

The active site of promoted ethylene-epoxidation catalysts

Citation for published version (APA):

Santen, van, R. A. (1988). The active site of promoted ethylene-epoxidation catalysts. In M. J. Phillips, & M. Ternan (Eds.), *Catalysis: Theory to Practice : Proceedings 9th international Congress on Catalysis. Volume 3: Characterization and Metal Catalysts* (pp. 1152-1158). Article 148-B4 Chemical Institute of Canada.

Document status and date:

Published: 01/01/1988

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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- The final published version features the final layout of the paper including the volume, issue and page numbers.

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THE ACTIVE SITE OF PROMOTED ETHYLENE-EPOXIDATION CATALYSTS

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ABSTRACT

The cooperative effect of chlorine moderation and alkali promotion on the initial selectivity of silver-catalysed epoxidation of ethylene have been investigated. To this end a study was made of the conversion ethylene catalysed by silver doped with alkali and non-doped in the presence and absence of chlorine. The silver powders were characterized by temperature programmed reduction as well as by oxygen adsorption studies. Also, the exchange reaction of C_2H_4O and C_2D_4 was studied.

The data were interpreted with the epoxidation model according to which the elementary step of the selective reaction is electrophilic attack of an adsorbed oxygen atom to the π -bond of ethylene and the non-selective reaction occurs by electro-positive attack of a different atomic oxygen species to the CH bond of ethylene. The role of alkali appears to be stabilization of that silver oxychloride phase that contains predominantly atomic electrophilic oxygen.

INTRODUCTION

The selectivity of the oxidation of ethylene catalysed by silver towards epoxide is significantly enhanced by the addition of chlorine (1) and alkali promoters (2). This finding has led to considerable speculation on the nature of the catalytically active site responsible for the epoxidation reaction. Although geometric (3) and electronic factors (4) have been distinguished, no definite explanation of the promoting effects can be given as long as the mechanism of epoxidation is not well understood.

It is now well established that the state of the oxygen adsorbed to the silver surface is critical for its epoxidation selectivity (5). It was found (6, 7) that in the absence of chlorine a high oxygen coverage is necessary. Silver powders only produced epoxide if O_{ads}/Ag_s atom ratio exceeded 0.5. O_2^{16} , O_2^{18} isotope experiments demonstrated (8) that atomic oxygen is incorporated into ethylene upon epoxide formation. These experiments provide strong indications that adsorbed oxygen atoms can give epoxide and that at least two kinds of adsorbed atomic oxygen atoms exist: At low O_{ads}/Ag_s atom ratio oxygen atoms are so strongly bonded that epoxide cannot be formed upon reaction with ethylene because the heat of formation of this elementary step becomes endothermic. As a result, total combustion is the only possible reaction. At high O_{ads}/Ag_s atom ratio, on the other hand, a weakly bonded adsorbed oxygen atom is formed, yielding epoxide (8). We will here report an experiment on the oxygen exchange between C_2H_4O and C_2D_4 that confirms this proposition.

The effect of Cl precoverage on the selectivity of the epoxidation has been extensively investigated on supported catalysts (3), on silver single

surfaces (9), (10), as well as on silver powders (11). On a clean silver surface the selectivity can change from 30 to 70 %. This effect was explained previously as being due to an epoxidation mechanism involving adsorbed molecular oxygen (3). Site blocking of silver by Cl decreases the probability of neighbouring silver atom, postulated necessary for dissociation of molecular oxygen.

It has been argued (5, 10, 12) that the chlorine effect can also be explained by a mechanism involving atomic oxygen. The role of chlorine is two-fold: firstly, it suppresses strongly adsorbed oxygen atoms, because chlorine will preferentially adsorb on these sites. Secondly, chlorine will favour the formation of weakly adsorbed oxygen (13), because it will also adsorb into the subsurface layer (14, 15). The bond strength of oxygen atoms bonded to silver atoms sharing chlorine atoms will weaken.

