feedstream to replace the Cl lost during reaction. Chlorine is deposited by the dehydrohalogenation of organic halides at the surface of the Ag catalyst. The deposition of surface Cl on the Ag surface is a function of the concentration and reactivity of the organic halide in the feedstream, as well as the concentration of vacant Ag sites. The surface Cl is in equilibrium with subsurface Cl, and the concentration of surface Cl controls the concentration of subsurface Cl. Thus, it is possible to chlorinate a Ag catalyst to levels considerably greater than one monolayer equivalent, based on exposed Ag surface, since the Ag subsurface is capable of “storing” substantial amounts of Cl. The excess Cl can be easily removed by reaction with paraffin reaction diluents, such as *n*-butane, to give an optimally Cl-modified catalyst. However, silver catalysts can also be overchlorinated by exposure to excessively high levels of organic halide and/or temperature, leading to the formation of bulk AgCl, which is catalytically inactive. Such catalysts cannot be regenerated by Cl removal.

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