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The selective epoxidation of conjugated olefins containing allylic substituents and epoxidation of propylene in the presence of butadiene

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Abstract

The epoxidation of isoprene (2-methyl-1,3-butadiene) and piperylene (1,3-pentadiene), both conjugated olefins containing allylic methyl groups, has been conducted using conventional, CsCl-promoted, Ag/α-Al_2O_3 catalysts. Selectivities to the allylic olefin epoxide isomers are over 20% and are much higher than expected due to the presence of the conjugated olefin structure. The epoxidation of propylene over the same catalyst under the same conditions is only 2.5%. The epoxidation of propylene in the presence of butadiene also yields PO in much higher selectivities. The presence of as little as 1% C_4H_6 in the reaction feedstream increases the selectivity to PO from 2.5% to over 40% at the expense of overall activity for C_3H_6 conversion. The upper limit of selectivity to PO in the presence of C_4H_6 appears to be approximately 50%, suggesting an upper limit for the effectiveness of this methodology. Epoxidation of C_4H_6 alone on similar Ag catalysts indicates that the consecutive reaction of EpB to CO_2/H_2O is strongly limited by the presence of excess C_4H_6 in the feedstream. In addition, the selectivity to EpB is directly proportional to the amount of C_4H_6 in the reaction feed stream. Selectivities $> 90\%$ are obtained only when there is sufficient C_4H_6 in the reaction feedstream to control the concentration of the reactive Ag–O surface. For C_4H_6 epoxidation, all CO_2/H_2O is formed by a consecutive reaction pathway from EpB; there is no parallel pathway for the direct formation of CO_2/H_2O from C_4H_6. Using the selective epoxidation of C_4H_6 as the model for understanding the enhancement in selectivity for allylic olefin epoxide formation, the most likely reason for improved selectivities is that strongly adsorbed C_4H_6 (or other conjugated olefins) limits the ensemble size of contiguous Ag–O surface sites. These ensembles are too small for PO combustion, but not too small for PO formation.

Keywords: Epoxidation; Allylic olefins; Propylene; Butadiene; Propylene oxide; Epoxybutene; Silver catalyst; Ensemble effect

1. Introduction

The direct epoxidation of allylic olefins, most notably propylene, has been one of the most elusive goals in catalysis research. Currently, over eight billion lb/year of propylene oxide are produced annually by either of two indirect routes [1,2]. The first is the so-called peroxidation process, whereby organic hydroperoxides or organic peracids are reacted with propylene in the presence of an early row transition metal complex to form equimolar amounts of propylene oxide and organic alcohols or acids, respectively. The potential drawback with this approach is that propylene oxide is produced as the minor weight fraction during the epoxidation reaction. The second indirect method is known as the chlorohydrin process, where propylene is reacted with hypochlorous acid to form propylene chlorohydrin. Following reaction with $Ca(OH)_2$, propylene oxide and $CaCl_2$ are produced. This reaction is both corrosive and environmentally unfriendly as well as generating large amounts of salt by-products, although this process has been very well integrated during its many years of commercial practice. As a result of these limitations, there has been a great deal of recent activity in exploring different alternatives for the direct epoxidation of nonallylic olefins, including propylene, by molecular oxygen. These alternatives include epoxidation of propylene by in situ generated H_2O_2 from H_2 and O_2 using size-specific gold crystallites supported on TiO_2 catalysts [3–5] as well as H_2O_2 generated in situ over Pd–Pt catalysts supported on TS-1 titanium silicalite [6,7]. The in

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situ H_2O_2 catalysts and processes are thus far too inactive, unstable, and nonselective for commercial application, although further research and development continues in these new areas.

Conventional, supported silver catalysts have also been tested for the epoxidation of allylic olefins such as propylene. However, due to the reactivity of the allylic C–H bonds (bond dissociation energy of allylic C–H in propylene is 77 kcal/mol), abstraction of the allylic hydrogen is preferred over the addition of adsorbed oxygen to the C=C bond, thus precluding the formation of propylene oxide [8,9]. More recently, however, data have been published suggesting that a new class of heavily modified, very high weight loading silver catalysts show unexpected selectivity for propylene oxide formation. Gaffney and co-workers [10–12] state that catalysts containing 30–60% Ag, 0.5–3.0% K, 0.5–1.0% Cl with balance $CaCO_3$ give propylene oxide at selectivities as high as 40–50% at temperatures of approximately 250 °C. Likewise, Bowman and co-workers [13,14] evaluated a catalyst containing approximately 60% Ag and high promoter loadings of Group IIA salts, mixed with sodium silicate, and found that at 180 °C the selectivity to propylene was 47% at 3.7% propylene conversion (10% C_3H_6 in feed and GHSV $= 200\ h^{-1}$). Most recently, Jin et al. [15] report that when a gas stream containing 15.6% C_3H_6, 12.2% O_2, and balance N_2 was passed over a catalyst containing 50% Ag and 50% MoO_3 at 400 °C and GHSV $= 4500\ h^{-1}$, the selectivity to propylene oxide was 53.1% selectivity at a propylene conversion of 2.1%.