Ethylene conversion experiments on alkali-promoted silver powders in the absence and presence of chlorine reported here are consistent with this point of view. It will be shown that there is no need to invoke an electronic effect to explain the role of alkali, but rather that it plays a role in the solid-state chemistry of the silver oxychloride layer. Finally, oxygen adsorption and reduction experiments on alkali-doped silver will be reported.

EXPERIMENTAL

Throughout the experiments we used spectroscopically pure silver from Johnson & Matthey. The surface compositions were determined by ESCA in a Varian IEE-15 apparatus. The relative atomic abundances of elements present on Ag, before impregnation, as measured by ESCA are 0.22 Cl, 0.03 S and 0.03 K. The rather large amount of chlorine present in the Ag powders was removed during the reaction whenever we used a chlorine-free feed (oxygen and ethylene).

The surface area of the silver powder stabilized by six oxidation and reduction cycles of 12 hours at 200 °C and 350 °C, respectively was 0.05 m²/g. Impregnated silver did not show any Cs⁺- or K⁺-containing crystalline material.

A circulation reactor, described elsewhere (8), was used for the isotope experiments. Typical pressures used in the recirculation apparatus were 1.3 kPa. The gas mixture was recirculated over the powder (WHSV \approx 31 Nl.h⁻¹.kg⁻¹), by means of a magnetically driven Pyrex pump, while the temperature was raised at a rate of 2.3 K/min. We used two quartz micro-flow reactors. One reactor, which had never been in contact with a chlorine-containing feed, was used for the measurements in the absence of chlorine. The other reactor was used for the measurements in the presence of a moderator. The total flow of gas through the reactors was 0.1 Nl/min. The gas composition was 8 % O₂, 24 % ethylene and 68 % nitrogen to which vinyl chloride could be added (ppm amounts). Atmospheric pressure was used. Samples of the exit gas could be pulsed into a gas chromatographic analysis system.

In the temperature-programmed reduction experiments reduced samples were oxidized for one hour at 200 °C in an O₂/H₂ stream with a partial oxygen pressure of 6.1 kPa. After cooling to -50 °C in a helium stream, the amount of hydrogen consumed at a partial H₂ pressure of 6.1 kPa in N₂ was measured as a function of temperature in a thermal conductivity cell.

Adsorption experiments were performed in an all-metal/Pyrex high-vacuum system, equipped with a Barotron 220 B pressure transducer.

RESULTS

C₂H₄O/C₂D₄ exchange experiments

Figure 1 shows the results of an experiment where ethylene epoxide and deuterated ethylene were reacted with each other using well reduced Ag (24 h, 350 °C, 1 bar) as a function of temperature. Whereas the epoxide decomposes to ethylene and adsorbed oxygen, C₂D₄ does not react with the adsorbed oxygen layer, except to give total combustion. We showed earlier (11) that the rate of ethylene epoxidation is higher for C₂D₄ than for C₂H₄.

The experiment clearly demonstrates that oxygen atoms can be generated on a silver surface by epoxide decomposition. So on the basis of the argument of microscopic reversibility adsorbed oxygen atoms should also be able to form epoxide from ethylene. In this particular situation no epoxide is formed, because at low oxygen coverage the high oxygen atom chemisorption bond strength inhibits epoxide formation.

