

## Epoxidation catalysis using heterogeneous catalysts

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## 4.6 Selective Oxidations

### 4.6.1 Epoxidation Catalysis Using Heterogeneous Catalysts

R. A. VAN SANTEN

#### 4.6.1.1 Introduction

Three large-scale selective oxidation processes are based on heterogeneous metallic catalysis. The epoxidation of ethylene, catalyzed by silver, produces ethylene epoxide, which is an important intermediate in the manufacture of glycols or polyols. Silver is also used as a catalyst for the oxidative dehydrogenation of methanol to formaldehyde. The third process is the production of vinylacetate by oxidative coupling of ethylene and acetic acid, catalyzed by palladium.

Whereas a main topic of this chapter will be the epoxidation of ethylene by silver, we will also discuss the reactivity of other metals in related reactions. This will help to explain why silver is the only metal for which ethylene epoxidation activity has been found.

Propylene epoxide, made by selective epoxidation of propylene, is an important intermediate for the production of polymers. Direct epoxidation of propylene to its epoxide can occur over silver, but only with very low yields. Large-scale production takes place by use of a peroxide. The heterogeneous catalyst used is a Ti/SiO<sub>2</sub> catalyst [1]. In the overall reaction, ethylbenzene and propylene are converted with oxygen to styrene, propylene epoxide, and H<sub>2</sub>O. The epoxidizing agent is ethylbenzene hydroperoxide. A related catalytic reaction is the epoxidation of propylene by hydrogen peroxide over the zeolitic Ti-MFI catalyst [2].

This review is limited to heterogeneous catalysis of the epoxidation of ethylene and propylene. The aim is to discuss the mechanistic basis of heterogeneous epoxidation catalysis based on a formulation of general principles of selective oxidation catalysis by transition metals.

A useful approach is to compare the proposed mechanistic steps and intermediates on surfaces with related coordination chemistry and organometallic intermediates in homogeneous catalysis. Recent advances in the understanding of the reactivity patterns of adsorbed oxygenates to transition metal surfaces,

obtained from model catalyst surface science studies, are providing a molecular basis for the a mechanistic description of selective oxidation reactions [3].

Selective oxidation catalysis can be categorized as follows:

- (i) redox catalysis
- (ii) oxygen activation and reactivity
- (iii) Surface acid-base catalysis.

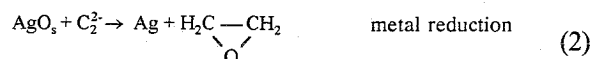
After a discussing these three basic aspects, a summary is given of our current mechanistic understanding of ethylene epoxidation and propylene epoxidation. This chapter focuses on the mechanism of the selective oxidation reactions. Details about the industrial processes are available elsewhere [4].

#### 4.6.1.2 Redox Catalysis

##### A Oxygenate Formation by Metal Reduction

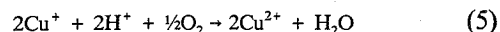
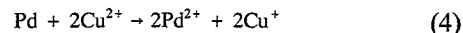
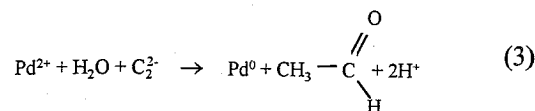
As explained more extensively in the next section an important mechanistic question in ethylene epoxidation catalysis is whether epoxidation occurs by reaction with atomically or molecularly adsorbed oxygen [5]. This question is of importance because selective oxidation of ethylene is in principle possible with 100% selectivity but, as discussed in Subsection B, selective epoxidation is only possible to 86% selectivity. Reactions which yield 100% selectivity are only possible when, in the elementary reaction step that leads to oxygenate formation, reduction of the metal occurs.

Ethylene epoxidation by atomically adsorbed oxygen requires the two elementary reaction steps of eqs 1 and 2.



In eq 1 dissociative adsorption of oxygen occurs and the silver surface is oxidized. In the second step the reduced silver surface is regenerated by oxidation of ethylene. There is not only 100% selectivity on the basis of ethylene, but also 100% selectivity on the basis of oxygen possible. Whether this will be realized will depend on the occurrence of nonselective ethylene combustion reactions, to be discussed later. A homogeneous process in which this catalysis is realized is the Wacker reaction in which ethylene is converted to acetaldehyde. The Wacker process requires three elementary reaction steps of eqs 3–5 to complete the catalytic reaction cycle.

