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The Oxidation of Ethylene over Silver-Based Alloy Catalysts

3. Silver–Gold Alloys

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Supported silver–gold alloy catalysts were prepared by impregnation of low surface area α-Al_2O_3 with mixed silver cyanide and gold cyanide solutions. Alloying was achieved by calcination at 250°C. X-ray diffraction analysis indicates that complete alloying was achieved. Surface composition of alloy particles was determined as a function of bulk composition by high resolution ESCA analysis. Surfaces were found to be significantly enriched in silver. Turnover numbers of ethylene epoxidation and combustion were found to exhibit maxima on surfaces containing 10–15% Au and drop to zero on surfaces containing 30% Au or more. Temperature-programmed desorption of oxygen from Ag–Au alloy surfaces revealed that oxygen desorbs in two modes from surfaces containing less than 30% Au. The high-temperature desorption peak was assigned to multicoordinated adsorbed atomic oxygen and the low-temperature peak to monocoordinated atomic oxygen. Based on these results a mechanism of ethylene epoxidation and combustion is formulated.

INTRODUCTION

Geometric and electronic factors in catalysis by alloys are investigated using ethylene oxidation as a probe reaction. In previous publications (*1–3*), the effects of alloying silver with Pd, Cd, and Zn on its performance in ethylene oxidation catalysis were described. The final metal which was selected for this study is gold, on the basis of its electronegativity, which is similar to that of Pd relative to silver. A major advantage that gold presents as an alloying metal in this catalytic system is the fact that it is totally inert toward most chemisorptive and catalytic processes. In addition, silver and gold form random solid solutions over the entire composition range. As a result, alloy catalysts with a large variation in surface composition can be formulated and studied. Finally, the formation of Ag–Au alloys is moderately exothermic, which ensures fairly rapid equilibration of the alloys.

It is probably for these reasons that gold is one of the few metals whose role as an additive to silver has been investigated in ethylene oxidation (*4–6*) and other catalytic systems (*7, 8*). Contradictory results concerning the effects of Au on kinetic parameters in ethylene epoxidation and combustion have been reported. Flank and Beachell (*4*) have concluded that activity for overall ethylene oxidation is dependent on lattice spacing of the alloy particles and that gold at low concentrations is a promoter of ethylene oxide formation, markedly improving selectivity. However, Geenen *et al.* (*5*) observed selectivity to decrease with increasing gold content and ultimately drop to zero over gold-rich alloys. Such discrepancies can probably be traced to the method of preparation of the catalysts and to different precursors of the metal components.

In the present communication, the effects of alloying silver with gold on kinetic

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parameters in ethylene oxidation are presented. In addition to ethylene oxidation, methanol oxidation–dehydrogenation was also investigated. Comparison of results of ethylene oxidation with methanol oxidation can lead to some conclusions concerning the nature of the adsorbed oxygen species which participate in the reactions since the only adsorbed species associated with methanol oxidation on Ag surfaces is monatomic oxygen (*9*, *10*). On the other hand, the nature of the oxygen species which participates in ethylene epoxidation and combustion has given rise to significant controvercy in the literature (*11*, *12*).

EXPERIMENTAL

Supported silver–gold alloy catalysts were prepared covering the entire composition range since gold is miscible with silver at any composition. Monometallic catalysts of Ag and Au were also prepared. All catalysts had a total metal loading of 5%. The support employed was low surface area α-alumina (Carborundum, SAHT-99), which was crushed to a particle size between 0.1 and 0.4 mm. Catalysts were prepared by simultaneous impregnation of the support with known amounts of mixed silver cyanide and gold cyanide. Metal cyanides, in appropriate quantities, corresponding to the desired alloy composition, were dissolved in an aqueous solution of ethylenediamine. The volume of solution used was in slight excess of the void volume of the support. The carrier was added to the cyanide solution while continuously stirring, at a temperature of 60°C. When nearly all the water evaporated, the resulting slurry was dried in an oven overnight at 100°C. The impregnated support was calcined in air at 250°C for a period of 24 h. This method of preparation, previously used by Geenen *et al.* (*5*) was adopted in this study in order to avoid using gold nitrate which is obtained by chemical reduction of gold chloride. Thus, the possibility of contamination of the catalyst with traces of chlorine, which is a well-known promoter of ethylene epoxidation, is avoided.

Catalysts were examined with respect to alloying achieved by X-ray diffraction, using a General Electric counter diffractometer with Ni-filtered Cu$K\alpha$ radiation. Scanning was performed between 30 and 80°(2θ). Total surface area was obtained employing the BET method, using argon as adsorbate at liquid nitrogen temperature. Surface composition of alloy particles was determined by electron spectroscopy for chemical analysis (ESCA). The instrument used is a duPont, Model 650-B, modified and automated for data collection. A magnesium anode was used to generate Mg–K radiation, which was used as exciting radiation without being monochromated. A double-sided sample holder was covered with sample powder and high resolution ESCA spectra were obtained. Carbon C$1s_{1/2}$ was used to calibrate binding energies.

Specific reaction rates of ethylene epoxidation and combustion were determined in the temperature range of 217–235°C, at a pressure of 15 atm. Details of the experimental apparatus and procedures have been reported elsewhere (*1*, *2*). For kinetic studies of methanol oxidation–dehydrogenation, the same reactor apparatus was used, modified by addition of a peristaltic metering pump to handle liquid methanol feed. Kinetic experiments were conducted at a temperature of 240°C and atmospheric pressure. Preliminary experiments showed that catalyst particles less then 0.4 mm in diameter and a total feed rate greater than 600 cm^3/min are adequate to eliminate intraparticle and interparticle heat and mass diffusional resistances. The feed mixture consisted of 6.5% methanol, 2.2% oxygen, and 91.3% nitrogen. Analysis of the feed and product mixtures was conducted by gas chromatography in two stages: Liquid components (water, formaldehyde, methanol, and formic acid) were condensed, and gases (nitrogen, oxygen, and carbon dioxide) were directed into a 100/120 mesh Carbosieve S column through a sampling valve. The liquid was separated over an 80/100 mesh Porapak T column. Further experimental details have been reported by Toreis (*13*).