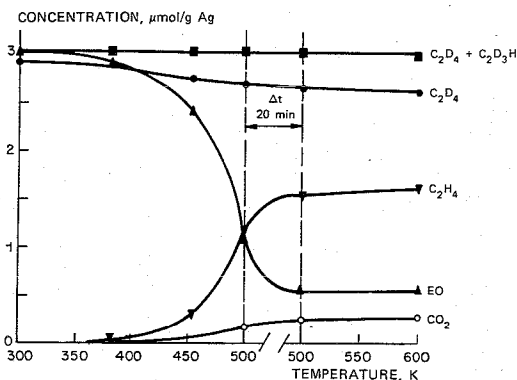


Figure 1. C₂H₄O (epoxide) and C₂D₄ exchange experiments

Microflow experiments

Figure 2a show the effect of Cs adsorption on the activity of silver powder. The silver powder was impregnated with CsNO₃, dried and reduced at 350 °C in H₂. Measurements were performed after careful start-up of the reaction and twenty four hours stable operation. Alkali measurements were done by ESCA. In the absence of vinyl chloride from the feed, the activity of the reaction is found to be strongly enhanced by Cs⁺ adsorption to silver powder. A very different result is found for the conversion dependence in the presence of chlorine adsorption (Figure 3a). Now the activity is found to be strongly suppressed by preadsorption of Cs⁺ ions.

As Figures 2b and 3b show, no large effects on the initial selectivity are found. In the absence of chlorine initially a small increase in selectivity is observed. In the presence of chlorine, the effect of the presence of Cs⁺ on the initial selectivity increases with temperature. Whereas in the absence of adsorbed Cs⁺ the selectivity decreases with increasing temperature, in the presence of adsorbed Cs⁺ no change in initial selectivity is observed.

Figure 4 compares the selectivity of C₂H₄ epoxidation and C₂D₄ epoxidation under the same conditions of the microflow experiment in a recirculation experiment catalysed by a silver catalyst with different Cs and Cl compositions. As reported earlier, the C₂D₄ selectivity is higher than the ethylene selectivity (11, 16, 17). The initial selectivity can become larger than 86 %, which is higher than the limit predicted according to the molecular epoxidation mechanism.

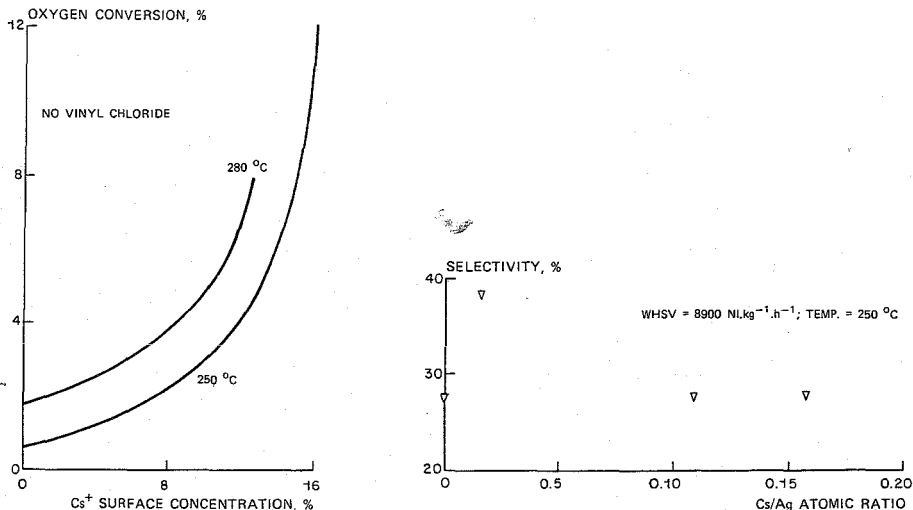


Figure 2. a. Oxygen conversion as a function of Cs⁺ surface concentration.
 b. Selectivity as a function of Cs⁺ surface concentration.
 No vinyl chloride present.