Again, as indicated by reaction eq 3, the metal is reduced in the oxygenate formation step. Oxidation

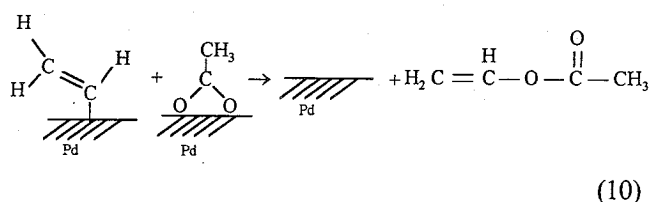
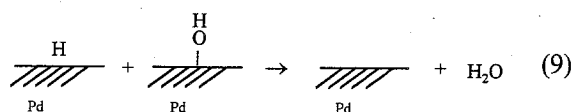
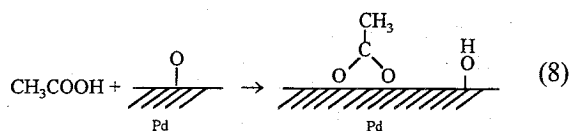
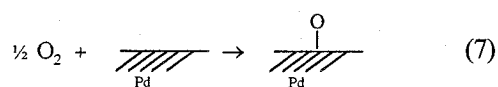
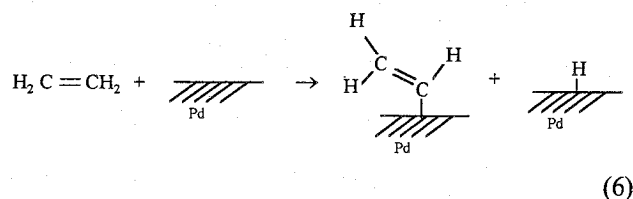


of Pd is catalyzed by  $\text{Cu}^{2+}$ . Also according to this reaction mechanism 100% selectivity of ethylene conversion to the oxygenate is possibly with 100% oxygen consumption efficiency.  $\text{O}_2$  dissociation occurs on oxidic  $\text{Cu}_x^+$  clusters. Because dissociation of oxygen generates two atoms, these clusters have to contain at least two  $\text{Cu}^+$  ions.

Thermodynamically the one-electron transfer reaction  $\text{Cu}^+ \rightarrow \text{Cu}^{2+}$  is favored over the two-electron transfer reaction  $\text{Pd}^0 \rightarrow \text{Pd}^{2+}$ .

Note that in ethylene epoxidation no C–H bond is broken, but that aldehyde formation requires C–H bond rupture and formation.

In the related oxidation reaction of ethylene with acetic acid to vinyl acetate and  $\text{H}_2\text{O}$ , it has been proposed [6] that on the Pd surface the ethylene molecule is converted to adsorbed vinyl, leading to the reaction sequence of eqs 6–10.



References see page 2252

Equation 8 will be discussed more extensively in the section on acid–base catalysis. The difference between eqs 6–10 and the previous schemes is that now adsorbed oxygen is not inserted into the product molecule, but is used to oxidize the reactant molecules by hydrogen abstraction, one from the acetic acid molecule, the other from ethylene. In the overall scheme again the metal is reduced in the product-forming reaction. No epoxide formation occurs on Pd because the CH activation reaction will lead to total combustion of ethylene in the absence of acetate. Whereas CH activation occurs readily on Pd, it does not occur on reduced Ag.

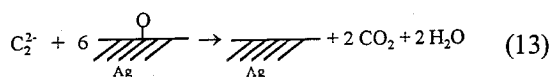
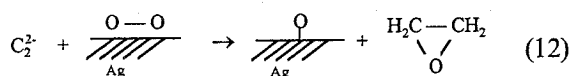
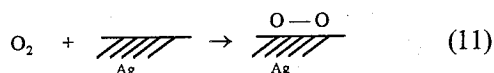
According to eqs 6–10 vinylacetate production is, in principle, again possible with 100% selectivity in ethylene and oxygen.

