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The Oxidation of Ethylene over Silver-Based Alloy Catalysts

II. Silver–Cadmium Alloys

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Silver–cadmium-supported alloy catalysts were prepared by impregnation of α-alumina with mixed silver nitrate and cadmium nitrate solutions. They were characterized in terms of exposed metallic area and surface composition employing selective chemisorption of oxygen and hydrogen. Surface enrichment in cadmium was observed which increased after the catalysts had been exposed to reaction conditions. Turnover frequencies of ethylene epoxidation and combustion reactions were determined. The former was found to increase significantly with increasing cadmium content of the surface while the latter was found to remain constant or slightly increase, resulting in improved selectivities. Activation energies were found to decrease with increasing cadmium content. The results are discussed in terms of geometric and electronic considerations of the alloy surfaces and it is concluded that electronic interactions between silver and cadmium atoms, affecting the rate-controlling step of the reactions, are primarily responsible for their observation.

INTRODUCTION

Because of its industrial and scientific importance, the selective oxidation of ethylene to ethylene oxide over silver catalysts has received great attention in the literature. A very interesting aspect of this catalytic system is the fact that silver is unique among metals in its ability to promote the epoxidation reaction so as to obtain significantly high selectivities. Fundamental aspects related to adsorption characteristics, kinetics, mechanism, and various parameters of the catalyst have been reviewed frequently (*1–3*).

Studies of ethylene oxidation over silver-based alloy catalysts can be very rewarding in understanding fundamental phenomena of this reaction system and of alloy catalysis in general. The oxidation of ethylene is suitable for such studies for a number of reasons. The reaction has been shown to be structure sensitive (*15*) which implies that kinetic parameters are affected by the details of surface structure. Furthermore, reaction parameters are sensitive to the particular support which is employed for the silver crystallites, to pretreatment conditions of the catalyst, and to the presence of various promoters which, at very low concentrations, alter selectivity significantly. These sensitivities have often been attributed to the mode of oxygen chemisorption on silver. Thus, according to Kilty and Sachtler (*1*), molecular oxygen adsorbed on one silver atom leads to ethylene oxide while atomic oxygen, adsorbed on ensembles of four silver atoms leads to combustion products. The electronic structure of the surface would also be expected to influence the mode of oxygen adsorption and subsequently the performance of the catalyst since dissociative adsorption requires transfer of two electrons from silver to oxygen while nondissociative adsorption requires transfer of only one electron.

In our studies, the oxidation of ethylene is investigated using silver-based alloy catalysts. In particular, geometric and electronic alterations of the surface silver ma-

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trix, brought about by alloying, are related to changes in measurable kinetic parameters and to the mechanisms of the epoxidation and combustion reactions. In an earlier publication (*4*) we reported results of ethylene oxidation over silver–palladium alloy catalysts. Specific reaction rates per exposed silver atom were found to decrease for the epoxidation and increase for the combustion reactions with increasing palladium content of the surface. Activation energies were found not to be affected by alloying. These results are in general agreement with those of other investigators (*5*, *6*) who used Ag–Pd alloy catalysts. The only other alloy catalysts which has been investigated under ethylene oxidation is silver–gold (*7*, *8*). Contradictory results have been reported from these two studies.

In the present paper we report results obtained using silver–cadmium-supported alloy catalysts. Cadmium was selected as the alloying metal because it forms solid solutions with silver within an appreciable composition range (0–42%), the alloy is formed exothermically thus resulting in random solid solutions which equilibrate rapidly, and, finally, because cadmium has a lower electronegativity than silver.

EXPERIMENTAL

Supported silver and silver–cadmium alloy catalysts were prepared with bulk-phase compositions in the range of 0 to 35% cadmium. A supported cadmium catalyst was also prepared. All catalysts had a metal loading of 5 wt%. The support which was used was low surface area α-alumina (Carborundum, SAHT-99), which was crushed to particle sizes between 0.1 and 0.4 mm. The preparation method involved impregnation of the support with known amounts of mixed silver nitrate and cadmium nitrate solutions of appropriate concentrations, drying of the impregnated support at 105°C in an oven overnight, and reduction of the dried and impregnated support at 250°C in flowing hydrogen for 24 h.