It is difficult to rationalize the performance of any of the catalysts containing such high silver loadings in terms of conventional supported catalysts, since, in many cases, the support is present as a minor component. In addition, the alkali or alkaline earth modifiers are present at much higher concentrations than the ppm levels commonly associated with promoted silver catalysts. It is more realistic to consider these catalysts as more or less uniform mixtures of silver, modifier, and inert support and to think of the changes in catalytic properties as being due to the well-known ligand and/or ensemble effects of catalysis [16,17]. In the case of these Ag catalysts, ensemble theory predicts that catalytic behavior may be influenced by either the electronic properties of silver sites interfaced with the support (ligand effect) or by the sizes of the contiguous arrays of the silver surface atoms resulting from the dilution of the silver surface by the modifier and/or the support (ensemble effect). For example, if the nonselective combustion of propylene to CO_2/H_2O requires a different sized silver ensemble from that needed for propylene oxide formation, then ensemble effects could play a critical role in selective propylene oxide formation. The ligand effect would require that the alkali or alkaline earth additive or support influences the electronic nature of the adjacent Ag surface sites. These types of electronic modifications are usually associated with very small metal crystallites, or even transition metal complexes, not large, bulk Ag crystallites.

For the past several years, we have studied the epoxidation of conjugated, nonallylic olefins over promoted silver catalysts supported on fused α-Al_2O_3 [18–21]. These catalysts are more typical of silver catalysts normally used for olefin epoxidation. Silver weight loadings are typically between 5 and 15%, promoter loadings are between 500 and 1500 ppm (not 1–5% as in the case of the catalysts of Gaffney and Bowman), and the support is fused α-Al_2O_3. In the case of butadiene epoxidation, we have observed that the selectivity for 3,4-epoxy-1-butene (EpB) from butadiene is directly proportional to the concentration of butadiene in the gas-phase feed stream. This is different from the situation for epoxidation of ethylene to ethylene oxide, where the selectivity to ethylene oxide is typically inversely proportional to the concentration of ethylene in the feed [22,23]. The situation for ethylene oxide formation is the expected relationship of feed concentration to selective product formation where there is a parallel reaction pathway for nonselective product formation (CO_2/H_2O in the case of olefin epoxidation). Vannice and co-workers [24] have also observed that the integral heats of adsorption of butadiene on O-covered Ag catalysts are much stronger than ethylene adsorption on the same surfaces, presumably due to the conjugated olefin structure of butadiene. These results, coupled with the direct relationship of EpB selectivity and butadiene feed concentration, strongly suggest that adsorbed C_4H_6 stabilizes EpB or its precursor against over oxidation to CO_2 and H_2O. One explanation is that strongly bound butadiene on the Ag–O surface may dilute the Ag surface into ensembles of Ag–O too small for CO_2/H_2O formation, but not EpB formation.

In this paper, we present the results for the epoxidation of olefins that contain both a conjugated olefin structure and a methyl group allylic to one of the C=C double bonds [25]. These olefins examined in this study are isoprene (2-methyl-1,3-butadiene) and piperylene (1,3-pentadiene). If the strongly bound, conjugated olefin structure exerts the same influence as it does during butadiene epoxidation, then it may be possible to increase the selectivity for the allylic epoxide isomer. By analogy, we also present data for the epoxidation of propylene in the presence of various concentrations of butadiene in the propylene and O_2-containing feedstream to see whether selectivity to propylene oxide can also be enhanced by the presence of butadiene. Finally, select data for the selective epoxidation of C_4H_6 are presented to illustrate the relationship of C_4H_6 feed concentration to the selectivity for EpB formation.

