

The Geometric Factor in Ethylene Oxidation over Gold-Silver Alloy Catalysts

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The gold-silver alloy system was chosen for a study of the effect of the geometric factor in the silver-catalyzed oxidation of ethylene because of the known promoting ability and inertness for oxygen chemisorption of metallic gold. Alloys with gold contents of 0, 5, 15, 30, 45, 60, and 80 atom % were prepared by a chemical reduction technique and examined for catalytic activity for ethylene oxidation in a microreactor assembly coupled to a gas chromatography unit. Dynamic adsorption measurements and lattice parameter measurements were also performed on the alloy samples. The results of these studies show that activity for overall ethylene oxidation over gold-silver alloys is dependent on lattice spacing, and that gold, at low concentrations, is a promoter for ethylene oxide formation, markedly improving ethylene oxide selectivity even though conversion falls off somewhat. Activation energy values indicate that the number of active sites decreases as gold concentration increases. Oxidation activity appears to be related to surface sites having fairly low adsorption energies for oxygen. Ethylene adsorption was found to be relatively unimportant.

INTRODUCTION

The silver-catalyzed oxidation of ethylene has received considerable attention in the past (see, for example, refs. 1-7), but many aspects of it remain unclarified. Gold is one of several materials reported to be a promoter for silver catalysts for ethylene oxide production (6, 8), but the literature shows no systematic studies of catalytic activity throughout the entire range of alloy composition.

The chemical reactivity of gold-silver alloys had been shown by Tamman to undergo a rather sudden change in the region of 50 atom % gold (9). This suggested that there may be a parallel change in the catalytic activity of alloys with high gold contents. Since the gold-silver alloy system is continuous throughout the entire compositional range, forming a solid solu-

tion crystallizing in a cubic lattice with the lattice constant varying smoothly with alloy composition and exhibiting a minimum at about 60 to 65 atom % gold (10), a test could be made of the importance of lattice geometry in catalytic oxidation with such a system.

Extension of geometric considerations to oxidation reactions such as the oxidation of ethylene has not heretofore been made, although the need for structural conformity of the catalyst with the reacting molecule has recently been emphasized (11). It may also be noted that some of the discussion concerning electronic mechanisms in catalysis recognizes the importance of geometric considerations and imparts physical meaning to them (12).

EXPERIMENTAL

Alloy preparation. Pure homogeneous alloys with gold contents of 0, 5, 15, 30, 45, 60, and 80 atom % were prepared according

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to the chemical reduction method of Hund and Trägner (13).

Formaldehyde reduction in strongly basic solution under intensive stirring was employed for reduction to the metal from a KNO_3 -saturated nitric acid solution containing the requisite amounts of gold and silver. Metal recovery was essentially quantitative, and the X-ray diffraction peaks indicated no significant broadening. Electron micrographs showed the alloys to consist of uniformly small irregularly shaped particles with surface detail that could, in some areas at least, be described as sets of chevrons. A commercial-type BaO_2 -stabilized silver catalyst supported on α -alumina was prepared for comparison purposes (7). Several of the alloy preparations, as well as some of the reactor experiments, were performed in duplicate and were found to be quite reproducible.

Microreactor. The stainless steel reactor tube had a catalyst capacity of 1 cc and employed upper and lower "deadmen" to minimize void volume. Sheathed thermocouples entered the top and bottom heads of the reactor through lava sealing rings and were reproducibly positioned just above and below the bed of catalyst. The upper junction signal was used to actuate a Wheelco proportional band temperature controller, and the lower one was read from a portable potentiometer. A snug-fitting phosphor-bronze core was placed around the microreactor and wrapped with insulated nichrome wire connected to the load side of the controller. This assembly was covered with insulation and fitted into a metal heater casing.

Flow system. CP grade ethylene and air from high-pressure cylinders were each passed through two-stage diaphragm regulators, capillary orifice differential manometer flow meters, and low-flow-type differential pressure controllers. The gases were then fed to a mixing tee and passed through a drying tube before entering the valve assembly leading to the upper reactor head. The exit gases entered the valve assembly from the lower reactor head and passed through a rotameter tube monitor before being vented.