The catalysts were examined with respect to the extent of alloying achieved by X-ray diffraction using a General Electric counter diffractometer, employing Cu$K\alpha$ radiation. Scanning was performed between 30° and 80° (2θ). The total surface area was obtained employing the BET method, using argon as the adsorbate at liquid-nitrogen temperature. The exposed surface area of the alloys and the composition of the surface of the alloy were determined by selective chemisorption of oxygen and hydrogen. The chemisorption experiments were conducted in a constant-volume high-vacuum apparatus (Micromeritics, Accusorb 2100E). The oxygen chemisorption experiments were carried out at 200°C, at oxygen pressures of up to 25 mm Hg. The hydrogen chemisorption experiments were carried out at 215°C, at hydrogen pressures of up to 400 mm Hg. Prior to the chemisorption experiments, a standard pretreatment procedure was followed. This procedure consisted of the following steps: (1) Degassing of the sample under dynamic vacuum at 140°C for 15 h. (2) Three-cycle oxidation–reduction of the sample under oxygen or hydrogen at 5 mm Hg pressure at 140°C for 30 min. A 15-min degassing period was used between each exposure to oxygen or hydrogen. (3) Degassing of the sample at the chemisorption temperature for 15 h. The chemisorption experiments were conducted after this treatment.

Details of the experimental procedures followed to determine specific reaction rates have been reported in a previous publication (*4*). Kinetic experiments were conducted at a pressure of 15 atm and at temperatures of 217, 224, and 235°C. The feed composition consisted of 3.0% ethylene, 3.3% oxygen, and 93.7% nitrogen. The oxygen concentrations was kept at low levels so as to avoid phase separation of the alloy catalysts during reaction.

RESULTS AND DISCUSSION

Precautions were taken in this study to form monophasic alloys by preparing sup-

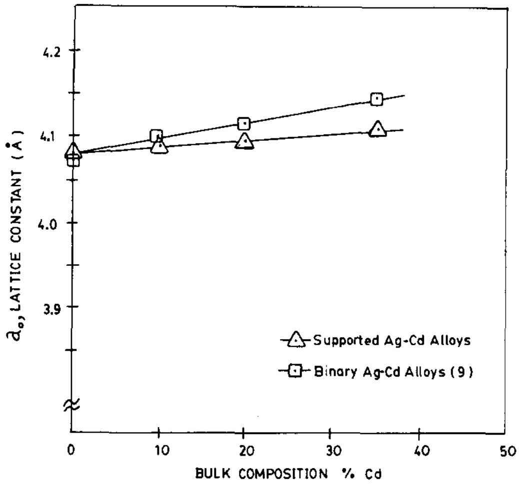

FIG. 1. Lattice constants of Ag–Cd alloys as a function of bulk composition.

ported catalysts with cadmium content up to 35% only. The alloys were subjected to X-ray diffraction analysis before and after exposure to reaction conditions. These analyses confirmed that alloy formation had been achieved and that neither phase shift nor separation to individual components had occurred during reaction. Lattice constants were calculated from the diffraction peaks of a number of crystal planes of the alloys by plotting $\cos^2 \theta$ versus a_0 and extrapolating to $\theta = 90°$. Lattice constants thus obtained are shown on Fig. 1 as a function of the bulk composition of the alloy. These results compare favorably with those reported in the literature (*9*) which are also shown on the same figure. The small differences may be attributed to the fact that our experiments were conducted with supported alloys while those of the referenced work were conducted with bulk alloys.

The total surface area of the catalysts was found to be 0.5 m^2/g by argon adsorption at liquid-nitrogen temperature. The exposed metallic area was found to be approximately 0.35 m^2/g as determined by oxygen chemisorption while the average crystallite volume–surface diameter was larger than 900 Å in all cases. All catalysts had a metal content of 5%.

(*a*) *Alloy Surface Composition*

Since the surface composition of alloys can vary dramatically from that of the bulk, an experimental scheme was developed to determine surface compositions. The total number of exposed silver and cadmium atoms were determined by selective chemisorption of oxygen. This technique was verified in preliminary experiments employing oxygen chemisorption and physical adsorption of argon on pure cadmium powders. The exposed surface area of the same sample was determined using these two methods and a good agreement was obtained. These results are shown on Table 1, while Fig. 2 shows typical oxygen adsorption isotherms on pure cadmium powder and a supported Ag–Cd alloy.