2. Experimental

The CsCl-promoted catalysts used in this study were prepared using methods that have been described earlier [18,19]. The CsCl loadings were determined using AA-ICP and the Ag weight loading was maintained at 12% (wt) for all catalysts. The catalyst support was fused α-Al_2O_3 rings, type SA-5562, which were supplied by

Norton Corporation. The surface area of the support was 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. The Ag crystallite diameters were measured from scanning electron micrographs and automatic particle counting/measuring software. The average Ag crystallite diameter was determined to be 0.14 µm; assuming hemispherical particle shapes, the Ag surface site density was calculated to be approximately 2.7×10^{18} sites/g. No allowances were made for Cs and Cl coverage on the Ag surface when estimating the Ag surface site concentrations. Before being evaluated, all catalysts were ground and sieved to give particle diameters of 0.4–0.8 mm.

Catalyst evaluations were made using the reactor and GC analytical system previously described [21], except that the reactor was constructed of $\frac{1}{4}$-inch o.d. stainless steel embedded in a 1-inch o.d. brass shell to help maintain isothermal conditions during catalyst evaluation studies. Catalyst bed temperatures were measured by means of a movable C/A thermocouple (0.020-inch o.d.) inside an axial, thin-walled stainless-steel thermowell running the full length of the reactor. Tylan FC-260 mass-flow controllers were used to regulate and maintain flows of C_3H_6, C_4H_6, O_2, CH_4, n-C_4H_{10}, and He in the various reaction protocols. The addition of gas-phase compositions of isoprene (bp = 34 °C), piperylene (bp = 44 °C), and 1,5-hexadiene (bp = 59.5 °C) was accomplished using vapor-liquid equilibrium (VLE) saturators that were maintained at the desired temperatures using close system refrigeration/heaters. By using a combination of the temperature of the VLE saturator (and incorporation into the appropriate Antoine equation), the flow rate of He sweep gas through the VLE, and the overall flow rate of the reactor feed stream, the desired feedstream compositions were made.

3. Results and discussion

Results for steady-state epoxidation of C_4H_6 to EpB are shown in Fig. 1 to illustrate the nature of the reaction network for CO_2 and H_2O formation. The plot of C_4H_6 conversion versus selectivity to EpB (as a catalyst activates to steady-state performance) intersects the y axis very near 100% selectivity, 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. These data are consistent with the earlier work of Monnier and co-workers [9,26]. The data in Fig. 2 show the effects of C_4H_6 feed concentrations on catalyst performance, most notably the selectivity for EpB formation. Fig. 2a indicates that at all reaction temperatures, the selectivity to EpB is higher for the feed stream containing 17% C_4H_6, relative to the feed containing 5% C_4H_6. The plot for 5% C_4H_6 feed concentration shows a sharp transition toward even lower selectivities at temperatures greater than 190 °C. This is because of the lower residual feed concentrations of C_4H_6 as conversion increases; the conversion of C_4H_6 increases from 20 to 35% as the reaction temperature proceeds from 190 to 210 °C, further confirming the dependence of EpB selectivity on C_4H_6 feed concentration. The results in Fig. 2b confirm that the lower selectivity values for the 5% C_4H_6 feed composition are not due to higher EpB concentrations. Since the data in Fig. 1 show that CO_2/H_2O are formed consecutively from EpB, selectivity should decrease as the concentration of EpB in the feed stream increases. Fig. 2b shows

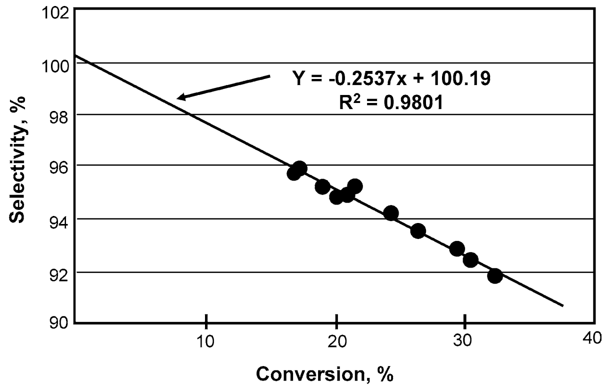
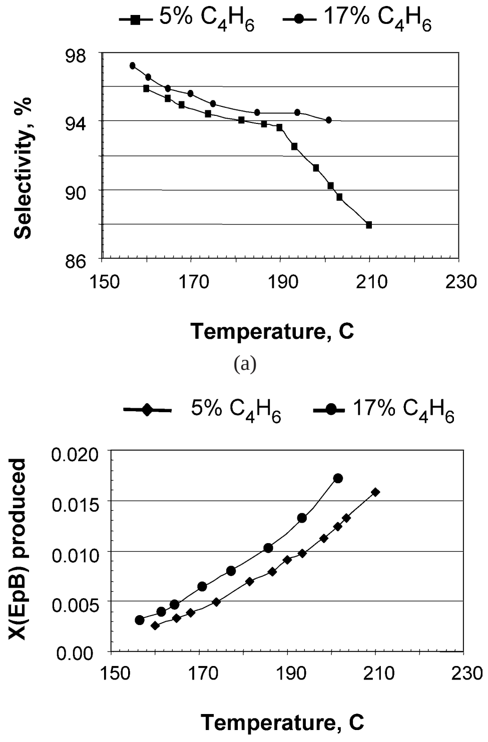