Valve assembly. Attached to the reactor heads was a multimode valve assembly consisting of (a) a pair of three-way toggle valves for choosing reactor bypass or reactor flow-through modes (feed samples could thus be passed through the chromatographic unit without disturbing any of the adjustments in the system), (b) a pair of three-way toggle valves for choosing which of the two parallel gas chromatographic analytical columns would be used for a given sample, (c) an eight-port two-position valve for selecting either continuous or slug modes of reactor operation, and (d) an eight-port two-position valve with two sample loops of nominal 1-cc capacity for introduction of product samples to the chromatographic unit without serious disruption of the various flow patterns in the system.

Analytical system. A parallel-column system employing two different lengths packed with 25% acetonylacetone supported on Chromosorb was developed for these studies (14). With this system connected to a thermistor bead thermal conductivity cell, quantitative estimation could be made for ethylene, air, carbon dioxide, and ethylene oxide. Individual peak areas were measured by a triangulation method to within 1 mm². Mass spectrometer analyses were used in obtaining appropriate mole response correction factors and in establishing the absence of any other major products under the conditions employed. Operating details are described in ref. (14).

Adsorption system. For the dynamic adsorption studies the microreactor system as described above was used with minor modifications. Catalysts were charged to the microreactor and heated to 232°C under flowing helium. With the valve assembly adjusted to permit the slug mode of reactor operation, slugs of air or ethylene were passed over the catalyst bed either by injection with a gas-tight syringe through a tee in the system, or by operation of the gas sampling valve with gas flowing through the feed system in the slug mode pattern. The amount of oxygen adsorbed by the sample was determined from the reduction in the area of the chromatographic peak for

oxygen using a molecular sieve column, compared with the area obtained from a set of calibration blanks.

X-Ray diffraction measurements. Lattice parameter measurements were made using a GE XRD-5 X-ray diffraction unit. Lattice constants were determined from the (420) planes with a precision of about two in the fourth decimal place, and an accuracy comparable to the best available literature values (10, 15). The alloy system was concluded to be homogeneous and face-centered cubic throughout the range of composition, with a minimum in the lattice constant occurring in the neighborhood of 60 atom % gold, in agreement with previously cited literature references.

Data evaluation. Calculations were made for ethylene conversion (mole percent disappearance of ethylene, based on ethylene in the feed), ethylene oxide selectivity (mole percent appearance of ethylene oxide in the product, based on ethylene disappear-

ance), ethylene oxide yield (mole percent appearance of ethylene oxide, based on ethylene in the feed), first order rate constant, apparent activation energy, and material balance (16). Normalization on the basis of product distribution was used, even though the material balances were consistently within about 2% of theoretical.

Data were taken at 204°, 232°, 260°, and 288°C, using a 10:1 air-to-ethylene feed ratio and a 1 sec nominal contact time at essentially atmospheric pressure. Ratios of 5:1 and 20:1 and contact times of 0.5 and 2.0 sec were run and showed that the product distribution was not unduly sensitive. Data taken at different contact times established that the results in this system could be fitted to a rate law having a first order dependence on ethylene pressure. It was also shown that no reaction took place in an empty reactor up to a temperature of 290°C. Various additional blank tests and calibrations were made wherever necessary