### B Oxygenate Formation by Metal Oxidation

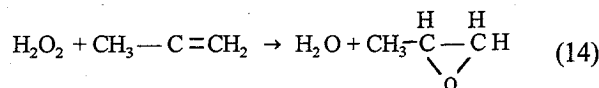
The mechanism in which the oxygenate formation step leads to metal oxidation requires molecularly adsorbed oxygen as an intermediate. The corresponding reaction scheme is given by eqs 11–13. In eq 12 molecularly adsorbed oxygen is reacted with ethylene to epoxide. One oxygen atom of the molecule is incorporated, the other oxygen atom remains adsorbed to Ag, formally oxidizing the surface. The reduced silver surface is regenerated when atomically adsorbed oxygen is removed by ethylene; eq 13 leads to total combustion of ethylene. Since six oxygen atoms can be removed by one ethylene molecule, six molecules of ethylene can react with molecularly adsorbed oxygen to the epoxide and a seventh ethylene molecule has to be consumed to remove the six oxygen atoms from the surface [7].

This reaction mechanism therefore predicts a maximum selectivity of ethylene conversion to the epoxide of 6/7. The oxygen consumption selectivity is 50%.

Whereas for many years this has been the preferred mechanism for ethylene epoxidation by silver, there is now considerable evidence that a mechanism akin to eqs 1 and 2 is to be preferred. This is discussed more fully in Section 4.6.1.5. Routes that proceed via oxidation of the metal in the oxygenation step require a coreductant to reduce the metal. In eqs 11–13 ethylene itself is the coreductant. In principle, however, also other reductant molecules can be used.



This in essence occurs in the reaction that uses hydrogen peroxide or a hydroperoxide as reaction intermediate. The reaction that produces propylene epoxide from propylene can be used as an example. The reaction of propylene with hydrogen peroxide produces H<sub>2</sub>O (eq 14).



From the two oxygen atoms present in H<sub>2</sub>O<sub>2</sub>, one gives the epoxide and the other H<sub>2</sub>O. Hydrogen peroxide is produced from H<sub>2</sub> and O<sub>2</sub>. One can consider H<sub>2</sub> to be the coreductant of the oxygen molecule next to propylene in the overall reaction of oxygen and propylene to propylene epoxide.

When hydroperoxide is used, for instance ethylbenzene hydroperoxide as in the Shell styrene monomer propylene epoxide (SMPO) process, ethylbenzene is the coreductant of oxygen.

As described in Section 4.6.1.6 the Ti/SiO<sub>2</sub> systems that are used for these reactions act as Lewis acids, without change in the valency of Ti<sup>4+</sup>. Therefore, this heterogeneous propylene epoxide catalyst does not strictly belong to the class of redox catalysts.

### 4.6.1.3 Oxygen Adsorption and Reactivity

On a transition metal surface oxygen can be adsorbed in four different states:

- (i) adsorbed molecular oxygen
- (ii) nucleophilic atomic oxygen
- (iii) electrophilic atomic oxygen
- (iv) subsurface atomic oxygen.

The states of oxygen on silver have been extensively investigated as powders, supported catalysts, and as single crystal surfaces. A review is available [5].

Molecular O<sub>2</sub> is stable at a silver(111) surface below 217 K. Above that temperature it will dissociate. The rate of oxygen dissociation is very strongly dependent on oxygen surface coverage. This is due to the surface atom ensemble requirement [7] for the dissociation reaction. Oxygen adatom adsorption to a silver surface takes place at sites of high coordination. Therefore, in order to dissociate, two neighboring sites on the surface have to be available. Each site requires three or four surface atoms. Because of the repulsive interaction between adatoms when they share a surface atom, they prefer ensembles in which the adatoms share a minimum number of surface atoms [8]. As a consequence the minimum ensemble requirement for oxygen atoms appears to be five surface atoms.

If no vacant neighboring adsorption sites are available, molecularly adsorbed oxygen will not dissociate and may remain molecularly adsorbed to higher temperatures [9].

The proposal of the epoxidation mechanism of ethylene according to eqs 11–13 was based on this suppression of molecular oxygen dissociation by site-blocking of the surface. It has been demonstrated experimentally [7, 10], that preadsorption of Cl to Ag catalysts dramatically reduces the sticking coefficient for dissociative oxygen adsorption to silver. As shown in Section 4.6.1.5, adsorbed chlorine acts as a promoter of the epoxidation reaction. It increases the initial selectivity of the epoxidation reaction nearly by a factor of 2.

