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A Study of the Vapor-Phase Epoxidation of Propylene and Ethylene on Silver and Silver–Gold Alloy Catalysts

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From kinetic and mechanistic studies of the oxidation of ethylene and propylene on Ag and Ag–Au alloy catalysts it is concluded that the comparatively low selectivity to propylene oxide is due mainly to the very slow formation of the epoxide and not to the consecutive oxidation to water and carbon dioxide. Oxidation experiments with N_2O have shown that propylene reacts with O^{2-} to form a stable "hydrocarbon" layer, which poisons the silver catalyst. Transient-response experiments have shown that during the oxidation of propylene with oxygen on silver a thick "hydrocarbon" layer is formed on the catalyst. With ethylene under identical conditions no contaminants are detected on the catalyst surface. On Ag–Au alloys that are rich in gold propylene is oxidized to acrolein, while no propylene oxide is formed. With increasing gold content the selectivity to acrolein increases, while in the oxidation of ethylene the selectivity to ethylene oxide decreases and ultimately drops to zero over gold-rich alloys. A model to explain these results is presented.

INTRODUCTION

It has been known for many years that on a silver catalyst in a gas-phase reaction ethylene can be selectively epoxidized with oxygen, whereas propylene is mainly converted to carbon dioxide and water. There are three possible explanations for this large difference in selectivity.

The first possible explanation is that propylene, unlike ethylene, can form an allyl-type intermediate, which is thought to react rapidly over silver to form carbon dioxide and water (*1*). However, as even compounds without allylic C–H bonds, such as 1,3-butadiene and propane, are known to be destructively oxidized over silver (*2*), the low selectivity to propylene oxide need not necessarily be related to the formation of allyl-type intermediates.

The second possible explanation is that the adsorbed oxygen species react in different ways with ethylene and propylene. Ethylene oxide is commonly thought to be formed by interaction of the ethylene molecule with molecularly adsorbed oxygen (*1, 3–12*), although Twigg (*13*), Hayes (*14*), Flank and Beachell (*15*), and Force and Bell (*16*) suppose that it stems from interaction with adsorbed oxygen atoms. As to the oxidation of propylene, Cant and Hall (*23*) have recently proposed a surface reaction between propylene and molecularly adsorbed oxygen resulting in a hydroperoxide. According to these authors this hydroperoxide decomposes rapidly over silver. As far as we know, the reaction of propylene with atomically adsorbed oxygen (N_2O as oxidant) has not yet been reported in the literature.

The third possible explanation is that propylene oxide once formed is rapidly oxidized in a consecutive reaction to carbon dioxide and water. In the literature there is some dispute about the occurrence of this consecutive oxidation of propylene oxide. Latyshev *et al.* (*17*) reported the rate of deep oxidation of propylene oxide to be several times higher than the rate of epoxidation of propylene, but this is in contrast

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with the results obtained by Gorokhovatskii and Rubanik (*18*), who found that propylene oxide is oxidized at a much lower rate than propylene. Cant and Hall (*12*) reported that under their reaction conditions only 2% of the carbon dioxide is formed from gas-phase propylene oxide.

No experimental results are available concerning the reaction of propylene with atomically and molecularly adsorbed oxygen. The reaction of propylene with atomically adsorbed oxygen can be easily performed by using N_2O as the oxidant. The reaction of propylene with molecularly adsorbed oxygen can in principle be effected in two ways, based on the following considerations:

(a) Tanaka and Yamashina (*11*) recorded an ESR spectrum of O_2^- associated with silver oxide (AgO) and found that this oxygen species reacts with ethylene to form ethylene oxide (selectivity ≈60%). This finding induced us to repeat their experiments using propylene as the olefin.

In the epoxidation of ethylene on silver catalysts the selectivity to ethylene oxide can be drastically improved by means of moderators, such as chlorine added as dichloroethane (*19*). This effect can be explained by assuming that the presence of chlorine on the surface of the catalyst favors nondissociative adsorption of oxygen (*9*). Attempts to obtain a similar increase in selectivity in the epoxidation of propylene failed (*20*). Force and Bell (*16*) proposed an alternative explanation of the moderator effect based on the assumption that atomic oxygen and Ag-adsorbed ethylene give total combustion. Chlorine is assumed to prevent coordination of ethylene to Ag.

Our experiments were based on the assumption that addition of an inactive metal to dilute the silver surface could, just like chlorine, enhance the formation of molecularly adsorbed oxygen. Because of its inertness in oxygen chemisorption (*21–27*) and its complete miscibility with silver (*15, 28–34*), gold is ideally suited to act as such an inert diluent. Although published results obtained with Ag–Au alloys in the ethylene epoxidation are contradictory (*14, 15*), we thought it worthwhile to test the Ag–Au alloy system in the oxidation of propylene and assess the influence of the assumed enhanced O_2^-/O^{2-} ratio on the epoxidation of propylene.