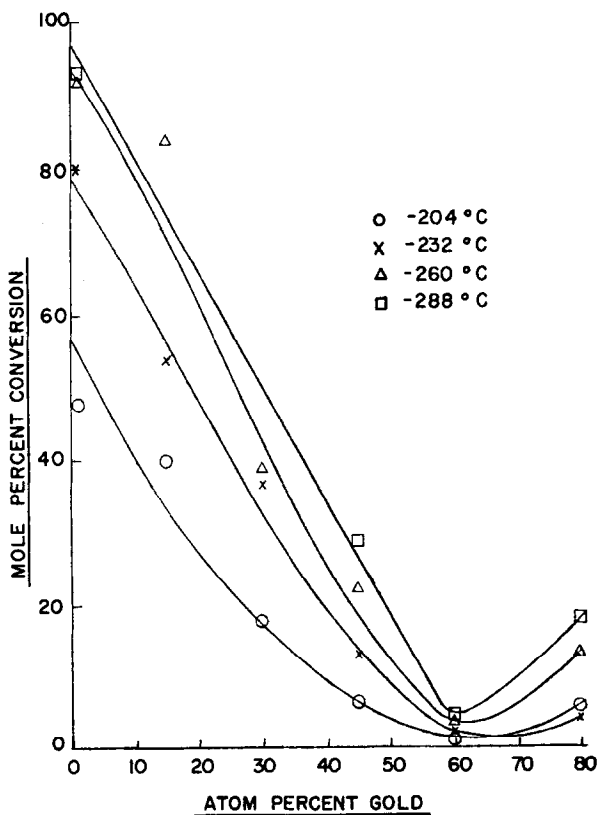


Fig. 1. Mole percent conversion vs. alloy composition.

in the system. Apparent activation energies were calculated from Arrhenius plots of the reaction rate constants obtained at the several temperatures previously noted, using a least-squares method.

RESULTS

The data obtained in this work are shown, in a series of plots against alloy composition, in Figs. 1 to 6. Since finely divided alloys of this type are subject to sintering, and the experiments at different temperatures were run in a random order, complete data could not be obtained for all of the catalyst samples charged to the reactor. It was necessary to rerun some of the alloy samples in order to obtain more complete data. Agreement in comparable cases was within a few percent.

The reaction rate constants as plotted in Fig. 4 have been recalculated on the basis of actual silver content of the alloys, and may thus be considered as representing the specific rate for silver catalysis when the silver is present in a given geometric environment.

The shape of the curve in Fig. 6, based on oxygen adsorption per gram of silver contained in the alloys, although unexpected, was confirmed in repeated experiments and could not be explained on the basis of differences in particle size or surface area, degree of heterogeneity, or experimental technique. Neither could it be explained on the basis of participation of the gold in oxygen adsorption, since gold is unique among metals in not chemisorbing oxygen (4, 8, 17). Indeed, one of the advantages of using the gold-silver alloy system in this study was that the effect of the geometric factor would not be masked by participation of gold in the reaction.

DISCUSSION

The most widely accepted mechanism for the oxidation of ethylene over silver is due to the work of Twigg (1, 2), but general agreement on this is still lacking (8). Twigg concluded from his studies in a flow system that at short contact times both ethylene oxide and carbon dioxide were formed, and established a parallel-consecutive mecha-

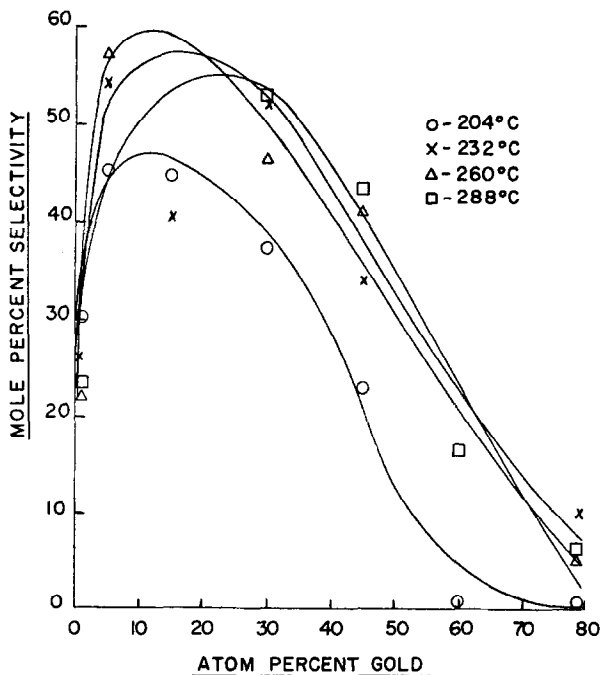


Fig. 2. Mole percent selectivity to ethylene oxide vs. alloy composition.