The number of exposed cadmium atoms was determined by selective chemisorptive of hydrogen which was found not to adsorb on silver or on the alumina support. Initial experiments on pure cadmium powders were used to develop experimental conditions under which monolayer coverage of cadmium could be achieved. Hydrogen adsorption isotherms on cadmium powders at temperatures of 100, 200, 215, and 250°C are shown on Fig. 3. The fact that the amount of hydrogen adsorbed increases with temperature is not viewed as a thermodynamic effect which would imply endothermic adsorption. It is more likely that this is a kinetic effect, in which case, the curves obtained at 100 and 200°C are not true isotherms. It is interesting to observe that the values of the monolayer equiva-

TABLE 1

Results of Preliminary Chemisorption Experiments

Adsorbent	Adsorbate	Temp. (°C)	V_m (ml/g)	Exposed area (m^2/g)
Cd, powder	Ar	−196		0.39
Cd, powder	H_2	215	0.165	0.40
Cd, powder	O_2	200	0.170	0.43
Cd/Al_2O_3	H_2	215	0.023	0.06
Cd/Al_2O_3	O_2	200	0.021	0.06

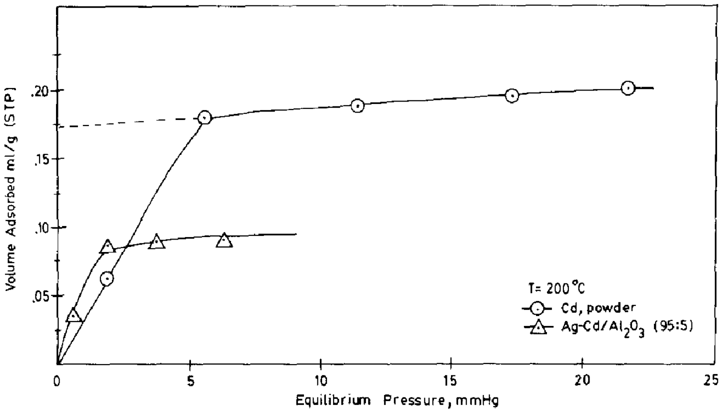

FIG. 2. Oxygen chemisorption isotherms on cadmium powder and Ag–Cd (95 : 5)-supported alloy catalyst.

lents obtained from extrapolation of the 215 and 250°C isotherms to zero pressure are nearly identical. Values of monolayer equivalents obtained from these isotherms were compared with areas obtained with argon physisorption on the same samples. From such comparisons it became evident that monolayer coverage of the cadmium surface with hydrogen could be achieved at temperatures of 215°C or higher (see Table 1). Thus, hydrogen chemisorption experiments on supported Ag–Cd catalysts were conducted at 215°C. Apparently, the amount of hydrogen adsorbed on Cd at 250°C is larger than the monolayer equivalent. Since cadmium neither dissolves hydrogen nor forms hydrides at this temperature, the excess amount is probably due to hydrogen adsorption on a preadsorbed hydrogen layer. A comparison of the areas obtained by oxygen chemisorption and hydrogen chemisorption on the same supported cadmium catalysts, which are also shown on Table 1, shows a very good agreement between the two methods.

The surface composition of the alloys used in this study is shown on Fig. 4 as a function of bulk composition of the alloys. Surface compositions before and after the catalysts had been exposed to reaction conditions are shown, as well as the theoretical surface composition computed from the model proposed by Williams and Nason (*10*), based on the thermodynamic proper-

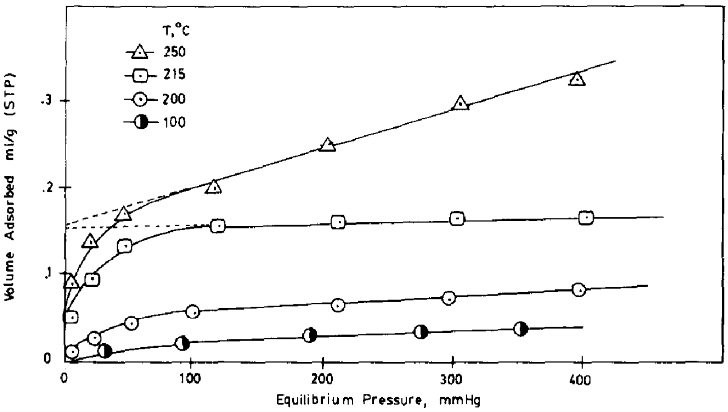

FIG. 3. Hydrogen chemisorption isotherms on pure cadmium powders at various temperatures.

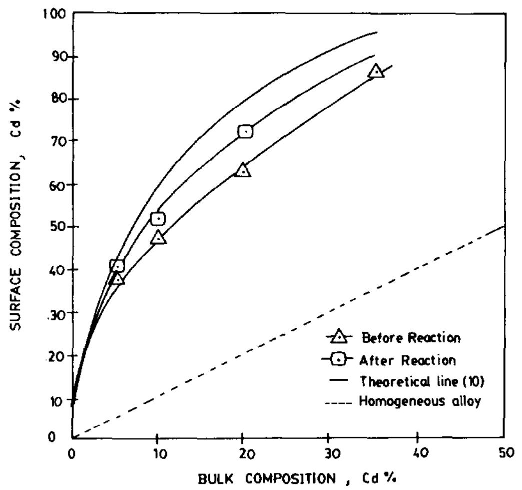

FIG. 4. Surface composition of supported Ag–Cd alloy catalysts as a function of bulk composition.