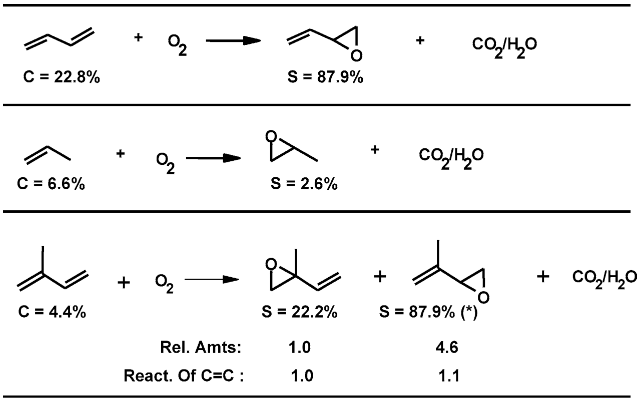
Fig. 1. Effect of C_4H_6 conversion on selectivity to EpB. Catalyst is CsCl-promoted, Ag/α-Al_2O_3. Promoter loading is 900 ppm Cs. Reaction temperature = 205 °C; feed is 9% C_4H_6, 18% O_2, balance n-C_4H_{10} + 2 ppm 2-chlorobutane at GHSV = 12,000 h^{-1}.



(a)

(b)

Fig. 2. Effect of C_4H_6 feed concentration on the selectivity to EpB. Catalyst is CsCl-promoted, Ag/α-Al_2O_3; promoter loading is 900 ppm Cs. Feed conditions are % C_4H_6 as stated, 18% O_2, balance n-C_4H_{10} + 2 ppm 2-chlorobutane at GHSV = 20,000 h^{-1}. (a) Selectivity versus reaction temperature. (b) Mole fraction EpB versus reaction temperature.

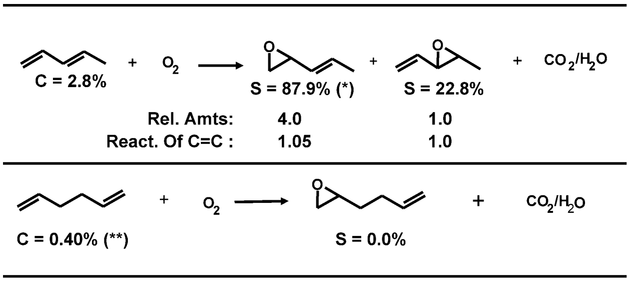


*Assumes selectivity same as for EpB.

Fig. 3. Epoxidation of isoprene over CsCl-promoted, Ag/α-Al_2O_3; Cs loading is 700 ppm. Reaction temperature is 205 °C and feedstream is 12% olefin, 17% O_2, balance n-C_4H_{10} + 2 ppm 2-chlorobutane at GHSV = 6200 h^{-1}. Epoxidation of butadiene and propylene are also included for comparison with the results for isoprene. Conversion of olefin is denoted as ‘C’ and molar selectivity to olefin epoxide as ‘S’.

that the effect of C_4H_6 feed concentration more than offsets the higher EpB concentration; the selectivity values are higher for the 17% C_4H_6 feed concentrations, even though the EpB concentrations are greater. It is noteworthy that even though C_4H_6 feed concentrations have increased by more than threefold (from 5 to 17% C_4H_6), the amount of EpB produced is only slightly higher, again consistent with the approximate zero-order C_4H_6 kinetics previously noted [9]. The results in Fig. 2a do suggest, however, that it is essential to maintain C_4H_6 concentrations at the end of a reactor tube high enough to keep selectivity to EpB at desired levels.