EXPERIMENTAL

Continuous-flow experiments. The oxidations of ethylene and propylene were carried out under atmospheric pressure in a stainless-steel reactor. The feed consisted of dry air, ethylene or propylene, and nitrogen as an inert diluent (olefin/oxygen/nitrogen volume ratio: 23.4/7.8/68.8). With a view to having a constant check on the feed composition, part of the feed was led via a by-pass to a sampling unit. Samples of the feed and the exit gas were analyzed by GLC and with a Beckman oxygen analyzer.

Pulsed-flow experiments. The adsorption studies with the pulsed flow were carried out in a microreactor under atmospheric pressure. The pulse consisted of approximately 1%v of the adsorbate gas in helium. The helium carrier gas was freed from water vapor and oxygen before being admitted to the reactor. The products formed during reaction were analyzed by GLC. Slowly desorbed products were collected in a liquid-nitrogen trap and analyzed.

The transient-response microreator. The transient-response oxidation experiments were carried out in the continuous-flow microreactor. After the catalyst had been kept in the reactor under the reaction conditions for a period long enough (several days) for steady state to be reached, the transient-response experiments were carried out by replacing the olefin in the inlet stream by nitrogen. The change in product composition was then monitored as a function of time.

X-ray diffraction measurements. The alloy composition is derived from the unit cell dimension of the alloy crystal, but since the unit cell dimension, measurable by X-ray diffraction (XRD), does not vary linearly with the alloy composition (*13*, *30–34*), a good calibration curve is necessary. We made such a curve using data from a number of Ag–Au alloys of accurately known composition (*35*). From each of these standards some material was filed off, which was subsequently annealed at 300°C in a hydrogen/nitrogen mixture to eliminate the distortion caused to the crystals by filing.

The XRD measurements were carried out in a standard powder diffractometer (Philips PW 1050). In order to achieve sufficient degree of accuracy we used the [333, 511] reflection at $2\theta = 158°$ throughout the measurements. An overall accuracy of approximately 3% in the alloy composition could be obtained for gold concentrations between 0 and 40%.

ESCA measurements. After an alloy catalyst had been kept under a steady state for several days in the continuous oxidation of ethylene with oxygen it was rapidly removed from the fluidized-bed heating system and cooled down to room temperature. The catalyst was then transported through the air. Since the catalytic experiments were performed under differential conditions, the alloys were exposed to a gas mixture containing $\geq 7\%$v oxygen prior to cooling. We therefore feel that transport through air at room temperature does not alter the alloy surface composition.

The spectra were recorded using a Varian IEE/15 spectrometer. From the Ag $3d_{5/2}$ (367 eV) and Au $4f_{7/2}$ (83 eV) intensities the silver fraction at the surface was calculated using the internal calibration method given by Bouwan *et al.* (35–37).

EPR measurements. The EPR spectra of AgO were recorded on a Varian E-line spectrometer connected to a Varian data 620/i integrator. The spectra were recorded at room temperature and at −180°C.

Catalyst preparation. The supported silver catalyst was prepared by impregnating an α-Al_2O_3 (surface area 0.8 m^2/g, 100–140 mesh) with an aqueous silver nitrate solution. The catalyst was dried at 100°C, calcined at 250°C for 16 hr in a flow of air, and reduced in a flow of hydrogen at 300°C for 15 hr. This method yields a catalyst with a homogeneous silver distribution and silver particle size of about 200 nm.

The supported Ag–Au alloy catalysts were prepared by coimpregnation of the α-Al_2O_3 with a solution of spectroscopically pure AgCN and AuCN in a water/ethylenediamine (1/3) mixture. The catalysts were dried at 100°C and calcined at 250°C. On-line analysis of the product gases by mass spectrometry showed that calcination at 250°C for 16 hr was sufficient to decompose the cyanides and to remove the ethylenediamine. The metal concentration in these catalysts was about 8%w. The BET surface areas of the alloy catalysts are given in Table 1.

The unsupported Ag–Au alloy was prepared according to the chemical reduction method of Hund and Trägner (*33*). The AgO was prepared following the method of Hammer and Kleinberg (*38*).

RESULTS

Kinetic Studies

Prior to the kinetic studies it was ascertained that at a linear gas flow of more than 4 cm/sec (STP) and with particles of 100–140 mesh film- and pore-diffusion limitation were absent in the oxidations of ethylene and propylene on all the catalysts used at the temperatures employed. Separate experiments demonstrated the α-Al_2O_3

TABLE 1

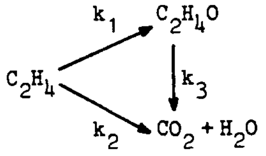
BET Surface Areas of the Calcined Ag–Au Alloy Catalysts

Bulk composition, (%w Au)	BET surface area (m^2/g catalyst)
0	1.4 ± 0.1
8	1.0
36	1.0
64	0.9
100	0.8
α-Al_2O_3	0.8

carrier to be inactive. All the continuous-flow experiments were performed under the conditions mentioned above.