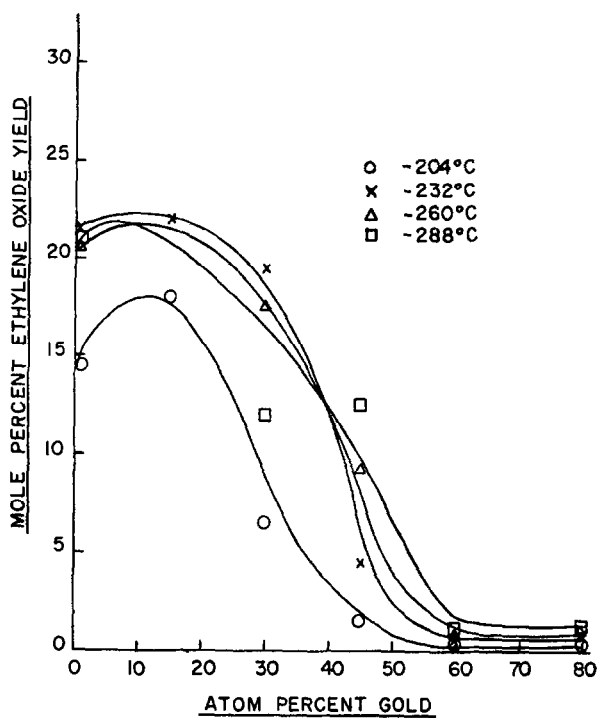


FIG. 3. Mole percent yield of ethylene oxide vs. alloy composition.

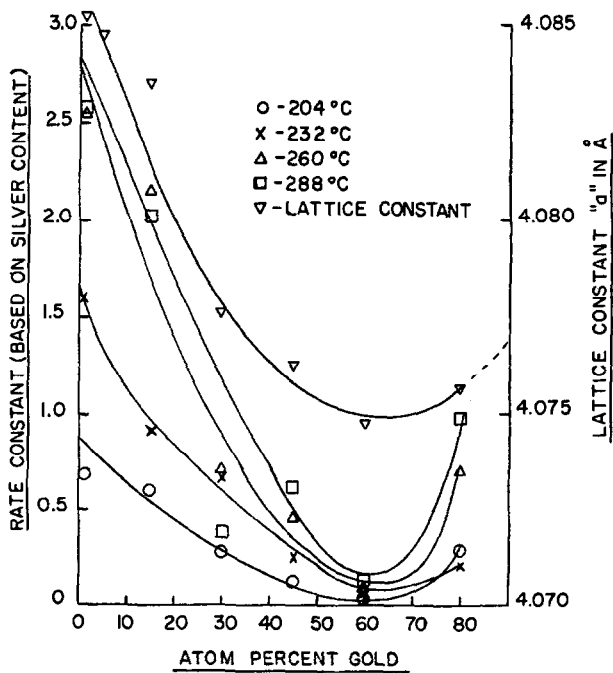


FIG. 4. Alloy composition vs. rate constant and lattice constant.

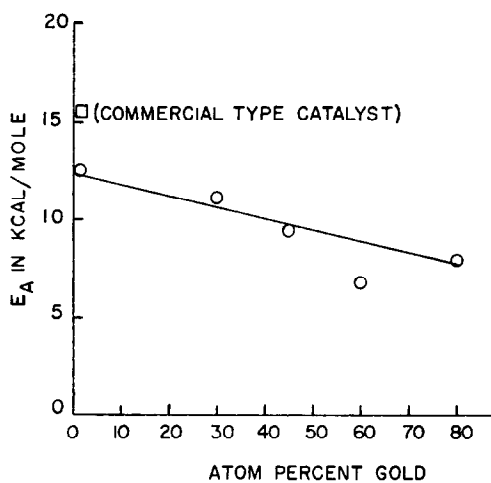


Fig. 5. Activation energy vs. alloy composition.

nism for the reaction. The rate of carbon dioxide formation was found to be somewhat slower from ethylene oxide than from ethylene. It was also shown by Twigg, in a static system, that at 200° to 350°C oxygen was chemisorbed as atoms on the surface of the silver, with a surface coverage of about 0.7, while ethylene was not chemisorbed on a clean silver surface. The fraction of the silver surface covered by oxygen was determined by means of electrical conductivity measurements. It was shown that ethylene could be oxidized by adsorbed oxygen atoms either to ethylene oxide or directly to carbon dioxide and water.

Kinetic measurements by Twigg in the static system indicated that the reaction mechanism involves first the chemisorption of oxygen as atoms on the catalyst surface, followed by the reaction of gaseous or physically sorbed ethylene molecules either with one oxygen atom to form ethylene oxide, or with two oxygen atoms to form products, presumably resembling formaldehyde, that are rapidly oxidized to carbon dioxide.