Temperature-programmed desorption (TPD) of oxygen from Ag–Au alloy surfaces was studied in an apparatus which consisted of a gas supply system, dual tubes, and a dual thermal conductivity detector. Ultrahigh purity helium and oxygen were used. Helium was further purified from traces of oxygen by passing it through an oxisorb unit. The catalyst was placed in one tube and an equal amount of α-alumina was placed in the second tube. Both tubes were heated simultaneously during experiments. The temperature was measured by a chromel–alumel thermocouple placed in the center of the catalyst sample. Oxygen detection in the helium stream passing through the catalyst sample was achieved by means of a dual thermal conductivity detector. The helium stream passing through the α-alumina sample was connected to the reference side of the detector. The detector was operated at 200°C with a current of 100 mA. A heating rate of 50°C/min was used in all cases and the sample was heated from 25 to 600°C.

The analysis cycle which was found to give reproducible results consisted of the following steps: (1) Sample and reference tubes were heated to 200°C in flowing helium. (2) The sample was exposed to flowing oxygen at 200°C for 30 min, then cooled to room temperature in presence of flowing oxygen. (3) Gaseous as well as physically adsorbed oxygen was removed by helium flow at room temperature. The effluent was periodically analyzed and the experiment started when no traces of oxygen were detected. Temperature in the catalyst sample was recorded continuously. Oxygen in the effluent stream was continuously monitored by the thermal conductivity detector.

RESULTS AND DISCUSSION

(*a*) *Bulk and Surface Characterization of Alloy Particles*

Silver and gold are completely miscible over the entire composition range, as phase diagrams reveal. Thus, monophasic alloys can be achieved at any desired composition. Formation of Ag–Au alloys is moderately exothermic, indicating that they equilibrate fairly readily. To ensure that alloying had been achieved with the preparation procedure adopted in this study, and that gross separation into metallic components did not occur upon exposure to reaction conditions, X-ray diffraction of all fresh and spent catalysts was conducted. Diffraction peaks of a number of crystal planes were recorded and lattice constants, a_0, were calculated by plotting $\cos^2\theta$ versus a_0 and extrapolating to 90°. Lattice constants obtained in this manner are shown in Fig. 1 as a function of bulk composition of the alloys.

Results shown in Fig. 1 compare favorably with values reported in Pearson's Handbook (*14*) which are also shown on the same figure. Small differences may be attributed to the fact that the results of this study are based on relatively small supported alloy crystallites while those of (*14*) are based on bulk alloys. Similar results

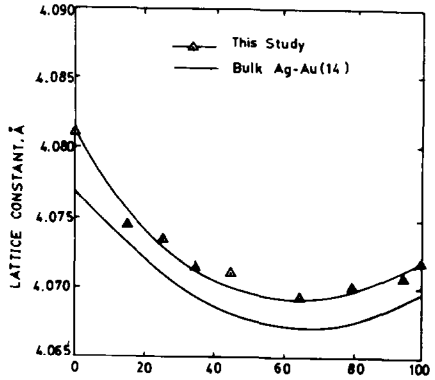


FIG. 1. Lattice constants of Ag–Au alloy catalysts as a function of bulk composition.

were obtained by Flank and Beachell (*4*), although their values of lattice spacing are somewhat higher than those observed in the present study. Differences might be due to the precision of the instruments used or in the method of preparation of the alloys.

It is well known (*15, 16*) that surface composition of equilibrated alloys can vary drastically from that of the bulk. Determination of surface composition is of great importance in catalytic studies with bimetallic catalysts. In other studies (*1–3*), selective chemisorptive titrations were employed to determine surface compositions of Ag–Pd, Ag–Cd, and Ag–Zn alloy catalysts. In the case of Ag–Au, this technique is of limited value since Au is inert toward most gases. To establish the surface composition, high resolution ESCA analysis of all samples was conducted.

Typical ESCA spectra, showing the $C1s_{1/2}$, Ag $3d_{3/2}/3d_{5/2}$, and Au $4f_{5/2}/4f_{7/2}$ photoelectron lines obtained with the 55 : 45 (Ag : Au) alloy catalyst are shown in Fig. 2. Integrated line intensities obtained from the areas under the peaks in the scans were corrected for differences in photoionization cross section (*17*) to approximate relative atom abundance, and were normalized to the $C1s_{1/2}$ photoionization line, which was used as a reference. The Ag/Au ratio was computed from the Ag $3d_{3/2}/3d_{5/2}$ and Au $4f_{5/2}/4f_{7/2}$ photoelectron lines. Results of surface composition obtained from ESCA spectra of various alloys are shown in Fig. 3.

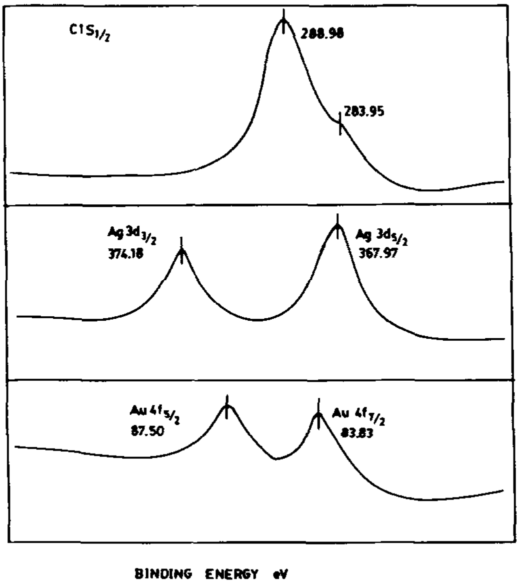


FIG. 2. ESCA spectra from (55 : 45) Ag–Au alloy catalysts.