Under differential conditions, in both the ethylene and the propylene oxidation an overall first order in oxygen was found. Because of the relatively low olefin conversion at a threefold excess of olefin the selective and deep-oxidation reactions were assumed to be pseudo-zero order with respect to the olefin.

There is a general consensus of opinion that the oxidation of ethylene with oxygen on silver catalysts can be described by a triangular scheme



Assuming that this model is also valid for the oxidation of propylene, then the selectivity should depend on the conversion, unless $k_3 = 0$. By measuring the oxygen conversion, residence time, and selectivity under differential conditions it is possible to determine k_1 and k_2, (selectivity = moles epoxide/moles epoxide + moles CO_2/n, where $n = 2$ for ethylene and 3 for propylene). The experiments with ethylene and propylene were carried out at 200°C on a 8%w Ag/α-Al_2O_3 catalyst. Table 2 gives the first-order rate constants based on residence time for both reactions. The results show that the low selectivity to propylene oxide as compared to that of ethylene oxide at low conversions (see Fig. 1) is due to differences in both rate constants, k_1 being 17 times smaller and k_2 six times larger for propylene than for ethylene; in other words, deep oxidation is faster and epoxidation much slower for propylene than for ethylene. The k_1/k_3 ratio was determined by measuring the selectivity as a function of conversion for the 8%w Ag/α-Al_2O_3 catalyst. The oxygen conversion, reaching to almost 100%, was varied by changing the gas flow. From these experiments it was found that in the temperature range 180–260°C the selectivity to propylene oxide lies between 4 and 6% and is independent of the oxygen conversion. This suggests that the consecutive reaction of gas-phase propylene oxide is of minor importance, i.e., $k_1 \gg k_3$. To verify this we examined the reaction of gas-phase propylene oxide with oxygen on the silver catalyst (Table 3). It is known from the literature that propylene oxide isomerizes to propionaldehyde and acetone on α-Al_2O_3, whereas it is completely oxidized to carbon dioxide and water on silver metal. Hence we conclude from the data in Table 3 that under our conditions, the consecutive oxidation of propylene oxide to carbon dioxide does not contribute much to the total formation of carbon dioxide.

TABLE 2

Oxidation of Ethylene and Propylene; First-Order Rate Constants Based on Residence Times

Rate constant (sec^{-1})	Ethylene	Propylene
k_1	3.4×10^{-3}	0.2×10^{-3}
k_2	7.9×10^{-3}	5.0×10^{-2}

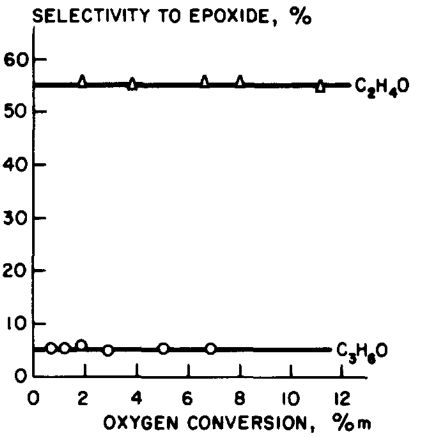


Fig. 1. Oxygen conversion versus selectivity to epoxide at 200°C over 8%w Ag/α-Al_2O_3 catalyst.

Mechanistic Studies

First, we repeated Herzog's experiments on the oxidation of ethylene with N_2O (*41*),

TABLE 3

Results Obtained with 8%w Ag/α-Al_2O_3 Catalyst in the Oxidation of Propylene Oxide[a]

C_3H_6O introduced (%m)	C_3H_6O converted (%)	Breakdown of products		
		CO_2 (%m)	Acetone (%m)	Propionaldehyde (%m)
0.01	70	Traces	30	70
0.05	40	30	20	50
0.10	33	50	8	42
0.50	20	70	5	25

[a] Experimental conditions of propylene oxide oxidation: temperature, 220°C; space velocity, 0.15 $g \cdot h \cdot Nl^{-1}$; $O_2/N_2/C_3H_6O$ volume ratio, 7.8/92.2/%v propylene oxide. (Experimental conditions for the comparative epoxidation reaction: temperature, 220°C; space velocity, 0.15 $g \cdot h \cdot Nl^{-1}$; $O_2/C_3H_6/N_2$ volume ratio, 7.8/23.4/68.8; products, carbon dioxide, propylene oxide (~0.01 %m), traces of propionaldehyde, and traces of acetone.)