The results in Fig. 3 compare the epoxidations of butadiene, propylene, and isoprene at 205 °C under steady-state reaction conditions for a CsCl-promoted, Ag catalyst. The catalyst shows the expected results for epoxidation of both C_4H_6 and C_3H_6. The selectivity of 2.6% for propylene oxide (PO) formation is typical for conventional Ag catalysts, either promoted or unpromoted. Epoxidation of isoprene yields both isomers; 2-methyl-3,4-epoxy-1-butene (2-Me-EpB) represents the nonallylic epoxide and is more similar to 3,4-epoxy-1-butene (EpB), while 3-methyl-3,4-epoxy-1-butene (3-Me-EpB) is the allylic epoxide and is more similar to propylene oxide. Interestingly, the selectivity for the formation of 3-Me-EpB is 8.5 times higher than for PO formation during C_3H_6 epoxidation. As noted in Fig. 3, the only assumption in the data is that the selectivity to 2-Me-EpB is the same as that for EpB, which seems reasonable given the structural similarities of the two epoxides. This assumption is necessary to establish CO_2 accountability for each isomeric epoxide. Although not shown in Fig. 3, the total selectivity for the formation of both epoxides was 56.9%, with the balance being CO_2/H_2O. Further, the reactivities of both allylic and nonallylic C=C bonds in isoprene are similar, indicating that steric effects are not controlling reactivity of the C=C bonds. If steric limitations are present, they may be offset by the increased electron density of the substituted C=C bonds. Since olefin epoxidation is considered to be due to the electrophilic addition of an adsorbed O atom to a C=C bond [23], the CH_3-substituted C=C bond should be intrinsically more reactive, thus potentially canceling any steric effect.



*Assumes selectivity same as for EpB.

**Catalyst deactivated quickly with time on-line.

Fig. 4. Epoxidation of piperylene and 1,5-hexadiene over CsCl-promoted, Ag/α-Al_2O_3; Cs loading is 700 ppm. Reaction temperature is 210 °C and feedstream is 12% olefin, 17% O_2, balance n-C_4H_{10} + 2 ppm 2-chlorobutane at GHSV = 6200 h^{-1}.

Similarly, the results in Fig. 4 compare epoxidation activities for piperylene and 1,5-hexadiene at 210 °C using the same catalyst as in Fig. 3. Epoxidation of 1,5-hexadiene was conducted to determine whether it was necessary for the two C=C bonds to be conjugated for the enhanced allylic epoxidation to take place. No epoxide formation was observed for this di-olefin; only CO_2/H_2O was formed. Conversion of 1,5-hexadiene declined with time on-line and the results shown are for activity after approximately 1 h of reaction time. Interestingly, as activity declined, a small peak corresponding to 1,3,5-hexatriene (from GC/MS analysis) was observed, indicating that oxidative dehydrogenation of 1,5-hexadiene had taken place. This compound, which is highly conjugated, is apparently very strongly adsorbed on the Ag–O surface and leads to catalyst deactivation. However, during the initial time on-line period, no epoxide was formed, indicating that conjugated olefins are required for allylic epoxidation to occur. It is also obvious that conjugated olefins can be so strongly adsorbed that all reaction is suppressed; of course, there may be some concentration of such conjugated olefins where epoxidation is allowed to take place. As in Fig. 3, both isomeric epoxides of piperylene are formed; 4,5-epoxy-2-pentadiene is the nonallylic epoxide and is obviously similar to EpB, while 3,4-epoxy-1-pentene is the allylic epoxide and represents the propylene oxide analog. As before, the selectivity for the formation of the allylic analog is approximately 8.5 times greater than for PO formation as shown in Fig. 3. Catalyst performance for the epoxidation of piperylene is very similar to that for isoprene, although reaction temperature is 5 °C higher. The total selectivity for formation of both epoxides was 56.0%, very similar to the results for the epoxidation for isoprene.