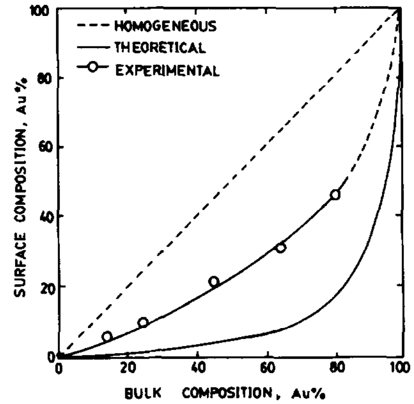


FIG. 3. Surface composition of Ag–Au alloys as a function of bulk composition.

A theoretical curve of surface composition obtained by application of the model proposed by Williams and Nason (*18*) is also shown in Fig. 3. This model is based on thermodynamic properties of individual components and was developed by minimizing alloy surface energy under the regular solution approximation. Both experimental and theoretical curves show significant enrichment of alloy surfaces with silver. This is primarily due to the fact that silver has lower heat of sublimation than gold, and as a result, tends to segregate at the surface. The degree of enrichment predicted by the theoretical model is higher than what was experimentally determined. This discrepancy cannot be attributed to chemisorption induced surface enrichment, a phenomenon which is not accounted for in the model since it assumes equilibrium of the alloy with vacuum. If chemisorption induced surface enrichment was operative, it would tend to enhance the concentration of Ag on the surface, not reduce it. This is due to the fact that oxygen forms strong chemisorption bonds with silver while it does not adsorb, at any appreciable extent, on gold. It is well known that the component which forms the strongest chemisorption bonds tends to segregate at the surface of the alloy particles. The alloys in this study were exposed to oxygen during preparation.

Discrepancies between theoretical predictions and experimental results as well as between experimental results of different investigators can be caused by factors such as temperature, particle size, and support material, in the case of supported alloy particles. It would be expected that equilibrium surface composition depends on size and morphology of alloy crystals. Therefore, different carriers and different metal contents may lead to different results. Furthermore, the regular solution model assumes ideal entropy of mixing and statistical distribution of atoms over lattice points. Deviations from such distributions can occur due to electronic or geometric factors, present at the surface of alloy particles.

The discrepancy between theoretical and experimental curves of surface composition cannot be explained at this point. Estimation of turnover frequencies of ethylene epoxidation and combustion and methanol oxidation, which are reported in subsequent sections, are based on the experimental curve.

(*b*) *Effects of Alloying on Oxygen Adsorption*

Temperature-programmed desorption of oxygen adsorbed on the surface of α-alumina-supported Ag–Au alloy particles was conducted to determine if the presence of gold on the surface affects the adsorption/desorption behavior of oxygen on silver. Desorption was conducted at a heating rate of 50°C/min, in the temperature range of 25 to 600°C. Spectra were recorded as a function of time and were translated to a function of temperature, since sample temperature was also recorded as a function of time. In preliminary experiments the adsorption/desorption cycle was conducted with α-alumina in the sample tube and with Au/α–Al_2O_3 catalysts. In both cases a horizontal line chromatogram was detected, indicating that oxygen does not adsorb irreversibly on either gold or α-alumina. Consequently, observed TPD peaks can be assigned to oxygen species originating from silver atoms only. TPD spectra obtained with Ag–Au alloy catalysts of various compositions are shown in Fig. 4. Two oxygen peaks are observed over alloys with low surface gold content (0–14%) while only a single peak is observed over alloys with higher gold content.

The position of peak maxima in the temperature scale is found to be a function of composition of the alloy particles. This is illustrated in Fig. 5 in which temperatures of peak maxima are shown as a function of alloy surface composition. It is observed that both, low-temperature and high-temperature peak maxima decrease with

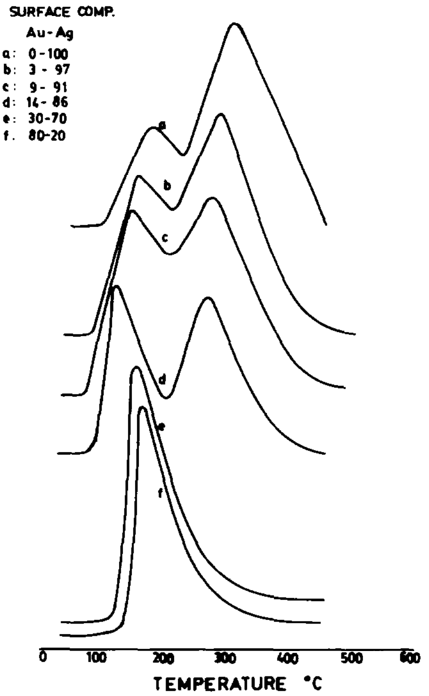


FIG. 4. TPD spectra of oxygen adsorbed on Ag and Ag–Au alloy catalysts.