using our 8%w/Ag-α-Al_2O_3 catalyst and confirmed his conclusion that the selectivity to ethylene oxide is much lower with N_2O than with O_2 (5 versus 55% at 8% N_2O (O_2) conversion at 260°C). In the oxidation of propylene with N_2O ($N_2O/C_3H_6/N_2$ volume ratio: 7.8/23.4/68.8) no reaction took place below 245°C. Between 245 and 250°C N_2O conversion set in at dramatic rate, ultimately reaching a level of 100%. Traces of carbon dioxide, propylene oxide, and 1,5-hexadiene were observed. In addition, eight products, all having retention times longer than that of propylene oxide, were detected by GLC. At 250°C N_2O conversion gradually decreased until after 15 run hours a constant level of 8% was reached. To find out whether the catalyst was poisoned we switched back to the "normal" feed ($O_2/C_3H_6/N_2$ volume ratio: 7.8/23.4/68.8) and indeed found that only 7% of the oxygen was converted instead of about 40% with a fresh catalyst. In order to clean the catalyst surface we raised the temperature to 275°C and used the $O_2/C_3H_6/N_2$ feed for 45 hr. However, hardly any change could be observed. Subsequently, we used a mixture of 8%v oxygen in nitrogen to burn off the contaminants from the catalyst. In this case large amounts of carbon dioxide and water were produced over a period of 2 to 3 hr. Then the carbon dioxide production decreased slowly until after about 4 hr only traces of carbon dioxide were detected. Assuming that the "hydrocarbon" is only deposited on the silver part of the catalyst surface (the carrier is inert for N_2O decomposition) and that the lateral spacing of the carbon atoms in the "hydrocarbon" layer is the same as the smallest lattice spacing in silver, we calculate from the amount of CO_2 formed a thickness of the "hydrocarbon" layer of about 55 nm.

The selectivity to propylene oxide and ethylene oxide as a function of the oxygen coversion was measured by changing the gas flow at a constant catalyst charge and temperature (200°C in the propylene oxidation and 260°C in the ethylene oxidation). We found that in the case of propylene, alloying of the silver with gold changed the product composition from propylene oxide and carbon dioxide to acrolein and carbon dioxide (Fig. 2). The formation of acrolein was confirmed by a combined GLC–MS analysis. The alloy catalysts were found to be stable (no deactivation) and the oxygen conversion/selectivity plots were all reversible.

In the oxidation of ethylene the selectiv-

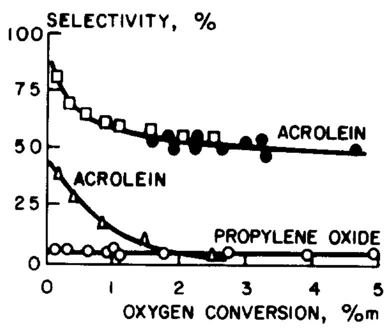


Fig. 2. Oxygen conversion versus selectivity to acrolein and propylene oxide at 200°C. ○, 8%w Ag/α-Al_2O_3; △, 61%w Ag–39%w Au/α-Al_2O_3; ●, 11%w Ag–89%w Au/α-Al_2O_3, □, 24%w Ag–76%w Au (Pure alloy). (Surface compositions from ESCA data.)

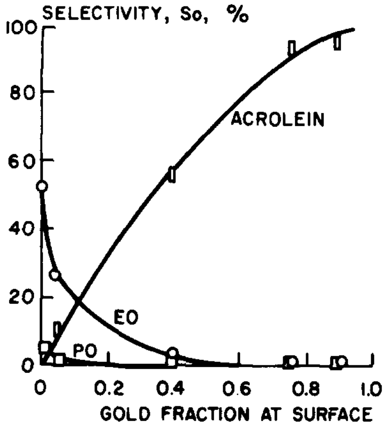


Fig. 3. Selectivities to propylene oxide (PO), ethylene oxide (EO), and acrolein over Ag–Au/α-Al_2O_3 catalysts (except for the catalyst with 76%w Au at the surface, which is a pure alloy). Propylene oxidation at 200°C; ethylene oxidation at 260°C.

ity to its oxide decreased sharply with increasing gold content of the alloy. On gold-rich alloys no ethylene oxide was formed, the only products being carbon dioxide and water. In Fig. 3 the selectivities extrapolated to zero oxygen conversion are plotted versus the gold fraction at the surface of the spent catalysts as measured by ESCA. (It should be noted that the surface composition deviated substantially from the bulk composition, as shown in Fig. 4.) The 8%w Au/α-Al_2O_3 catalyst was found to be inactive in the oxidations of both propylene and ethylene.