The Twigg mechanism has been confirmed by several subsequent workers, including Margolis and Roginskii (18) and Kummer (19), who also found that the rate of reaction was independent of the crystal face. The existence of two independent paths for carbon dioxide formation, in a

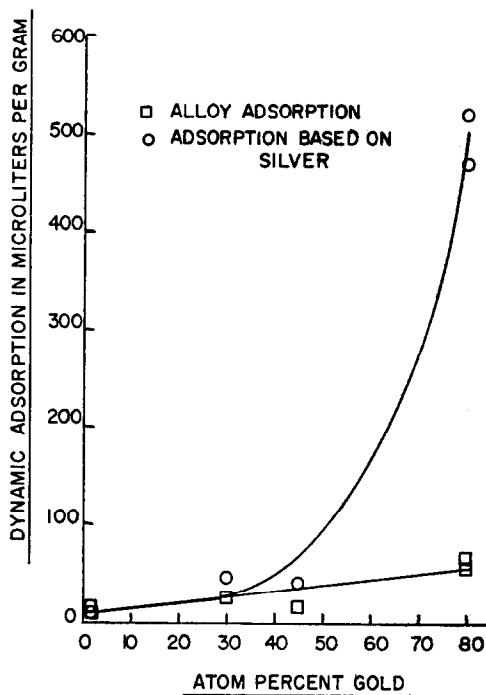


Fig. 6. Dynamic oxygen adsorption vs. alloy composition.

parallel-consecutive mechanism, was supported by a tracer study (18) in which a mixture of ethylene containing carbon-14 and inactive ethylene oxide was oxidized. The activity of the carbon dioxide formed was much higher than that of the ethylene oxide in the product, showing that the direct oxidation route for ethylene does indeed occur also.

It is generally agreed that ethylene is not chemisorbed by silver surfaces, and that oxygen is quite strongly adsorbed as atoms (8), although this view is not universally held (5). The rate of oxygen adsorption approximates the rate of ethylene oxidation so that one or the other may be the slow step in the overall process. When the oxide film on the silver surface is fairly thick, on the order of several tens of atomic layers, as has been shown by Temkin and Kul'kova (20), the chemical and electronic characteristics of the catalyst surface will be determined by the oxide film properties, the metal itself exerting little effect. But with a thin oxide layer, the catalytic properties

will depend on the nature and geometry of the underlying metal support (6).

Recent work by Czanderna on the chemisorption of oxygen on silver, using a vacuum ultramicrobalance, indicates that three processes are operative on a silver surface (21). Measured activation energies of 3, 8, and 22 kcal/mole are related to the processes of dissociative adsorption, molecular adsorption, and surface mobility of adsorbed oxygen atoms, respectively. This supports the conclusion of Margolis, based on homolytic oxygen exchange, that both atomic and molecular oxygen exist on a silver surface (22), a view recently challenged by Sandler and Hickam on the basis of their isotopic exchange data (23), which they interpreted as showing that only one form of oxygen is present on the surface.

The physical structure of the oxygen adsorbed on the outer surface of the silver remains a subject of speculation, according to these authors. The more loosely bound oxygen is often assumed to be bound in molecular form. Oxygen molecules as well as atoms provide a perfect geometrical fit with the two smallest lattice spacings (2.88 and 4.08 Å) of the face-centered cubic silver lattice. In the catalytic oxidation of ethylene to ethylene oxide and carbon dioxide, where the existence of different types of oxygen is indicated by the alternative reaction paths, Sandler and Hickam suggest that a distinction between different types of oxygen may have to be made on the basis of the way in which the oxygen is embedded into the surface lattice, in the limit as surface or subsurface oxygen. The difference in coordination with surrounding silver atoms might be an essential factor in determining the chemical properties of the oxygen present. That this plays a role in the gold-silver alloy series is shown by the comparison of the Hall coefficients for the alloy series with the lattice constant curve (24). The number of current carriers in the semiconducting oxide layer is seen to be directly related to the lattice geometry of the alloys, in accordance with Vol'kenshtein's interpretation (12).