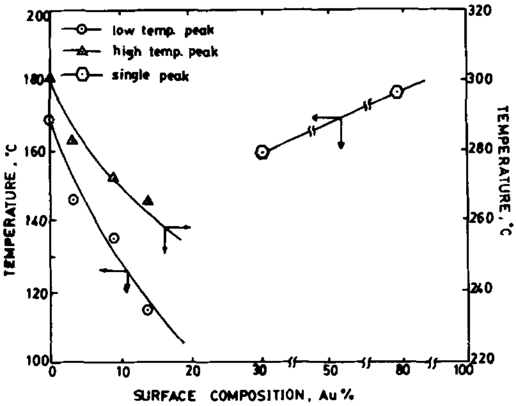


FIG. 5. Variation of TPD peak temperatures with alloy surface composition.

increasing gold content of the surface. The maximum of the low-temperature peak is found to vary from 170°C at 0% gold to 115°C at 14% Au at the surface. Similarly, the maximum of the high-temperature peak varies from 300 to 265°C, within the same composition range. In cases in which only a single peak is present, its maximum shifts to higher temperatures as Au content of the surface increases.

Many studies of oxygen adsorption on silver have attempted to characterize the nature of adsorbed species. Most single crystal studies have led to the conclusion that adsorption of oxygen at temperatures exceeding 300 K results in one stable species, thought to be monatomic, which desorbs at 560–600 K (*19–23*). A second stable species, thought to be diatomic, exists at low temperatures and desorbs below 200 K (*21–23*). Grant and Lambert (*24*), however, who studied oxygen adsorption on Ag (111) at 300 K in the pressure range 0.01–1.0 Torr, concluded that adsorbed dioxygen species coexist with adsorbed monatomic oxygen. The former desorbs at approximately 380 K while the latter at approximately 600 K.

On the basis of these findings the H-T peak observed in the present study at 300°C can be assigned to adsorbed atomic oxygen. The L-T peak cannot be easily identified because of lack of general consensus in the literature. Nevertheless, there are two extreme cases to be considered. First, this peak may correspond to a molecularly adsorbed species. The stability of this species at temperatures higher than those observed in UHV single crystal experiments may be due to higher exposures (oxygen pressure and time) employed in the present study (1 atm as opposed to a few Torr) or it may exist on crystal faces other than the principal ones, (111) and (110), which have been used in those experiments. On the other extreme, both peaks may be assigned to oxygen adatoms of different spatial and energetic configuration. Campbell and Paffett (*22*) also observed two desorption peaks, at 570 and 610 K, upon exposing Ag (110) single crystals to 50 Torr oxygen at 490 K. They assigned both peaks to atomic oxygen on the basis of XPS analysis. The temperature difference between the TPD peaks observed by Campbell and Paffett (*22*) is significantly smaller than the one observed in the present study (40 versus 130 K). This might be due to different surface coverages and different planes exposed ((110) versus polycrystalline). The fact that the L-T peak was not observed at lower surface coverages indicates that this species is indeed sensitive to surface coverage. Based on the discussion above and in view of the fact that molecularly adsorbed oxygen on silver surfaces has only been observed to desorb at temperatures in the range of 190–220 K (*21–23, 25*), while the L-T TPD peak observed in this study appears at 440 K, it is reasonable to believe that this peak corresponds to an atomic oxygen species.

Alloying silver with gold results in significant changes in the TPD spectra of oxygen. The position of the maxima of the two peaks in the temperature scale move to lower temperatures while the magnitude of the H-T peak decreases relative to the L-T peak. At gold contents greater than or equal to 30%, a single peak appears at an intermediate temperature, but closer to the temperature of the L-T peak.

The population of an adsorbed species is proportional to the area under its desorption peak in a TPD spectrum. Thus, it can be concluded that the coverage of the H-T adsorbed atomic oxygen species decreases while that of the L-T species increases with increasing gold content. Dissociative adsorption of oxygen on silver has been proposed to proceed on sites of four adjacent silver atoms (*26*). Recent work by Campbell and Paffett (*22*) has also shown that multiatom sites are required for dissociative adsorption. The decrease of the H-T adsorbed oxygen species with increasing gold content can then be explained by the following reasoning: Gold acts as a diluting agent, destroying a number of four adjacent silver atom sites, thus hindering the dissociative adsorption of oxygen on such sites. As a result of this process, not only the surface population of multiatom site-adsorbed species decreases but also the population of other species which require sites of a smaller number of silver atoms (presumably one) increases. This is precisely what is observed in the present study. After all four adjacent silver atom sites are destroyed (30% Au or higher), then only one species dominates the surface, the species which requires adsorption sites composed of a fewer number of atoms. A Monte Carlo simulation of Ag–Au alloy surfaces also showed that the number of four adjacent silver atom sites on surfaces containing 30% Au or more is extremely small or zero (*13*). Then, the H-T desorption peak can be assigned to multicoordinated atomic oxygen, while the L-T peak can be assigned to monocoordinated atomic oxygen species.

Figure 5 indicates that a significant shift of the position of peak maxima to lower temperatures occurs upon alloying silver with gold. In the range of 0 to 14% Au, the L-T peak shifts from 170 to 115°C while the H-T peak shifts from 300 to 265°C. Such shifts indicate that the strength of the silver–oxygen bond decreases with increasing gold content. Gold atoms, in addition to their spacer role on the catalytic surface, also affect the electronic structure of silver atoms by near-neighbor interactions. It has been suggested (*27*) that in Ag–Au alloys, *d*-electrons of gold are transferred to silver, a transfer that is partially compensated by transfer of conducting *s*, *p*-electrons in the opposite direction. Isomer shift determinations also suggest *s*-charge transfer from Ag to Au atoms (*28*). XPS analysis indicates that the ratio of *d*-depletion (i.e., gold to silver) to conduction electron gain (i.e., silver to gold) is 0.6 ± 0.2 for $Ag_{0.5}Au_{0.5}$ (*29*). This indicates that, upon alloying silver with gold, a net transfer of electrons from silver to gold is expected, rendering silver deficient in electrons. The same conclusion is drawn by examination of the work function of the two metals. The work function of Ag is reported to be 4.73 eV while that of gold 4.82 eV. Since the work function of silver is lower than that of gold, electronic interactions between Ag and Au atoms are expected to result in electron transfer from silver to gold.