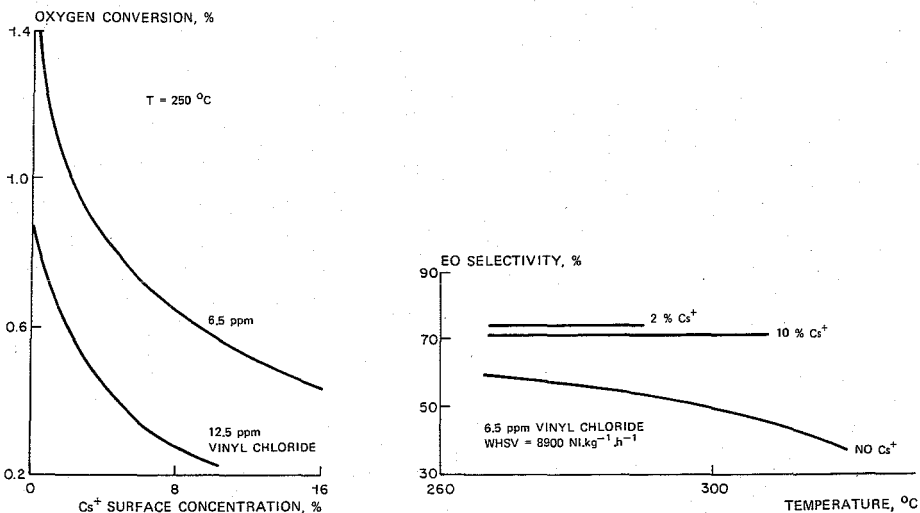


Figure 3. a. Oxygen conversion as a function of Cs⁺ surface concentration.
 b. Influence of Cs⁺ concentration on selectivity.

Temperature-programmed reduction and oxygen adsorption results

Figure 5 presents results of temperature-programmed reduction of Cs⁺-impregnated and Cs⁺-free silver powder samples. A clear shift to a higher oxygen reduction temperature is observed upon Cs⁺ impregnation, indicating an increased bond strength of adsorbed oxygen.

In Figure 6 the rate of oxygen adsorption to K⁺-impregnated and non-impregnated Ag powder are compared at different temperatures. The preparation of potassium-doped silver was similar to that of the cesium-impregnated

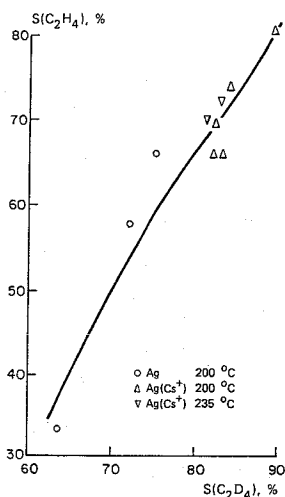


Figure 4. Initial epoxidation selectivity of C_2H_4 versus C_2D_4 .

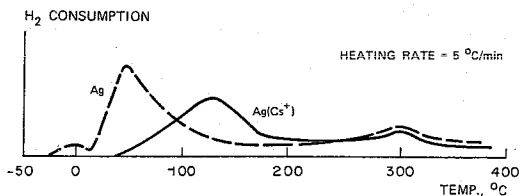


Figure 5. Temperature programmed reduction of alkali-free and Cs^+ -doped silver powder.

material. The initial oxygen pressures were 0.5 kPa. The change in pressure after oxygen adsorption was ~ 0.03 kPa. The adsorption time was of the order of 30 minutes.

The rates of adsorption have been plotted as a function of the amount of oxygen adsorbed. Although the initial rates increase with temperature, it can be seen that at higher temperatures the maximum amount of oxygen that can be adsorbed starts to decrease with temperature. Apparently at those temperatures equilibrium between gas phase and adsorbed oxygen is reached. Similar results were reported earlier by Kilty (3). Alkali doping not only increases the rates of adsorption, but also shifts the adsorption equilibrium to higher oxygen coverage. These results also indicate increased oxygen bond strengths of oxygen adsorbed to silver induced by alkali adsorption. It should be noted that the results presented apply to a situation where the presence of metallic adsorbed alkali can be excluded.

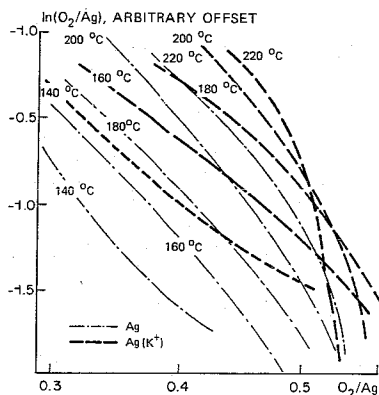


Figure 6. Rate of oxygen adsorption as a function of oxygen coverage to silver powder promoted with potassium and non-promoted.