ties of the individual components. Both, the theoretical and the experimental curves show that the surface is enriched with cadmium, the metal with the lower heat of vaporization. Nevertheless, the degree of enrichment is not as high as the theoretical model predicts. The enrichment of the surface with cadmium is higher after the alloys had been exposed to reaction conditions. This can be attributed to the presence of oxygen in the reaction mixture. Cadmium–oxygen bonds have been reported (*11*) to have a heat of formation of 67 kcal/mole while silver–oxygen bonds 51 kcal/mole. Since the cadmium–oxygen bonds are stronger than those with silver, diffusion of cadmium atoms from the bulk to the surface would be expected. Other factors, such as carbonate formation from adsorbed oxygen and CO_2, might also be contributing to changes in surface composition during reaction. Finally, it must be mentioned that the total exposed surface area of the alloys, before and after reaction, was found to be the same.

(*b*) *Specific Reaction Rates and Selectivity*

Specific reaction rates per exposed silver atom (turnover frequencies) were determined employing an isothermal reactor which was operated in the differential mode, utilizing the alloy surface compositions obtained from selective chemisorption experiments. Initial experiments performed on supported cadmium catalysts indicated that cadmium did not exhibit any catalytic activity under the conditions employed in this work. Thus, specific reaction rates for the epoxidation and combustion reactions were computed in terms of the silver component only and any changes in activity or selectivity can be attributed to some type of interaction between the cadmium and silver surface atoms.

Turnover frequencies of the epoxidation and combustion reactions are shown on Figs. 5 and 6, respectively, as a function of the surface composition of the alloy catalysts, at temperatures of 217, 224, and 235°C. These plots show that the specific rate of the epoxidation reaction increases with increasing cadmium content of the surface while that of the combustion reaction either increases very slightly or remains constant. As a result of these trends in specific reaction rates, selectivity is found to increase with increasing cadmium content of the surface. The dependence of selectiv-

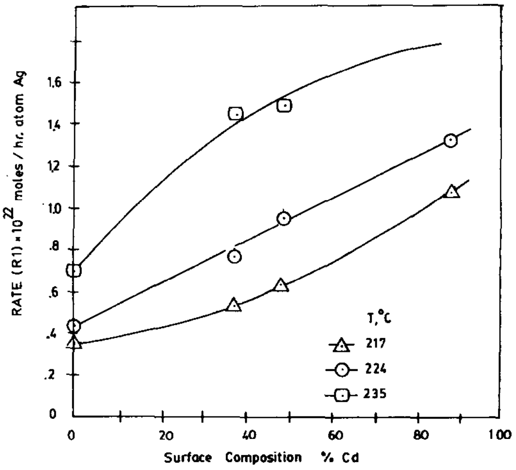

FIG. 5. Turnover frequency of epoxidation reaction as a function of alloy surface composition.

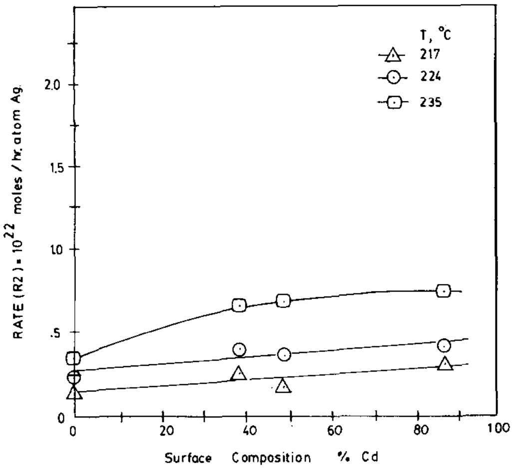

FIG. 6. Turnover frequency of combustion reaction as a function of alloy composition.

ity on the surface composition of the alloy catalysts is shown on Fig. 7.

Activation energies of the epoxidation and combustion reactions of ethylene were determined within the temperature range of 217 to 235°C and are shown on Fig. 8 as a function of alloy surface composition. The activation energies of both reactions are shown to decrease with increasing cadmium content of the surface. Nevertheless, the activation energy of the epoxidation reaction decreases much more drastically than the activation energy of the combustion reaction.