The dissociative adsorption of oxygen on silver requires transfer of electrons from silver to oxygen. Dissociative adsorption of oxygen on silver atoms in Ag–Au alloys is hindered since these silver atoms are electron deficient due to near-neighbor interactions with gold atoms. Thus, the resulting silver–oxygen bonds are weaker and the adsorbed species tend to desorb at lower temperatures, in accordance with results observed in the present study.

At high surface gold contents (>30%), the opposite phenomenon is observed. The single TPD peak tends to shift to higher temperatures with increasing gold content. This is probably due to the fact that at high Au contents, surface Ag atoms are mostly coordinated to Au atoms rather than to other Ag atoms on which oxygen would be adsorbed. Ag atoms with oxygen adsorbed on them are highly electropositive and they would tend to abstract electrons from near-neighbor silver atoms not occupied by oxygen, much more so than Au does. As a result, isolated Ag atoms in the alloy matrix are less deficient in electrons than their counterparts in a pure silver matrix, in the presence of oxygen. This results in stronger oxygen adsorption on the isolated Ag atoms, and thus higher desorption temperature.

In the analysis presented above it was assumed that all oxygen detected in the desorption process originates from silver atoms. To justify this assumption, the possibility of spillover of atomic oxygen species onto Au sites must be addressed. In static chemisorption experiments of oxygen on gold powders and α-Al_2O_3-supported gold crystallites at temperatures as high as 200°C, no measurable chemisorption was detected (*13*). Nevertheless, it is conceivable that in Ag–Au alloy particles oxygen dissociates on Ag atoms and spills over onto Au sites. The L-T peak cannot be assigned to oxygen originating from Au sites because it also appears in pure Ag samples and because it composes all oxygen detected from high Au content catalysts. Such an assignment would imply that Ag atoms in an Au atom matrix do not adsorb any oxygen. The H-T peak cannot be assigned to oxygen originating from Au sites either because the magnitude of this peak decreases with increasing gold content and it is eliminated at high Au contents. Thus, both peaks must be assigned to oxygen originating from Ag sites. If any spillover of adsorbed oxygen does occur onto Au sites, these species are probably very weakly bound and desorb during the He purging process, or at low temperatures and are not detected because their concentration is very low.

The TPD results discussed above clearly demonstrate that alloying silver with gold results in significant changes in the mode of oxygen desorption. Major changes are rationalized in terms of a geometric factor. Multiatom sites (presumably 4-atom ones) responsible for dissociative multicoordinated oxygen adsorption are destroyed by introduction of Au atoms in the silver surface matrix. As a result, the population of multicoordinated oxygen species decreases and eventually is eliminated as the Au content of the surface increases. Electronic near-neighbor interactions between silver and gold atoms, rendering Ag atoms electron deficient, are thought to be responsible for observed changes of silver–oxygen bond strengths.

(*c*) *Effects of Alloying on Kinetic Parameters*

Initial specific rates of ethylene epoxidation and combustion were determined in a plug flow reactor which was operated in the differential mode. Turnover frequencies (specific rates per surface silver atom) were computed from knowledge of surface composition as a function of bulk alloy composition. Pure, α-alumina-supported gold catalysts were found to be inactive in either reaction under conditions employed in this study. Thus, specific rates were computed in terms of the silver component only, and any changes in kinetic parameters can be attributed to some form of interaction between Ag and Au atoms at the surface of the catalyst.

Turnover frequencies of ethylene epoxidation and combustion are shown on Figs. 6 and 7, respectively, as a function of surface composition of alloy catalysts. It is observed that, at all temperatures, both

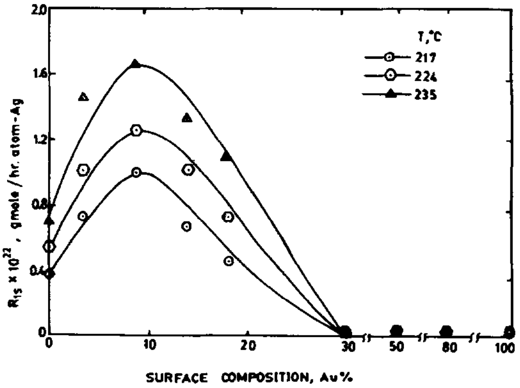


FIG. 6. Variation of turnover frequency of ethylene epoxidation with surface composition of Ag–Au alloy catalysts.

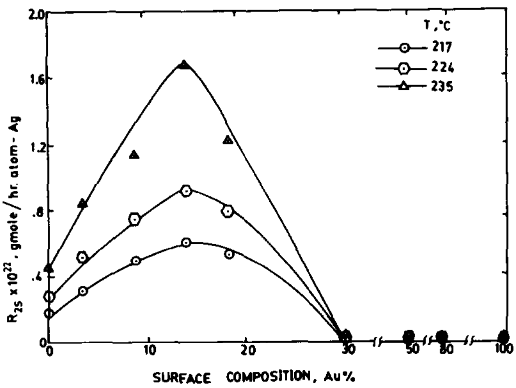


Fig. 7. Variation of turnover frequency of ethylene combustion with surface composition of Ag–Au alloy catalysts.

specific rates initially increase with increasing gold content of the surface, go through a maximum, and then decrease, dropping to zero at surface compositions exceeding 30% gold. In ethylene epoxidation, maximum turnover frequency is observed at approximately 10% gold, while in combustion at approximately 15% gold. Selectivity, defined as the ratio of the rate of formation of ethylene oxide, R_{1s}, to total rate of consumption of ethylene ($R_{1s} + R_{2s}$), is shown in Fig. 8 to remain approximately constant up to 10% Au content of the surface and drop at higher gold contents. This behavior is the result of different rates of change of turnover frequencies of epoxidation and combustion, with respect to surface composition of the alloy catalysts.