The adsorption of Cl together with eqs 11–13 provides a plausible rationale for this increase in selectivity; the alternative explanation is given later.

When present, molecular oxygen will also react with reactive surface intermediates formed in the reaction path leading to total combustion.

When the molecule has been dissociated, the adatoms originally adsorbed to the external surface may move to subsurface lattice positions. This may be the onset of bulk oxidation, when thermodynamics favors the bulk oxide, or may remain limited to the subsurface layer next to the outer layer. Subsurface oxygen atoms have been shown to exist for several transition metals, e.g. Rh, Pd, and Ag [11a]. Subsurface oxygen atoms and coadsorbed surface atomic oxygen have been observed using Raman spectroscopy [11b]. Earlier they were indirectly proved to exist using isotope-labelled experiments [11c]. On silver surfaces titration and microbalance experiments have demonstrated that maximum oxygen coverages obtainable have a stoichiometry of one oxygen adatom to one surface silver atom, as in AgO [5].

Surface crystallographic experiments, however, have never reported the presence of an external adatom oxygen layer with a stoichiometry in excess of one oxygen adatom to two surface Ag atoms, as in Ag<sub>2</sub>O. Therefore it has to be concluded that at a maximum surface coverage of one silver surface atom to one adsorbed oxygen atom, half of the atoms will be adsorbed to external surface positions and the other half of the atoms will be located in subsurface positions.

The presence of subsurface oxygen atoms will reduce the electron density on neighboring silver atoms, hence the oxygen adatoms adsorbed to the external surface that share bonding to silver surface atoms with the subsurface oxygen atoms are highly polarizable. When contacted with an alkene, the interaction between ethylene  $\pi$  electrons and oxygen electrons will lead to a flow of oxygen electrons to the positively charged surface metal atoms [12]. Surface oxygen adatoms then behave chemically as electrophilic oxygen atoms, that

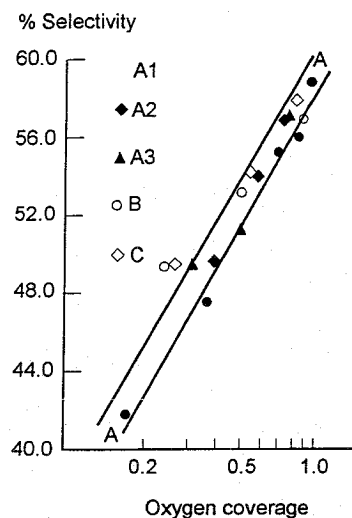
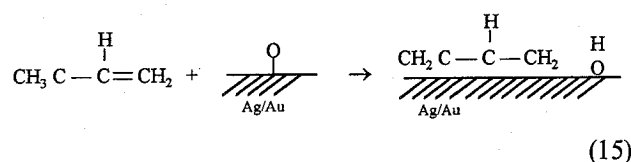


Figure 1. Selectivity versus coverage for various catalysts [13].

preferentially react with the high electron density part of the molecules, as for instance the  $\pi$  bond of ethylene. This has been experimentally demonstrated by a study of the selectivity of ethylene epoxidation as a function of oxygen coverage. Shown in Fig. 1 is the strong increase in the epoxidation selectivity with enhanced oxygen surface concentration.

Whereas oxygen adatoms at high surface coverage behave as electrophiles, this reactivity changes dramatically for oxygen atoms adsorbed to silver at a low surface coverage. This is best illustrated by an experiment in which the surface coverage was altered by alloying (Fig. 2) silver with gold [14]. Due to its low reactivity oxygen will not dissociate on Au, hence dilution of the silver surface by Au reduces the steady state coverage of oxygen per metal atom exposed. A sharp decrease in selectivity is observed for ethylene epoxidation, but an increase in the selective oxidation of propylene becomes acrolein. The main product from propylene with Au concentration. The mechanism of acrolein formation is well understood from other systems [15]. Propylene activation occurs by abstraction of a proton to produce the allylic intermediate (eq 15).



Hence adsorbed oxygen atoms now behave as nucleophiles. In a second step acrolein is produced by insertion of a second oxygen atom.