DISCUSSION

The strong increase in epoxidation rate induced by doping of silver powder with cesium is consistent with the enhanced rates of oxygen adsorption measured on alkali-doped silver, because the epoxidation reaction is known to be first order in oxygen (18) under the particular conditions applied.

The decrease of the epoxidation rate in the presence of chlorine observed with increasing Cs^+ coverage implies increased site blocking of oxygen adsorption sites because of competitive adsorption with chlorine. Chlorine is generated from vinyl chloride by combustion of the organic material. Chlorine is removed from silver by reaction with ethylene. The increased site blocking by chlorine implies that, relatively speaking, the bond strength of adsorbed chlorine is more affected by alkali coadsorption than the bond strength of adsorbed oxygen (19).

It indicates a larger steady-state coverage of chlorine on an alkali-doped catalyst at the same effective partial pressure of Cl than on a non-doped catalyst. This is also evident from the temperature dependence of the selectivity in the presence of chlorine. Whilst the initial selectivity decreases with temperature on non-doped Ag, it is independent of temperature on a Cs^+ -doped catalyst. This result shows that at higher temperatures in the presence of Cl, Cs^+ significantly affects the initial selectivity, in contrast to the behaviour reported on the absence of Cl (10). As the activation energies of the two parallel selective and non-selective reactions are very close (18), the temperature dependence is probably due to the decreasing surface equilibrium concentration of Cl with temperature on non-alkali-doped silver. The $\text{C}_2\text{H}_4\text{O}/\text{C}_2\text{D}_4$ exchange experiment, as well as the observed selectivity of 90 % observed for an optimally promoted catalyst using C_2D_4 corroborate the proposition, that the epoxidation reaction occurs by reaction of ethylene with adsorbed atomic oxygen.

The isotope dependence of the initial selectivity was discussed earlier (11, 16, 17). It indicates that the rate-limiting step of ethylene combustion appears to be C-H bond breakage.

The oxygen adsorption experiments show that under reaction conditions equilibration between gas phase and adsorbed oxygen occurs. The resulting low oxygen surface coverage during reaction conditions explains the low epoxidation selectivity of non-promoted silver.

Chlorine adsorption on silver results in a decrease in the activity because of the high surface coverage of Cl. This not only reduces the activity because fewer surface vacancies are present to accommodate oxygen, but it increases the selectivity because adsorbed oxygen atoms now share silver atom neighbours with chlorine. This reduces the adsorbed oxygen atom bond strength, probably decreases its silver coordination number and makes them suitable for electrophilic attack to the π bond of ethylene, resulting in epoxide. The oxygen atoms adsorbed at low oxygen surface coverage are nucleophilic and attack ethylene at the positively charged hydrogen atoms (7, 8, 11).

In the absence of chlorine, alkali adsorption does not increase the selectivity or does so only slightly, because not only the surface coverage with oxygen, but also the bond strength of adsorbed oxygen is increased.

In the presence of chlorine, the main role of alkali appears to be to maintain a high surface coverage of adsorbed Cl. The resulting adsorption site is schematically shown in Figure 7.

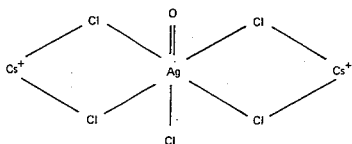


Figure 7. Schematic drawing of ethylene epoxidation site on Cs^+ -promoted silver in the presence of chlorine.

Our model implies that alkali acts to change the solid-state chemistry of the silver oxychloride layer formed at the silver surface. Alkali is well known to stabilize salts (20) and this appears to be its main effect on the silver catalysts. In this particular case it appears to stabilize the formation of the silver oxychloride anion, which is the ethylene epoxidation agent.

ACKNOWLEDGEMENT

I wish to thank C.P.M. de Groot and J. Moolhuysen for their careful assistance with the experiments.

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