Activation energies of ethylene epoxidation and combustion are shown in Fig. 9 as a function of surface composition. Activation energy of combustion is shown not to be affected by the presence of gold on the surface. However, activation energy of epoxidation decreases with increasing gold content, goes through a minimum at approximately 10% Au, and increases, approaching the activation energy of combustion at high gold contents of the surface. Surface composition at which minimum activation energy is exhibited corresponds to the composition at which maximum turnover frequency of epoxidation is observed.

Methanol oxidation–dehydrogenation was used as an additional probe reaction in studying geometric and electronic effects of alloying silver with an inert metal, gold. Preliminary experiments in which feed mixtures were passed through empty reactor tubes or over Au/α-Al_2O_3 catalysts, at 240°C, resulted in no measurable conversions. Thus, homogeneous reactions or reactions on metal surfaces of the apparatus (stainless steel tubes) or independent reactions on gold surfaces do not occur under conditions employed in this study. Specific reaction rates were then computed based on the silver component of the catalyst only.

Total rate of methanol conversion and apparent rates of conversion to formaldehyde, formic acid, and carbon dioxide were estimated. Specific rates per surface silver

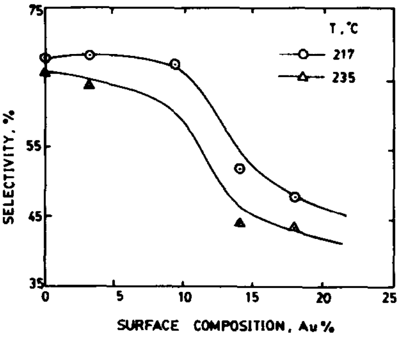


Fig. 8. Effects of gold content on epoxide selectivity.

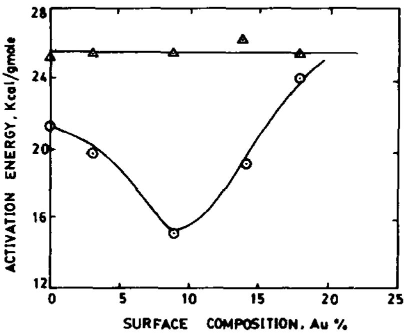


Fig. 9. Effects of surface gold content on activation energies of ethylene epoxidation and combustion.

atom at 240°C, are shown in Fig. 10 as a function of alloy surface composition. A behavior similar to that observed with ethylene epoxidation is apparent in Fig. 10. All rates exhibit maxima at a surface containing approximately 10% gold, while catalysts with surface gold contents exceeding 30% are inactive in all reactions. Selectivity to formaldehyde formation, defined as the ratio of the apparent rate of formaldehyde formation over the rate of methanol consumption, was observed to decrease with increasing gold content of the surface.

Significant controvercy, concerning the effects of alloying silver with gold on activity and selectivity in ethylene oxidation, exists in the literature. Flank and Beachell (*4*) observed activity to decrease with increasing gold content and selectivity to exhibit a maximum at 10–15% Au (bulk). Herrera *et al.* (*6*) observed that activity remained constant at lower temperatures and increased at higher temperatures over samples containing up to approximately 11% Au, then decreased at higher gold contents. Selectivity was also found to exhibit a maximum at ~16% Au (bulk). Geenen *et al.* (*5*), on the other hand, found selectivity to decrease monotonically with increasing gold content, although more rapidly than what was observed in the present study. These discrepancies might have their origin in the method of preparation of the alloy catalysts since widely different methods were used. In addition, the presence of various species which, at extremely low concentrations are known to be promoters of ethylene oxide selectivity, in impregnating solutions, might be responsible for the observed selectivity enhancements at low gold contents. Results of the present study are in general agreement with those reported by Geenen *et al.* (*5*). In both studies, metal cyanides were used as precursors, eliminating the possibility of promotion by residual species from impregnating solutions.

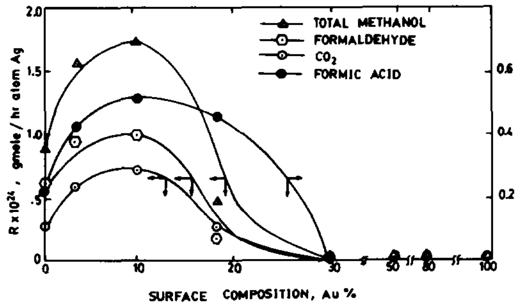


FIG. 10. Variation of turnover frequencies of methanol oxidation–dehydrogenation reactions with surface composition.

A striking result of the present study is the complete loss of activity for ethylene and methanol oxidation of surfaces containing 30% gold or more, as shown in Figs. 6, 7, and 10. This result was carefully checked by preparing and testing three different batches of catalysts and by conducting reactions at temperatures as high as 280°C. No activity was detected in any case, even at high temperatures. This finding cannot be attributed to reorganization of surfaces under reaction conditions with subsequent loss of surface silver. Oxygen chemisorption experiments on fresh and used catalysts indicated no measurable changes of surface composition upon exposure to reaction conditions. In addition, if chemisorption-induced surface reconstruction was operable in this system, the alloy surface would be expected to be further enriched with silver which forms strong chemisorption bonds with oxygen. Oxygen, on the other hand, does not adsorb on gold. Thus, there is no reason to believe that Au atoms diffuse to the surface, while Ag atoms diffuse to the bulk of the alloy particles.