The formation of acrolein on the Ag/Au alloys was surprising. Raising the temperature at constant space velocity did not deactivate the Ag–Au alloy catalyst and the selectivity/temperature/conversion plot (Fig. 5) was completely reversible.

The Pulsed-Flow Experiments

As acrolein is formed with high selectivity on Ag–Au alloy catalysts but is not formed at all on the Ag catalyst, we have tried to identify the cause of this difference by studying the adsorption and subsequent reaction(s) of acrolein on the surfaces of an oxygenated silver catalyst, on the one hand, and on an oxygenated Ag–Au alloy catalyst, on the other.

A freshly prepared silver catalyst and carrier were pretreated by subjecting them to an oxidation–reduction (OR) cycle (calcination at 300°C for 4 hrs in air followed by reduction in a flow of hydrogen at 300°C for 4 hrs) (42, 43). The conditions for subsequent oxygen adsorption were: total amount of catalyst, 2; carrier flow, 25 ml (STP)/min; temperature, 200°C; time between two pulses, 210 sec; O_2 content of one pulse, $(0.12 \pm 0.006) \times 10^{18}$ molecules. A characteristic graph of an oxygen–adsorption experiment is given in Fig. 6. The total amount of oxygen uptake as a function of the OR cycle number is presented in Fig. 7. The decrease of the total oxygen uptake as a function of the OR cycle number is most probably due to a decrease in silver surface area. After roughly 10 cycles a constant oxygen uptake is attained. We found, however, that the α-Al_2O_3 carrier adsorbs up to 20% of the amount of oxygen adsorbed by the corresponding silver catalyst. Repeated OR cycling does not render the carrier inert.

The adsorption of acrolein on the oxygenated 8%w Ag/α-Al_2O_3 catalyst in pulse operation resulted in *polymerization* of the acrolein. The amount adsorbed corresponded to approximately 15 acrolein mole-

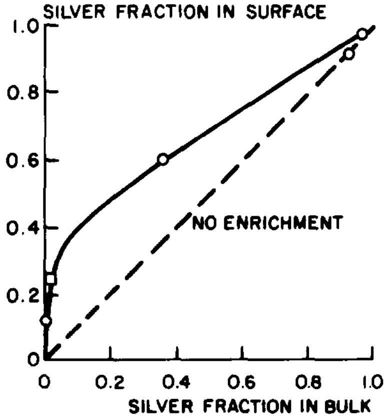


Fig. 4. Surface enrichment for spent Ag–Au alloy catalysts. ○, Ag-Au/α-Al_2O_3; □, pure Ag-Au alloy.

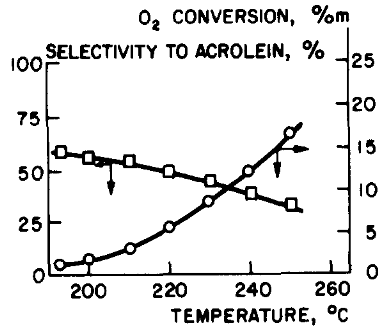


Fig. 5. Selectivity to acrolein and oxygen conversion as a function of temperature over 11%w Ag–89%w Au/α-Al_2O_3 catalyst.

cules per adsorbed oxygen atom. There was no slow desorption of the acrolein. Subsequent admission of gaseous oxygen resulted in a slow liberation of carbon dioxide and water. When more oxygen was admitted and adsorbed or absorbed, the amount of carbon dioxide liberated as a function of time did not change. Hence the polymer formed is capable of retaining the pulsed oxygen without immediately forming more carbon dioxide. That carbon dioxide is not held by the α-Al_2O_3 carrier follows from the fact that the amount of CO_2 adsorbed when pulsed on the oxygenated carrier can be neglected.

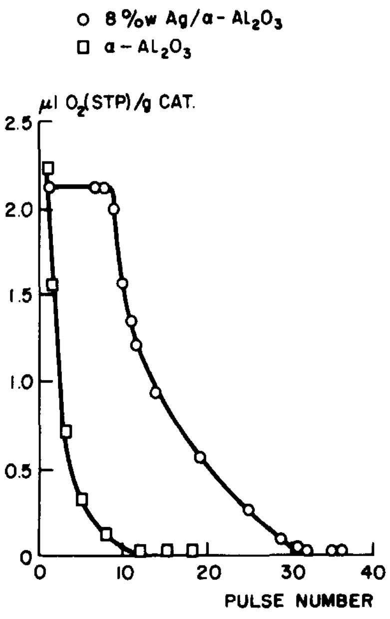


Fig. 6. Oxygen adsorption at 200°C as a function of pulse number.