In order to determine whether the positive effect of the conjugated olefin structures in Figs. 3 and 4 toward allylic epoxidation was limited to intramolecular conjugation, or

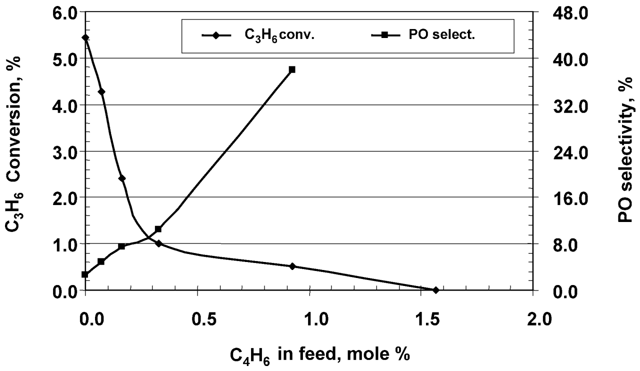
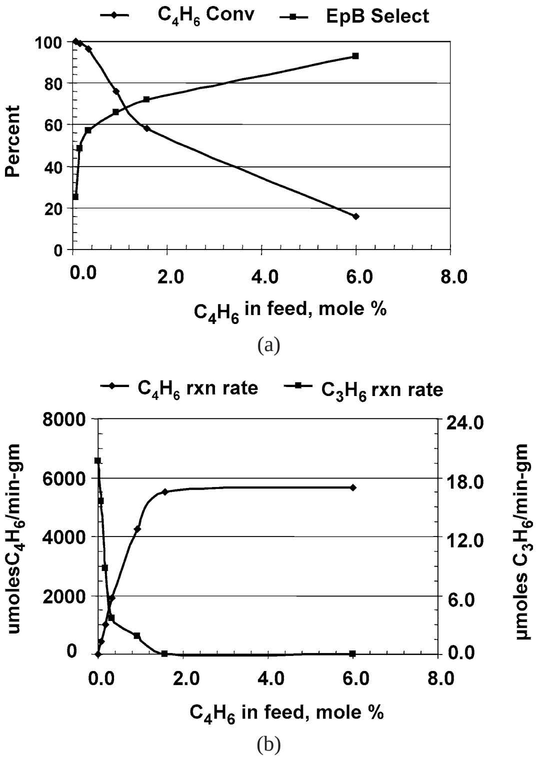


Fig. 5. Effect of C_4H_6 on epoxidation of propylene. Catalyst is CsCl-promoted, Ag/α-Al_2O_3; Cs loading is 580 ppm and reaction temperature is 210 °C. Feed composition is 6% C_3H_6, 12% O_2, variable C_4H_6, balance CH_4 + 1 ppm ethyl chloride at GHSV = 6000 h^{-1}.

was general to the existence of any conjugated olefin in the reaction feed stream, varying amounts of C_4H_6 were added to a feed stream containing C_3H_6, O_2, CH_4 diluent, and 1 ppm ethyl chloride at a reaction temperature of 210 °C. These results, which are summarized in Fig. 5, show that C_4H_6 has a similar effect on increasing selectivity to PO at the expense of overall activity for C_3H_6 conversion. As the feed concentration of C_4H_6 increases from zero to 0.9 mol%, the selectivity to PO increases from approximately 2.5 to 40%. The concurrent decrease in C_3H_6 conversion indicates that C_4H_6 is much more strongly adsorbed on the Ag–O surface sites than C_3H_6, consistent with the observations of Vannice and co-workers [24]. At C_4H_6 levels as low as 0.2 mol%, the conversion of C_3H_6 is lowered by more than 50% even though the ratio of $C_3H_6/C_4H_6 = 30$. Clearly, the strongly adsorbed C_4H_6 is limiting both selective and nonselective reactions.

To illustrate even further the powerful effect of C_4H_6 on selectivity for EpB formation, the plots in Fig. 6 show C_4H_6 conversion and EpB selectivity during the C_3H_6 and C_4H_6 cofeed experiments. When C_4H_6 conversion is 80% or greater, the selectivity to EpB ranges from 25% (at 100% C_4H_6 conversion) to 65% (at 80% C_4H_6 conversion of a 1% C_4H_6 feed composition). Selectivity values to EpB of $> 90\%$ are attained only when the concentration of C_4H_6 in the feed is increased to 6%. At 20% C_4H_6 conversion of a 6% C_4H_6 feed composition, the concentration of C_4H_6 at the reactor exit is approximately 4.8%. The curves in Fig. 6b show again that the conjugated structure of C_4H_6 greatly suppresses overall conversion of C_3H_6 and that the rate of reaction of C_3H_6 is completely suppressed for C_4H_6 concentrations greater than 2% in the feed. The curve representing C_4H_6 reaction rate as a function of C_4H_6 feed concentration also illustrates the transition from first-order to zero-order C_4H_6 dependency as the C_4H_6 concentration increases to values commonly used for EpB production [9,18].