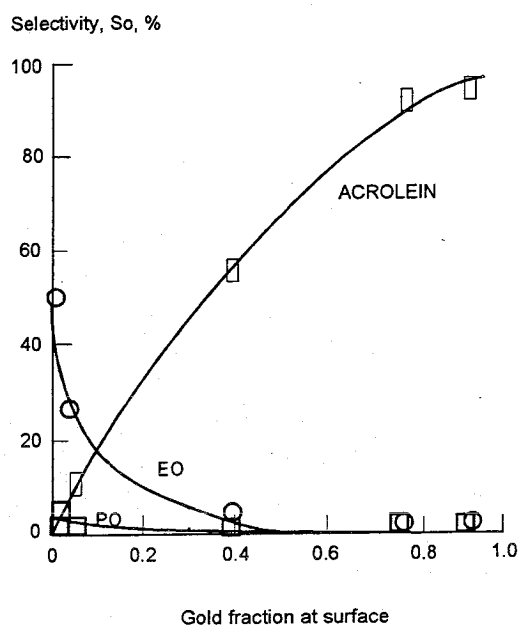
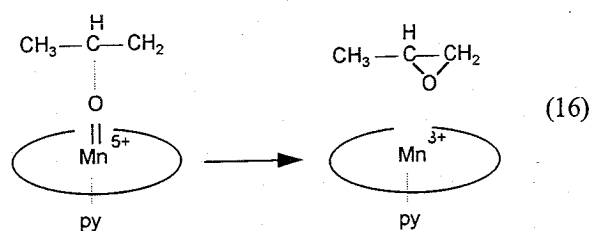


Figure 2. Selectivity of ethylene and propylene oxidation as a function of Au:Ag ratio; EO=ethylene epoxide, PO=propylene epoxide.

The presence of nucleophilic oxygen adatoms on silver surfaces with a low oxygen surface adatom concentration must also be responsible for the enhanced total combustion of ethylene at low oxygen surface coverage. The next section discusses more extensively the surface basicity of nucleophilic oxygen adatoms.

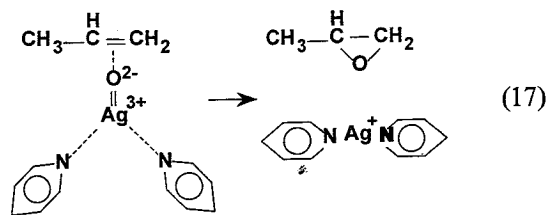
This section concludes with a short discussion of organometallic analogs of the electrophilic epoxidation reaction. It appears that monometallic oxygen complexes exist that produce epoxide upon contact with alkenes. The main requirement appears to be that the complexed oxygen atom is bonded to a highly charged metal atom.

In the cytochrome P-450 analog a Mn ion that formally is five-valent donates a coordinated oxygen atom selectively to an alkene: (eq 16).



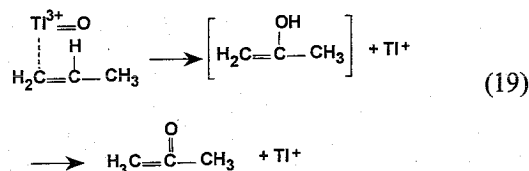
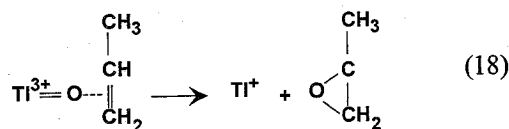
This reaction occurs under mild conditions in  $\text{H}_2\text{O}$ . Silver complexes have also been found that can be activated to produce epoxide from an alkene (eq 17).

Silver in a formally three-valent state reacts with propylene to give the epoxide. The reduced Ag com-



plex can be electrochemically oxidized, so that the oxygen atom in the complex on the left-hand side of eq. 17 can be generated from  $\text{H}_2\text{O}$  [16]. The highly charged state of silver results in highly electrophilic oxygen. This complex is possibly the organometallic analog of the electrophilic surface reaction oxygen center.

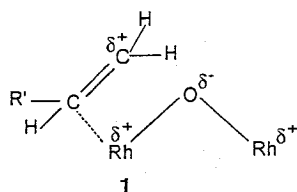
Epoxidation tends to compete with keto formation. This has been found for the reaction of propylene with  $\text{Tl}_2\text{O}_3$ . The corresponding reactions are shown in eqs 18 and 19.



The high charge on the cation tends to lead to competition between the electrophilic reaction to give the epoxide and a radical reaction, possibly activated by a direct interaction between the  $\pi$  bond of propylene and  $\text{Ti}^{3+}$ . The radical reaction will lead to formation of an OH radical. The resulting intermediate vinylalcohol will rapidly isomerize to the ketone.