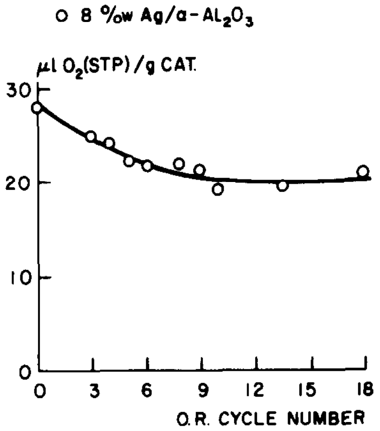


Fig. 7. Oxygen uptake at 200°C as a function of OR cycle number.

The adsorption of acrolein on an unsupported 24%w Ag–76%w Au alloy (surface composition) showed an entirely different behavior. After oxygen coverage the alloy did not adsorb more than approximately one acrolein molecule per three oxygen atoms. Part of the acrolein was reversibly adsorbed (i.e., a slow desorption was observed). The irreversibly adsorbed part yielded carbon dioxide and ethylene as products, indicating that the molecule is cleaved at the C_2H_3–CHO bond. In contrast to what was observed on the supported silver catalyst, the carbon dioxide (as well as the ethylene) formed was desorbed immediately and no carbon was left on the surface.

The Transient-Response Experiments

The response of a component Y in the outlet gas mixture to a step change to nil in the concentration of X in the inlet gas stream is called X (dec., 0)–Y response. Fig. 8 illustrates the decrease of the propylene concentration in the outlet gas stream as a function of time after the olefin has been replaced by nitrogen at $t = 0$. It also demonstrates a difference (see A in Fig. 8) between the olefin concentrations under reaction conditions (T = 230°C) and at room temperature where no reaction takes place.

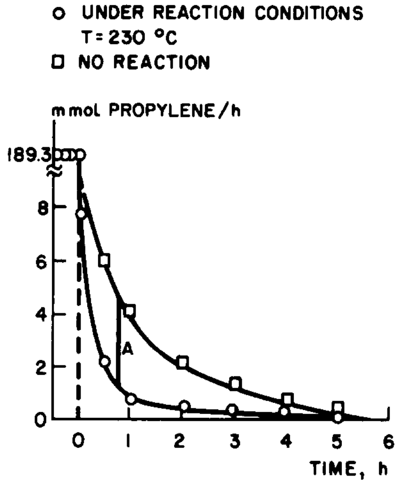


Fig. 8. The propylene (dec., O)–propylene response.

This difference must be taken into account when the amount of propylene present on the catalyst surface is calculated. This implies that one has to make an assumption as to the selectivity to the epoxide as a function of time after $t = 0$.

After the 8%w Ag/α-Al_2O_3 catalyst had been kept under a steady state at 230°C for several days, the C_3H_6 (dec., O)–CO_2 and C_3H_6 (dec., O)–C_3H_6O responses were followed. Fig. 9 shows the C_3H_6 (dec., O)–CO_2 response. After correcting the C_3H_6 (dec., O)–response curve for the amount of CO_2 evolved from the reacted propylene (A in Fig. 8) one obtains Fig. 10. The correction is based on the C_3H_6 (dec., O)–C_3H_6O response measured, which was found to follow almost exactly the amount of propylene converted (A in Fig. 8). This implies that the selectivity to propylene oxide is practically constant, suggesting that propylene oxide is produced by reaction between gaseous propylene and some form of adsorbed oxygen. The integrated amount of desorbed CO_2 was calculated from Fig. 10 and the layer thickness of the intermediate was estimated.

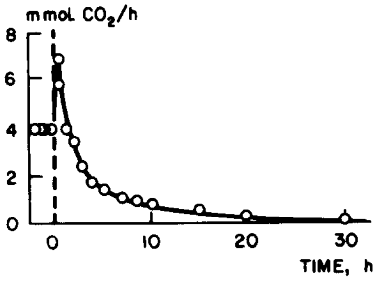


Fig. 9. The propylene (dec., O)–carbon dioxide response.

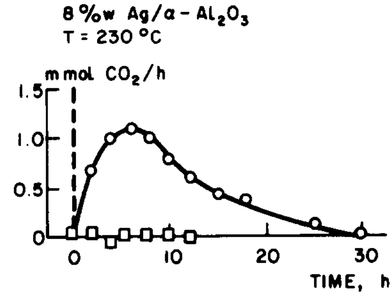


Fig. 10. ○, The propylene (dec., O)–carbon dioxide corrected response. □, The ethylene (dec., O–carbon dioxide corrected response.

During the time necessary to reach steady state (see p. 500) before the transient experiment was conducted, traces of propionaldehyde and traces of acetone were detected (see also Table 3). These trace amounts disappeared immediately after the start of the transient experiment. As we have not quantified these traces, we cannot quantify accurately the part of the α-Al_2O_3 carrier that may have been covered with the "hydrocarbon" layer. Since approximately the same trace amounts of isomerization products were found during continuous flow experiments and the αAl_2O_3 carrier itself proved to be inert under identical conditions in separate transient response experiments, we feel justified in assuming that the "hydrocarbon" layer is deposited only on the silver particles. This then results in a thickness of the layer of ~155 nm.