To more clearly identify the effect of conjugated olefins on allylic olefin epoxidation, it is helpful to examine again the effect of C_4H_6 toward C_4H_6 epoxidation. The data in



(a)

(b)

Fig. 6. Reactivity of C_4H_6 during the C_4H_6 and C_3H_6 co-feed experiments. Catalyst and reaction conditions are the same as for Fig. 5. (a) Relationship of C_4H_6 conversion to selectivity for EpB. (b) Comparison of C_4H_6 and C_3H_6 reaction rates during co-feed experiments.

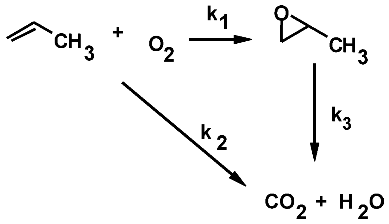


Fig. 7. Mechanistic scheme for epoxidation of C_3H_6 to PO showing parallel and consecutive pathways for formation of CO_2 and H_2O.

Figs. 1 and 2 indicate that nonselectivity arises from the consecutive oxidation of EpB and/or its precursor. Thus, the effect of C_4H_6 on selectivity is limited to controlling the extent of the consecutive oxidation of EpB, not in suppressing a parallel pathway for the formation of CO_2/H_2O from a different type of adsorbed C_4H_6. If we argue that the effect of butadiene (or other conjugated olefin structures) is manifested similarly during C_3H_6 (or other allylic olefin) epoxidation, then the presence of strongly bound C_4H_6 suppresses the overoxidation of PO to CO_2/H_2O. This is best viewed by considering the mechanistic scheme shown in Fig. 7, for the Ag-catalyzed reaction of C_3H_6 with O_2 to form PO and CO_2/H_2O. The formation of the reaction products is shown as a parallel-consecutive reaction network, in the same way that the reaction of C_2H_4 and O_2 is commonly represented [23].

Referring to Fig. 7, the selectivity to PO or allylic epoxides is enhanced by lowering the rate of the reactions having rate constants k_2 and k_3. From analogy to C_4H_6 epoxidation over similar promoted Ag catalysts, the parallel pathway with rate constant k_2 is not preferentially affected by the presence of conjugated olefins, although from the overall lower activity in the presence of C_4H_6, it is obvious that the strongly adsorbed C_4H_6 is adsorbed on sites leading directly to both PO formation (k_1) and CO_2/H_2O formation (k_2). The apparent upper level of selectivity in Fig. 5 is approximately 50% at vanishing C_3H_6 conversion, very similar to the corresponding values reported by Gaffney and co-workers [10–12] and Bowman and co-workers [13,14] for their heavily modified, high weight loading Ag catalysts. This suggests that the parallel pathway for CO_2/H_2O formation occurs at approximately the same rate as PO formation under normal reaction conditions, thus leading to 50% selectivity. The observed limit of 50% selectivity for PO formation, obtained by either modification of the Ag surface during catalyst preparation (Gaffney and Bowman) or by cofeeding conjugated olefins, possibly suggests a real upper limit of performance of Ag catalysts for allylic olefin epoxidation. It is also interesting to note that the selectivity values for formation of the allylic epoxide isomers in Figs. 3 and 4 were limited to 22–23%, considerably below the values observed for PO in the presence of C_4H_6. This may simply mean that the intramolecular conjugated olefin structure is less capable of site blocking Ag–O sites from the allylic moiety than C_4H_6, which is smaller and is a separate molecule from C_3H_6.

The surface reaction steps summarized in Fig. 8 illustrate the proposed role of adsorbed conjugated olefins in suppressing the combustion of allylic olefin epoxide precursors. The adsorbed PO species is meant only to represent an adsorbed PO precursor, the structure of which may actually more closely resemble an oxametallocycle intermediate of the type proposed by Barteau and co-workers [27,28]. The upper reaction step represents the Ag–O surface state in the presence of preferentially adsorbed C_4H_6 (or other adsorbed conjugated olefin, such as isoprene or piperylene), which limits accessibility of Ag–O species to the reactive allylic –CH_3 group by forming Ag ensembles too small for PO combustion, but not too small for PO formation. While changing Ag ensemble sizes by adsorption of conjugated olefins is desirable for increasing selectivities for allylic epoxides, ensemble formation greatly decreases the concentration of available Ag–O surface sites, resulting in an overall lowering of catalytic activity. It is tempting to also assume this ensemble effect is occurring for the catalysts prepared and evaluated by Gaffney and co-workers [10–12], Bowman and co-workers [13,14], and Jin et al. [15] but direct evidence is lacking.