To explain this phenomenon, results of TPD analysis must be considered. Figure 4 shows that the H-T peak, which corresponds to multicoordinated adsorbed atomic oxygen, decreases in magnitude with increasing gold content and it is eliminated at surface gold contents greater than or equal to 30%. As discussed earlier, this peak is attributed to dissociative oxygen adsorption on multiatom silver sites (4 adjacent Ag atoms). At 30% gold, all such sites are eliminated, thus oxygen cannot adsorb on the surface in this mode. The fact that catalytic activity is eliminated at exactly the same surface composition strongly indicates that oxygen species adsorbed on multiatom silver sites are either responsible for adsorption of ethylene or are the ones which participate in surface reactions. Since turnover frequencies increase while the concentration of multicoordinated adsorbed atomic oxygen decreases, at low surface Au contents, it is unlikely that this particular oxygen species directly participates in surface reactions. It is well known that ethylene does not adsorb on well-reduced silver surfaces but it does adsorb (although weakly) on oxygenated silver surfaces (*11*, *12*). For these reasons the former explanation is favored. It can then be concluded that ethylene adsorption sites are created by the dissociative adsorption of oxygen on multiatom Ag sites. Results of methanol oxidation–dehydrogenation which also show no activity at 30% Au also support this conclusion. Methanol, in order to react, must adsorb to form a methoxide species ($CH_3O\langle ads\rangle$), which is believed to be responsible for further activity. Like ethylene, methanol does not adsorb on reduced silver surfaces but it does adsorb on oxygenated ones.

If the alloy is not well formed, islands or clusters of silver atoms might exist on the surface, even at higher gold content, which would provide sites for dissociative multiatom adsorption of oxygen, subsequent adsorption of ethylene, and catalytic action. In that case, elimination of catalytic activity would be expected to occur at much higher Au content. Alloy preparation techniques might be crucial in this respect.

Alterations in turnover frequencies and other kinetic parameters, brought about by alloying silver with gold, must be explained in terms of geometric and electronic considerations of catalytic surfaces. The most obvious effect of gold atoms on the surface is to reduce the number of multiatom silver sites required for adsorption or surface reactions. The model of Kilty *et al.* (*26*), important elements of which are supported by the work of Campbell (*30*), cannot alone explain observed results. According to this model, dissociative adsorption of oxygen on ensembles of four adjacent silver atoms leads to combustion products, while diatomic adsorption on single silver atoms leads to ethylene oxide. If it is assumed that gold simply plays an inert spacer role, then the ratio of adsorbed molecular to atomic oxygen would increase with increasing surface gold concentration, leading to increased epoxidation and decreased combustion activity. Results of this study and previous ones (*1*, *2*) clearly contradict this premise. Thus, geometric alterations of catalytic surfaces are not solely responsible for observed changes in catalytic behavior of silver under ethylene oxidation conditions.

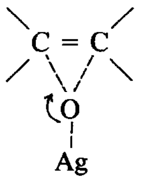
Results of the present investigation can only be explained in terms of a mechanism of ethylene epoxidation and combustion. Experimental observations lead to the following conclusions: (1) The fact that all three reactions—partial and complete oxidations of ethylene and methanol oxidation—behave in a similar manner with increasing gold content of the surface implies that all reactions are affected similarly by the presence of gold. (2) Since methanol oxidation does not require the presence of adsorbed diatomic oxygen species to proceed, then either molecular oxygen does not participate in ethylene oxidation either, or, if it does, the presence of gold on catalytic surfaces does not influence the mode of its participation. (3) Activation energies of epoxidation and combustion are different and are differently affected by the presence of gold. This observation implies that rate controlling steps of the two reactions are different. (4) Results of TPD and kinetic experiments discussed earlier imply that ethylene participates in the reactions from an adsorbed state, in agreement with many other investigators. Sites for ethylene adsorption are created by dissociative adsorption of oxygen on multiatom sites. (5) A correlation between concentration of monocoordinated adsorbed atomic oxygen and turnover numbers of ethylene epoxidation and combustion and methanol oxidation is observed. This indicates that this species participates directly in these reactions. (6) Molecularly adsorbed oxygen on silver or alloy surfaces was not observed in the present work. In fact, such species have never been detected on Ag surfaces at temperatures close to those of oxidation activity.

The following mechanism can be formulated based on these observations: Oxygen adsorbs on Ag surfaces in two modes. A strongly adsorbed, multicoordinated, monatomic species and a weakly adsorbed monocoordinated species which is also atomic. The presence of strongly adsorbed species is necessary for catalytic action. Ethylene adsorbs on electropositive silver sites created by the multicoordinated adsorption of oxygen, and it reacts with the weakly adsorbed monocoordinated oxygen to form an intermediate complex which either branches to ethylene oxide or to total combustion products. This branching is affected by the presence or absence of adsorbed species in neighboring silver atoms and by the electronic configuration of silver atoms.

Results of the present study as well as previous ones employing silver-based alloy catalysts (*1–3*) can be explained in terms of the mechanism outlined above. At low gold surface contents, turnover frequencies of ethylene epoxidation and combustion and methanol oxidation increase with increasing gold content. This is accompanied by a similar increase in the amount of adsorbed monocoordinated atomic oxygen. The fact that a direct correlation between these two phenomena exists indicates that this oxygen species is the one which directly participates in all reactions. The fact that the multicoordinated oxygen species follows the exact opposite trend indicates that this species does not participate directly in the reactions. Nevertheless, this species is responsible for generation of electropositive silver sites for ethylene adsorption. Although ethylene adsorption decreases with increasing Au content, its effect is not immediately felt because this adsorption step is not the slowest one in the sequence. The proposition that both reaction routes proceed through the same intermediate complex arises from the observation that both rates are affected identically by the presence of gold, in the low concentration range. Nevertheless, activation energies of the two reaction routes are different and are differently affected by the presence of gold atoms on the surface. This observation implies that rate-controlling steps of the two routes are also different.