The present results show, in agreement with previous work (6), that gold in moder-

ate concentrations is indeed a promoter for silver catalysts for ethylene oxide synthesis. It can be seen from examination of Figs. 1 to 3 that while conversion of ethylene decreases with increasing gold content, the selectivity to ethylene oxide passes through a rather steep maximum, allowing an optimum yield of ethylene oxide to be achieved in a gold-promoted catalyst system. The improvement, however, is rather small in these experiments, which were of course not conducted in a manner duplicating commercial practices. It should be noted also that maximum ethylene oxide yield is achieved at temperatures somewhat lower than those giving maximum conversions of ethylene.

A comparison of the plots of alloy composition versus rate constant corrected for actual silver content by volume, and versus lattice constant, shown together in Fig. 4, shows remarkable agreement between the two curves, both having a minimum in the neighborhood of 60 atom % gold. This agreement furnishes support for concluding that lattice spacing plays an important role in the catalytic activity of the system under consideration. Both structural and energetic conformity between the gas-phase reactant molecule and the catalytic surface with its adsorbed species are required for maximum efficiency of reaction (11).

The occurrence of a minimum in the lattice constant curve might be explained on the basis of a principle in solid state physics. In order to maintain a constant number of electrons in the unit cell, or, more realistically, an electron concentration in the valence band, the lattice parameter may change to accommodate small compositional changes in the alloy (25). Addition of silver to gold causes a shrinkage until the system is overwhelmed, whereupon steady expansion of the lattice occurs until pure silver is reached. This type of behavior is seen in a number of alloy systems and is commonly referred to as deviation from Vegard's rule of monotonic change in lattice parameter for a continuous alloy system. The electronic principle of valence band electron concentration conservation may thus be suggested as a basis for both lattice

change and catalytic activity paralleling such change.

The apparent activation energy versus composition curve plotted in Fig. 5 appears to be almost a linear one, although the data have some degree of uncertainty. It is noted that the highest activity is associated with the highest activation energy, and that the reaction over a commercial-type catalyst preparation has a comparably high activation energy. This latter value agrees reasonably well with others reported in the literature (4).

The general slope of the activation energy curve requires some explanation. Since the plot of activation energy against the logarithm of the frequency factor was found to be linear, and ethylene adsorption or reaction from the gas phase would not have a high entropy of activation—it should in fact remain constant in the series—the low activation energies observed are indicative of a small number of active sites (3). Since these sites may well be formed in association with defects or layer edges on the alloy surface, further dilution with gold would decrease the chances of such sites being formed, and would decrease their number. This effect would not be expected to overshadow the lattice spacing effect, and was not found to do so in this work. It should be pointed out that the activation energy for adsorption of oxygen on silver varies with surface coverage, indicative of a heterogeneous surface and of metal-oxygen bonds of varying energies (21).

The nearest-neighbor distance in a silver lattice, as noted above, coincides with the oxygen-oxygen distance in an oxygen molecule. Chemisorption of oxygen can thus be easily accomplished, from the geometric point of view. The slight change in this distance brought about by promotion of the silver catalyst with gold would tend to decrease the total amount of oxygen adsorbed, but it would promote the dissociation of the oxygen molecule into adsorbed atoms, which then can migrate rather freely over the surface. The shapes of the curves for conversion and ethylene oxide selectivity and yield in Figs. 1 to 3 can be visualized on this basis. As the amount of gold in the

alloy increases, the surface mobility of the oxygen would be expected to fall off, since gold alone of all the metals does not chemisorb oxygen. The selectivity at very high gold concentrations, therefore, would not be expected to rise again. Rather, a shift toward molecularly adsorbed oxygen would be expected, leading to the results shown in Figs. 2 and 3. Strong dilution with gold thus enhances CO_2 formation by favoring molecular adsorption rather than the atomic form. The rate of oxidation per unit of silver, however, is seen in Fig. 4 to depend on the lattice constant.

The dynamic adsorption studies showed the rather surprising result that the least active catalysts for ethylene oxidation, i.e., those alloys with high gold content, adsorbed the greatest amount of oxygen per gram of silver, and also held on to it the most strongly. Several duplicate experiments were in good agreement regarding this point.