As a reference, ethylene was oxidized under the same experimental conditions and the C_2H_4 (dec., O)–C_2H_4O and C_2H_4

(dec., O)–CO_2 responses were monitored. The curves could perfectly well be matched by assuming the selectivity to ethylene oxide to remain constant throughout the experiment. Hence the catalyst surface does not contain contaminants (Fig. 10, the C_2H_4 (dec., O)–CO_2 corrected response: the detection limit in these experiments is one monolayer of "hydrocarbon").

The Reaction of O_2^- *Species with Propylene*

AgO was characterized by DTG analysis, and by XRD and ESR experiments. Its Ag_2O content, if any, was too low to be detectable by XRD. DTG analysis showed two peaks, which were assigned to the decomposition of AgO into Ag_2O (100–230°C) and to the decomposition of Ag_2O into Ag metal (300–480°C); the accuracy of the DTG experiments was 97%. The ESR spectrum of O_2^- associated with the AgO was exactly the same as the one reported by Tanaka and Yamashina (*11*).

When a fresh AgO sample was evacuated and contacted with 20 Torr of propylene at 25°C the O_2^- ESR signal did not change. This suggests that the adsorption of propylene on the O_2^- species does not take place at room temperature. Only above approximately 100°C was a reduction of the ESR signal intensity observed: after reaction at 100°C for 4 days the O_2^- signal had disappeared and the low-temperature DTG peak was reduced by 15%. Analysis of the reaction gas by mass spectrometry revealed that the only reaction products, besides traces of acetone, were carbon dioxide and water.

DISCUSSION AND CONCLUSIONS

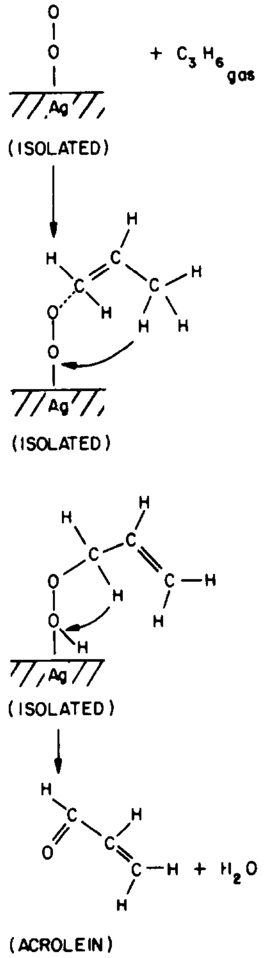
Our kinetic study has shown that the consecutive oxidation of propylene oxide to carbon dioxide and water does not contribute much to the overall formation of carbon dioxide and therefore this route can be ruled out as a possible cause of the low selectivity to propylene oxide. The results, presented in Table 2, further show that the low selectivity to propylene oxide, as compared to the selectivity to ethylene oxide, is partly caused by an increase of the total oxidation rate and is mainly due to the very slow formation of propylene oxide.

When reacted with N_2O ethylene forms carbon dioxide, whereas propylene forms strongly adsorbed products which poison the catalyst. These adsorbates could only be removed through further oxidation to carbon dioxide. It is, however, surprising that with the $O_2/C_3H_6/N_2$ feed the reaction does not stop when enough "hydrocarbon" has formed to cover the silver surface. Since the liberation of carbon dioxide is much more pronounced with the O_2/N_2 mixture than with the $O_2/C_3H_6/N_2$ feed, it would seem that propylene is continuously deposited onto the "hydrocarbon" layer to form rather stable high-molecular-weight products. This deposit is then oxidized to carbon dioxide and water. As to the mechanism by which this occurs one can only speculate. Just like N_2O, oxygen forms O^{2-} when adsorbed on a silver surface. Hence, it is likely that with propylene these strongly adsorbed products are also formed when use is made of oxygen instead of N_2O. Indeed, the transient-response technique has unambiguously shown that under continuous-flow conditions a thick polymer layer is present on the silver particles. Propylene from the gas phase must continuously react with this polymer, as is concluded from the strong initial increase in carbon dioxide production observed after replacement of the propylene by nitrogen (Fig. 9). The formation of carbon dioxide from the polymer may result from a reaction of the gas-phase oxygen with the polymer layer and/or from an indirect oxidation after incorporation of the oxygen.