As seen in the Wacker reaction,  $\text{Pd}^{2+}$  produces the aldehyde instead of the epoxide, which also indicates a different mechanism. In the case of  $\text{Pd}^{2+}$  ethylene became bonded to  $\text{Pd}^{2+}$ . Subsequently an  $\text{OH}^-$  ion is reacted with now electron-deficient ethylene. It has been demonstrated using isotope-labelled  $\text{H}_2\text{O}$  that the hydrogen atoms in the resulting aldehyde derive from the original ethylene molecule [6].  $\text{Pd}^{2+}$  induces hydrogen transfer within the molecule, Pd becomes reduced, and  $\text{H}^+$  is desorbed in the final aldehyde-forming step.

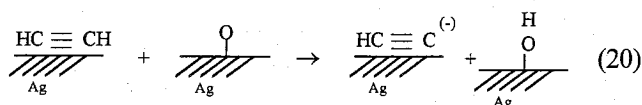
Interestingly, coadsorption of alkenes with atomic oxygen on transition metal surfaces of Pd and Rh, also results in the ketone or aldehyde upon desorption<sup>3</sup>. Structure 1 shown the proposed reaction intermediate on Rh.



$\pi$ -Bonding of an alkene to electron-deficient Rh induces a favorable interaction with nucleophilic adsorbed oxygen. Similar to the Wacker reaction,  $\text{Rh}^{\delta+}$  induces hydride transfer within the molecule.

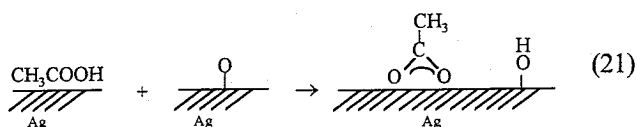
#### 4.6.1.4 Acid-Base Catalysis

The nucleophilic oxygen atoms adsorbed at low coverage to Ag(111) surface behave chemically as Lewis-basic reagents. A classical example has been provided by Madix and co-workers [3]. They have demonstrated that acids such as acetylene, when coadsorbed with O to a Ag(111) surface react rapidly to the adsorbed hydroxyl and corresponding anion (eq 20).

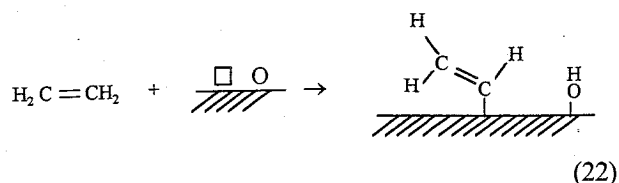


A surface vacancy next to the adsorbed oxygen atom is needed to stabilize the  $\text{C} \equiv \text{CH}^-$  anion generated. The requirement of a vacant site next to the oxygen atoms has, as a consequence, that this reaction can become suppressed when the concentration of such vacancies becomes reduced by site blocking.

A reaction with a Lewis basic oxygen can be responsible for strong chemisorption. Whereas, for instance, acetic acid only adsorbs weakly to the dense surfaces of Pd and Rh, it adsorbs strongly when oxygen atoms are present on such surfaces. The coadsorbed oxygen atoms initiate dissociative adsorption according to eq 21.



The decomposition of acetate occurs at a higher temperature. The presence of excess oxygen atoms may assist decomposition of the acetate by a Lewis-basic reaction with the acidic acetate  $\text{CH}_3$  groups. In the presence of gas-phase oxygen this will lead to total combustion. The total oxidation reaction of ethylene is also initiated by the reaction of nucleophilic oxygen and ethylene (eq 22).



Whereas Ag will not activate the C-H bond, eq 22 is exothermic. An Ag surface vacancy next to the adsorbed basic oxygen atom is required in order that the reaction proceeds. The resulting adsorbed vinyl reacts rapidly with additional oxygen to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Using  $\text{C}_2\text{D}_4$  instead of  $\text{C}_2\text{H}_4$  eq 18 has been shown to be rate limiting to total oxidation. There is a large isotope effect on the initial selectivity of the epoxidation reaction.