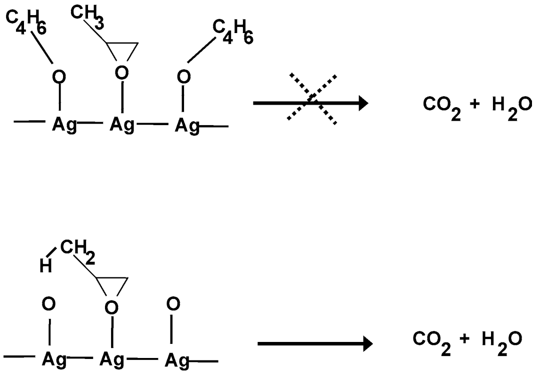


Fig. 8. Proposed surface intermediate schemes showing effect of strongly adsorbed C_4H_6 on lowering combustion of adsorbed PO or PO precursor.

This model for conjugated olefin addition is not limited to adsorbed butadiene or other simple conjugated olefins, but is likely valid for many other olefins containing extended C=C compounds, such as aromatic compounds. Indeed, Law and Chitwood [29] claimed in one of the earliest patents for EO production that aromatic compounds such as benzene and xylene could be added to the feedstream to improve selectivity for EO formation. The authors claimed that the moderating effect of aromatic compounds was not as long-lived as was the effect from Cl addition to the Ag catalyst, consistent with strong, reversible adsorption of such aromatic compounds on the Ag surface. More recently, Evans and Chipman [30] have also claimed that aromatic compounds can be added to reaction feedstreams for EO production to lower the rate of combustion of EO to CO_2 and H_2O. Thus, C_4H_6 may not even be the preferred conjugated olefin additive for enhancing selective allylic olefin epoxide formation. Regardless, the presence of a conjugated olefin, either intramolecular, as in isoprene or piperylene, or added separately, as in the case of butadiene, gives much higher selectivities for the formation of allylic epoxides relative to conventional, supported silver catalysts.

4. Conclusions

The presence of conjugated olefin structures in feedstreams containing allylic olefins or allylic olefin moieties results in dramatic increases in selectivities for allylic olefin epoxides. This enhancement in selectivity is related to the strength of adsorption of conjugated olefins on Ag–O surfaces relative to the more weakly adsorbed allylic olefins. For the case of C_3H_6 epoxidation in the presence of as little as 1% C_4H_6 in the reaction feedstream, selectivity to PO is increased from 2.5% to over 40% at the expense of overall activity for C_3H_6 conversion. The upper limit of selectivity to PO in the presence of C_4H_6 appears to be approximately 50%, suggesting an upper limit for the effectiveness of this methodology, since the parallel pathway for direct combustion of C_3H_6 to CO_2/H_2O is not preferentially inhibited. Epoxidation of C_4H_6 on similar Ag catalysts indicates that the consecutive reaction of EpB to CO_2/H_2O is strongly limited by the presence of excess C_4H_6 in the feedstream. Rather, the selectivity to EpB is directly proportional to the amount of C_4H_6 in the reaction feed stream. Selectivities $> 90\%$ are obtained only when there is sufficient C_4H_6 in the reaction feedstream to control the concentration of the reactive Ag–O surface. For C_4H_6 epoxidation, all CO_2/H_2O is formed by a consecutive reaction pathway from EpB; there is no parallel pathway for the direct formation of CO_2/H_2O from C_4H_6. Using the selective epoxidation of C_4H_6 as the model for understanding the enhancement in selectivity for allylic olefin epoxide formation, the most likely reason for improved selectivities is that strongly adsorbed C_4H_6 (or other conjugated olefins) limits the ensemble size of contiguous Ag–O surface sites. These ensembles are too small for PO combustion, but not too small for PO formation. The conjugated olefin structure and allylic olefin can also be coexistent within the same molecule for this desirable ensemble effect to occur. Epoxidation reactions of both isoprene and piperylene give approximately 10 times more allylic epoxide isomer products than epoxidation of propylene alone.

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