From the formation of 1,5-hexadiene in the N_2O experiment it is evident that allyl-type intermediates are formed. This, of course, does not imply that such an intermediate is also the precursor in the formation of the "hydrocarbon" layer. Additional evidence of the abstraction of an allylic hydrogen atom from propylene is the formation of substantial amounts of acrolein on the Ag–Au alloys. From these results we conclude that on silver the formation of the allylic intermediate is followed either by total oxidation to carbon dioxide or by further polymerization/polycondensation to carbonaceous residues, whereas on the gold-rich alloy surfaces this allylic intermediate is preferentially oxidized to acrolein and desorbed in this form. This effect of alloying silver with gold is quite conceivable since on the alloy surface the allylic groups are separated by poorly adsorbing gold atoms. The above conclusion is substantiated by the results of pulsed acrolein experiments. Acrolein was found to *polymerize* on oxygenated silver. The adsorption was completely irreversible and the polymer formed proved capable of accumulating oxygen from the gas phase, resulting in a deep oxidation of this polymer. On the Ag–Au alloy adsorbed acrolein behaved in an entirely different way; no polymerization took place, irreversible as well as reversible adsorption occurred and the carbon balance was 100%, indicating that the surface was left clean.

The observed formation of a polymer on the silver surface may also provide an explanation for the experimental results reported by Belousov *et al.* (2), who found that the oxidation of ethylene was suppressed by the presence of propylene, whereas the oxidation of propylene was hardly influenced by the presence of ethylene.

With increasing gold content of the Ag–Au alloy catalysts the probability of finding an isolated silver atom and therefore an isolated O_{2ads}^- could increase. We observed that the selectivity to acrolein also increases with the gold content, reaching almost 100% on the gold-rich alloys. We therefore favor the following mechanism for the acrolein formation:

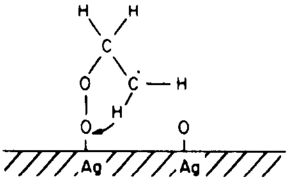


Molecular orbital studies (*44*) have shown that the formation of the propylene hydroperoxide anion from propylene and O_2^- is energetically possible. As proposed by Cant and Hall (*12*), hydrogen from the methyl group is used in an intramolecular hydrogen transfer, resulting in an adsorbed hydroperoxide and a doulbe bond shift. Because of the absence of any other absorbed species in the vicinity, this hydroperoxide then decomposes to form the aldehyde and water, a reaction which is well known in homogeneous catalysis (*45*). The decrease in selectivity at higher oxygen conversions (i.e., at higher acrolein pressures) is consistent with a consecutive scheme in which acrolein molecules react with each other to form adsorbed products that are further oxidized to carbon dioxide and water. In 1971 Cant and Hall (*46*) reported that on gold catalysts propylene is converted to acrolein with selectivities as high as 50%. However, as we found our gold catalyst to be inactive, while our alloys (Fig. 4) showed a pronounced silver surface enrichment at high gold concentrations, it may well be that the gold catalysts used by Cant and Hall (*46*) contained traces of silver at the surface.[1] If so, our results agree very well with their data as far as product-distribution and selectivity decrease at higher conversions are concerned.

The observation that O_2^- reacts with propylene to form acrolein-type intermediates has been reported before by other workers. Using ir and ESR spectrometry Kugler and Kokes (*48*) observed that on the surface of zinc oxide a reaction occurs between the allyl and O_2^- species. The reaction was followed by ir spectroscopy and acrolein was found as the major product adsorbed on the surface. Cant and Hall (*49*) also proposed a very important role of diatomic oxygen species in the oxidation of propylene to acrolein over Rh and Ru on α-Al_2O_3. Our results strongly suggest that acrolein can be formed as a gas-phase product if the O_2^- species are isolated. This, we think, also explains our results with AgO, where the adsorbed propylene is only desorbed at the decomposition temperature of the AgO, resulting in the formation of carbon dioxide and water.

It seems much more difficult to explain the effect of alloying silver with gold on the selectivity to ethylene oxide in the oxidation of ethylene, as shown in Fig. 3. This result seems to disprove the simple expectation that the predominant effect of alloying silver with inert "spacer" atoms of gold would be to favour the adsorption of oxygen as O_2^- rather than as O^{2-}.

However, from results of this laboratory (*50*) it could be concluded that the reaction of ethylene with O_2^- results only in ethylene oxide if the adsorbed complex



is sterically hindered by adjacent adsorbed species, such as O^{2-} or Cl^-, such that abstraction of hydrogen from the ethylene molecule in the way depicted above cannot occur. In the case of the alloys, the O_2^- species are separated from one another and hence the adsorbed ethylene complex will react to form carbon dioxide and water.

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[1] We have found that high-purity gold often contains trace amounts of silver at the surface as a result of chemisorption-induced enrichment because silver forms strong bonds with oxygen. A similar chemisorbed enrichment was invoked by Bouwman *et al.* (*47*) to explain enrichment with Pd of Pd–Au alloys after exposure to CO, as Pd forms strong bonds with CO molecules.

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