In Fig. 3 the initial selectivity of the ethylene epoxidation reaction of  $\text{C}_2\text{H}_4$  is plotted against the ratio of the rates of epoxidation and total combustion of  $\text{C}_2\text{D}_4$  versus that corresponding to  $\text{C}_2\text{H}_4$ . Note the larger isotope effect for lower selectivity. Since no hydrogen activation is involved in the oxygen insertion reaction, it demonstrates that CH activation is rate limiting to the total combustion reaction.

#### 4.6.1.5 Chemistry of Ethylene Epoxidation Catalysis

The catalyst applied in ethylene epoxidation is a low-surface-area  $\alpha\text{-Al}_2\text{O}_3$  on which large silver particles are dispersed. The size of the particles can become as large as the micropores of the catalyst support. Catalyst preparation usually occurs by impregnation with basic

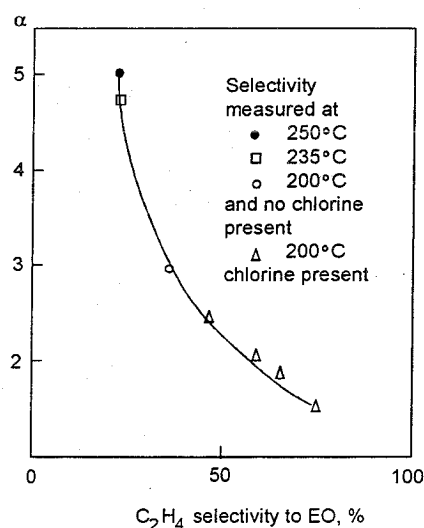
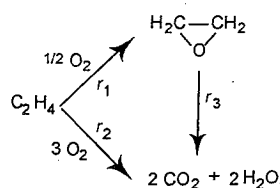


Figure 3. Isotope effect dependence on selectivity [17].



Scheme 1

silver complex solutions. Alkali promotion of the support and of the silver particles has a beneficial effect on catalyst performance (see below).

In addition to catalyst promotion by basic components, the selectivity also benefits from the addition of chlorine-containing compounds to the reaction stream.

One such a promoting compound is vinylchloride. Upon contact with Ag the hydrocarbon part of vinylchloride rapidly combusts over silver and chlorine becomes adsorbed to the silver surface. Because Cl is also removed from the silver surface by reaction with ethylene, a few ppm vinylchloride is continuously added to the feed in order to maintain a constant Cl surface concentration.

We will first discuss the elementary principles of epoxidation kinetics and relate them to the dependence of reaction rates on catalyst composition. We will use the reactivity principles discussed in the previous sections to elucidate the role of alkali promotion and chlorine promotion. For a more complete discussion see Ref. 5. It has been established by Voge and Adams [18] that ethylene epoxidation kinetics proceeds as scheme 1.

The initial selectivity of the epoxidation reaction is determined by  $r_1/r_2$  and is controlled by the reactivity of the silver particle. At higher conversion the selectivity becomes reduced by the consecutive reaction  $r_3$ . The elementary reaction steps responsible for  $r_3$  are the acid-catalyzed isomerization of the epoxide to the acetaldehyde and rapid combustion of acetaldehyde by silver. The rate of epoxide oxidation by silver is slow in comparison to the other reactions. The acid groups responsible for isomerization of the ethylene epoxide reside on the alumina surface. The consecutive reaction  $r_3$  becomes suppressed when the concentration of acidic protons on  $\text{Al}_2\text{O}_3$  is reduced. The acidity of the alumina derives from the changes of the  $\alpha\text{-Al}_2\text{O}_3$  surface due to its contact with catalyst impregnation solution. Alkali cations present in the solution decrease support acidity because of ion exchange. Alkali promotion of the catalyst contributes mainly to the improved selectivity of the catalyst by suppression of  $r_3$ . Therefore it will be most important at high ethylene conversion.

The initial selectivity parameter  $r_1/r_2$  is mainly determined by the housekeeping of adsorbed oxygen on

silver. The essential selectivity features have been discussed in the earlier sections. The epoxidation reaction requires the silver surface atoms to be electron deficient. Isotope exchange and chemisorption experiments have excluded adsorbed  $\text{O}_2$  as the active intermediate [11]. The atomic oxygen epoxidation mechanism is also supported by the observation of initial selectivities higher than 6/7 [5]. The nonselective reaction path of ethylene that leads to total combustion is initiated by a silver surface with a low surface concentration of oxygen atoms, with surface vacant sites next to them [19].