The dynamic adsorption experiments with ethylene showed that, within the range of detectability, a high gold content alloy adsorbed a very small amount of ethylene which was easily removed completely by a subsequently injected air slug, forming carbon dioxide. In passing ethylene over this alloy, a possible trace of ethylene oxide appears to be formed, presumably by reaction with labile oxygen remaining after heating to 232°C in a helium flow stream, or present by virtue of having diffused to the surface from the subsurface layers. This is not unexpected, considering the persistence of some of the oxygen adsorbed on silver (23).

A pure silver preparation exhibited little or no ethylene oxide formation with slug operation using ethylene or air. Water and quite appreciable amounts of carbon dioxide were observed as being formed from ethylene slugs, but neither of these were formed with injected slugs of air. These observations are indicative of appreciable oxygen adsorption and negligible ethylene adsorption. Continuous operation with a pure ethylene feed stream did not show prolonged carbon dioxide formation.

The dynamic oxygen adsorption data in-

dicates that at high gold concentrations a large amount of oxygen is adsorbed and held quite strongly. Pure silver apparently adsorbs little oxygen under these conditions and appears to hold it comparatively weakly. However, consideration must be given to the type of oxygen involved in this adsorption. Silver actually chemisorbs quite appreciable amounts, and oxygen on a silver surface readily migrates into the subsurface layers. This oxygen is very strongly held and does not readily participate in chemical reactions, nor is it readily desorbed. The adsorption measurements made in this study do not involve such strongly chemisorbed species.

It is also noted that the actual contact time for the slug of air passing over the catalyst bed in the adsorption experiments is fairly short and that the catalyst is being continually purged with a flowing helium stream at 232°C. Therefore, it is not the very weak adsorption sites having very low heats of adsorption for oxygen chemisorption that are involved. The observed adsorption involves sites of moderate to moderately strong strength, and the high-gold alloys would seem to have an adsorption energy distribution displaced somewhat toward the higher energy range. Pure silver would seem to have a distribution with maxima near both ends. This effect might be explained in terms of electron availability at a silver defect site as well as lattice geometry; it is probably dependent on both the number and spacing of silver atoms.

The oxygen involved in oxidizing ethylene must, then, be that which is adsorbed on moderately low energy sites, and these would have a somewhat higher activation energy for adsorption. Oxidation activity is concentrated in sites with adsorption energies which can fulfill the conditions of effecting adsorption and holding the oxygen on the surface loosely for a long enough time to react, allow freedom to migrate somewhat on the surface and effect dissociation, and not permit simple desorption upon the approach of an ethylene molecule. The addition of small amounts of gold increases the number of stronger sites while

decreasing the total number, promoting oxygen dissociation, and leading to an increase in selectivity, while the total conversion of ethylene decreases.

The double bond in an approaching oxygen molecule may be ruptured as a consequence of the transfer of electrons from the silver surface to the oxygen molecule, and formation of corresponding localized holes. Trapping of a free electron, or hole delocalization, then converts the oxygen atom into a reactive chemisorbed atom, but it retains some residual electron affinity for attack upon the ethylene double bond. This dissociative chemisorption depends on the nature and lattice structure of the surface, and the importance of geometric factors here can be readily seen.

CONCLUSIONS

In summary, we can interpret our results as supporting the following:

(a) Activity for overall ethylene oxidation over gold-silver alloys is dependent on lattice spacing, as shown by the coincidence of the curves for the rate constant and the lattice constant versus alloy composition.

(b) Gold, at low concentrations, is indeed a promoter for ethylene oxide formation, markedly improving ethylene oxide selectivity even though conversion falls off somewhat. These phenomena are explained on the basis of the data concerning adsorption energies and lattice spacing.

(c) The number of active sites decreases, as shown by activation energy values, as gold concentration increases; this effect does not appear to be as strong as the lattice spacing effect.

(d) Oxidation activity appears related to surface sites having fairly low adsorption energies for oxygen, as shown by the dynamic adsorption data. Strong sites bind the oxygen too firmly to permit a high reaction rate, and these are found in the alloys with high gold content. Ethylene adsorption is relatively unimportant. A surface reaction mechanism can be formulated on this basis, involving sites with a restricted range of adsorption energies for oxygen chemisorption.

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