These considerations are valid as long as there is sufficient ethylene on the surface. When the concentration of gold is sufficiently high so as to reduce multicoordinated adsorption of oxygen and subsequent adsorption of ethylene, turnover numbers begin to decrease and finally fall to zero at sufficiently high surface gold content. At that level (≥30%), no ethylene can adsorb on the surface and thus no reaction occurs.

In addition to these geometric effects, an electronic effect is also operable. As discussed earlier, near-neighbor electronic interactions between Ag and Au atoms result in electron transfer from Ag to Au, rendering surface silver atoms electropositive. The fact that the activation energy of epoxidation decreases with increasing gold content at low gold concentrations implies that the transformation of the intermediate complex involves electron transfer from this complex to Ag atoms. This is satisfied by the breaking of an Ag–O bond during this transformation which involves electron transfer from the complex to the silver atoms:



An electropositive silver surface facilitates breaking of such a bond which manifests itself as lower activation energy since this is the rate-controlling step. At higher gold contents the activation energy of epoxidation begins to increase as the reduced population of ethylene oxide on the surface is felt. Thus, the rate-controlling step shifts from the transformation of the intermediate complex to ethylene oxide, to the formation of the intermediate complex. As a result, activation energy of epoxidation gradually increases with increasing gold content and approaches that of combustion. Activation energy of combustion is not affected by electronic near-neighbor interactions between Ag and Au atoms since the rate-controlling step for this route is the formation of the intermediate complex. This conclusion is derived from the observation that at high Au content, activation energy of epoxidation approaches that of combustion. In this region, the formation of the intermediate complex controls both rection routes.

There is yet another very important factor which must be considered. This is related to hindrance effects of species adsorbed on atoms neighboring the adsorbed intermediate complex (*5*). The intermediate complex results in ethylene oxide if it is sterically hindered so that abstraction of hydrogen from the ethylene molecule cannot occur easily. This consideration explains why the maximum in epoxidation turnover number occurs at a lower gold content than that of combustion. Since gold does not adsorb oxygen, such a hindrance is not present and the intermediate complex decomposes to CO_2 and H_2O at the expense of ethylene oxide.

Results of previous studies in this laboratory employing other silver-based alloy catalysts (*1–3*) can also be explained in terms of the mechanism outlined above. The case of Ag–Pd alloy catalysts is obscured from the fact that ethylene reacts on Pd as well as on Ag. In addition, there is a strong possibility that ethylene oxide, formed on Ag atoms, is further oxidized on Pd atoms. For these reasons, apparent epoxidation turnover number was found to decrease with increasing Pd content. Results of Ag–Zn alloy catalysts (*3*) were explained on the basis of structural information obtained by EXAFS analysis. In the case of Ag–Cd alloys, turnover frequency of epoxidation was found to rapidly increase with increasing Cd content, while that of combustion to increase at a lower rate. This behavior is similar to the one observed over Ag–Au alloy catalysts of low gold content. The increase in turnover numbers is due to increased concentration of monocoordinated atomically adsorbed oxygen. The increase of epoxidation activity is higher than that of combustion due to the steric hindrance effect mentioned above. This effect comes about from oxygen species adsorbed not only on Ag but also on Cd atoms, neighboring the intermediate complex. At higher Cd contents, in contrast to the case of Au, turnover numbers continue to increase because, unlike Au, Cd adsorbs oxygen and, in cooperation with Ag atoms, it provides sites for the multicoordinated dissociative adsorption of oxygen. Thus, the adsorption of ethylene on the alloy surface is not hindered. For this reason, rates per surface Ag atom continue to increase, even at very high Cd contents. The different effects of Cd and Au on turnover frequencies and selectivity is due to the fact that Cd provides sites for the multicoordinated adsorption of oxygen and simultaneously provides the hindrance effect which is necessary for selective oxidation.

In terms of electronic interactions, an apparent discrepancy is obvious. Although Au and Cd are on opposite sides in terms of work function or electronegativity relative to silver, they influence activation energy in the same direction. This discrepancy can be explained by the fact that surface Cd atoms are oxidized under reaction conditions. Therefore, the Cd atoms neighboring Ag atoms are not of the same electronic configuration as reduced metallic Cd. In fact, Cd atoms in CdO would be electron deficient in comparison to metallic Cd. Thus, near-neighbor electronic interactions would tend to result in electron charge transfer away from Ag atoms, as is also the case in Ag–Au alloy catalysts.

The mechanism outlined above is not an entirely original one. Important elements of this mechanism have also been proposed by other investigators, most recently by Grant and Lambert (*31*) and van Santen and de Groot (*32*). Significant differences between these mechanisms also exist. The proposed mechanism is based on experimental observations of the effects of alloying Ag with various metals. Details of mechanistic steps and chemical transformations have not been presented since they cannot be substantiated with experimental results of this study. The most important aspect of ethylene oxidation catalysis is the nature of the adsorbed oxygen species which participates in the reactions. TPD results of the present study strongly indicate that weakly adsorbed monocoordinated atomic oxygen participates in both reactions. This weakly adsorbed oxygen has not been detected in ultrahigh vacuum single crystal experiments. Van Santen and de Groot (*32*) attribute this to the conditions under which oxygen is adsorbed, surface treatment, or lack of steps and edges of single crystals. The present work offers experimental evidence of the existence of a weakly adsorbed atomic oxygen species on Ag surfaces which participates directly in ethylene epoxidation and combustion chemistry.

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