At the reaction temperature ( $\approx 500$  K) in the absence of chlorine, the steady state oxygen coverage of silver will be such that the corresponding initial selectivity will be only  $\approx 40\%$ . Coverage of the silver by coadsorbed Cl enhances this selectivity to  $\approx 75\%$  [20]. The enhancement of the initial selectivity due to coadsorbed chlorine arises from two effects:

- (i) suppression of vacant silver sites;
- (ii) enhancement of electron deficiency of silver.

Because of its ability to also adsorb in subsurface layers [20], chlorine may replace the role of subsurface oxygen (Fig. 4).

Alkali appears to affect both the consecutive reaction  $r_3$  and the ratio  $r_1:r_2$ . The absence of chlorine also increases the overall reaction rates. The rate-limiting step of the reaction is the dissociative adsorption of oxygen which, as explained in Section 4.6.1.3 is strongly reduced on a high-coverage silver surface [21].

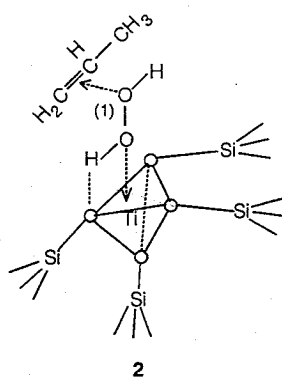
The rate of ethylene epoxidation is first order in oxygen and zero order in ethylene [22]. The presence of coadsorbed alkali compounds increases the rate of dissociative oxygen dissociation and hence the rate of the epoxidation reaction. This enhanced rate of oxygen dissociation is due to a reduction in the activation energy of dissociative oxygen adsorption.

Interestingly, when a comparison is made of the relative rates on alkali-promoted silver in the presence of chlorine moderator in the feed, the effect is reverse. The activity of the catalyst now decreases with increasing coverage of silver by alkali [2]. This implies that the presence of alkali enhances the surface steady-state chlorine coverage with a corresponding decline of available reactive free silver sites.

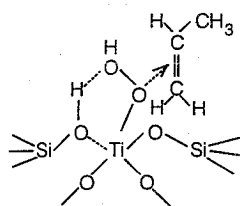
The initial selectivity for epoxidation is not affected by the presence of alkali promoters, when measurements are made around 500 K in the presence of the chlorine containing moderator. However, at higher temperatures, the initial selectivity is increased by alkali coadsorption. At higher temperatures the strongly adsorbed chlorine now maintains an oxy-chloride-silver boundary layer composition, such that the surface silver atoms remain in an electron-deficient state.







2



3

The structure of the intermediate that leads to epoxidation is not precisely known, but probably close to one of structures 2 or 3. According to 2 hydrogen peroxide does not dissociate, but coordinates to the Lewis acidic  $\text{Ti}^{4+}$  ion, analogous to eq 23. This induces electron deficiency on the oxygen atoms, favorable to epoxidation. The  $\text{OH}^+$  group can insert into the alkenic bond. The  $\text{H}^+$  then reacts with  $\text{OH}^-$  to  $\text{H}_2\text{O}$ . According to proposal 3 hydrogen peroxide first dissociates. Protonation of the bridging  $\text{TiOSi}$  proton creates a silanol, that weakly coordinates to Ti. Ti becomes five coordinated. The peroxide group bonded to Ti is stabilized by formation of a five-atom ring, resulting in a strongly acidic entity. This would agree with reported strong acidity. Again oxygen within the peroxide becomes electron deficient and suitable for the epoxidation reaction. UV spectroscopic evidence indicates coordination of the hydrogen peroxide to the Ti site and infrared spectroscopy has shown a weakening of the  $\text{Ti}-\text{O}$  bond. No redox catalysis is involved. On the anatase or rutile surface, the Ti atoms are more easily accessible than tetrahedrally coordinated Ti. The surface atoms of anatase or rutile occupy truncated octahedra. Now the hydroperoxide can coordinate side-on and  $\text{O}-\text{O}$  bond cleavage occurs.

The catalytic selectivity for epoxide formation catalyzed by the amorphous  $\text{TiO}_2/\text{SiO}_2$  [1] system is also based on the presence of four-coordinated Ti.

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