These results can be viewed in terms of both geometric and electronic consideration of the catalytic surfaces. Following the model of oxygen adsorption proposed by Kilty and Sachtler (*1*), the dissociative adsorption of oxygen which leads to combustion products requires an ensemble of four adjacent silver atoms, while the diatomic adsorption, which leads to ethylene oxide, requires a site of one silver atom. If it is assumed that cadmium atoms simply play an inert spacer role, then the ratio of adsorbed molecular to adsorbed atomic oxygen would increase with increasing surface cadmium concentration. This, in turn, would lead to increased specific rates of the epoxidation reaction and decreased specific rates of the combustion reaction since, it is generally accepted (*2*) that the adsorption of oxygen is at pseudoequilibrium during reaction. In this study, the specific rate of the epoxidation reaction was found to increase with increasing cadmium content of the surface but the rate of the combustion reaction was found to also slightly increase. Furthermore, if the observed alterations of the specific rates were due to changes in the

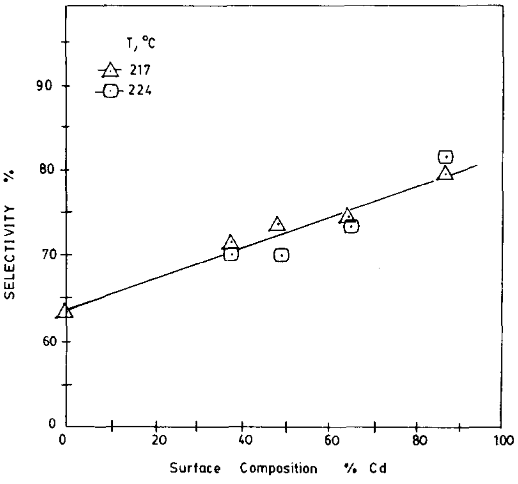

FIG. 7. Effects of surface composition on selectivity of alloys.

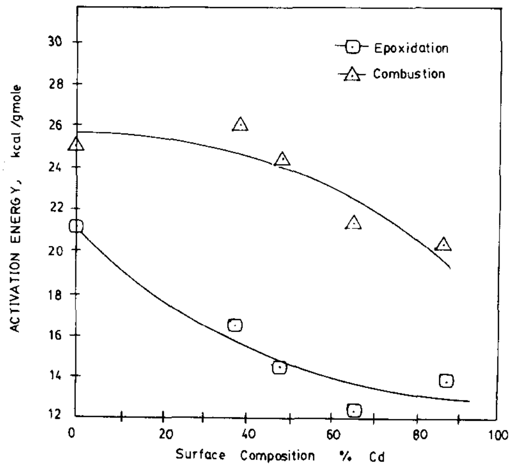

FIG. 8. Effects of surface composition on activation energies of epoxidation and combustion reactions.

ratio of adsorbed molecular to atomic oxygen, no changes in the activation energies would be expected, contrary to what was observed in this study.

The conclusion from this analysis is that geometric alterations of the silver surface, due to alloying with cadmium, are not solely responsible for the observed alterations in the catalytic behavior of silver under ethylene oxidation conditions. This conclusion is supported by the work of Geenan *et al.* (*8*) who studied ethylene oxidation over silver–gold alloy catalysts. They observed selectivity to decrease and ultimately drop to zero over gold-rich alloys. The opposite trend would be expected from purely geometric considerations.

The modes of oxygen adsorption on silver can also be viewed in terms of electronic considerations. The dissociative adsorption of oxygen requires transfer of two electrons from silver to oxygen according to $O_2 + 2e \rightarrow 2O^-$. The nondissociative adsorption requires transfer of one electron from silver to oxygen according to: $O_2 + e \rightarrow O_2^-$. Since cadmium has a lower electronegativity than silver, alloying silver atoms with cadmium atoms would affect the electron structure of the silver atoms, by near-neighbor interactions, in the direction of becoming more electropositive. Then, the potential of oxygen adsorbing dissociatively is reduced at the expense of nondissociative adsorption. Assuming that molecular oxygen leads to ethylene oxide while atomic oxygen leads to combustion products, the turnover frequency of the epoxidation reaction would be expected to increase, as it was observed to, but the turnover frequency of the combustion reaction would be expected to decrease, while, in this study it was found to increase slightly. Furthermore, such considerations can not explain the changes in the activation energies of both reactions which were found to be functions of the surface composition of the alloys, as shown in Fig. 8.

The possibilities discussed so far, related to both geometric and electronic considerations of the alloy surfaces, could explain the trends observed in the specific reaction rates if the ethylene oxidation reaction network is extended to include further oxidation of ethylene oxide or isomerization of ethylene oxide to form acetaldehyde which could decompose to carbon dioxide and water (*12*). Further oxidation of ethylene oxide cannot be a significant contributor to combustion products because of the very low concentration of ethylene oxide in the reaction mixture due to small conversions (less than 5%, total) of ethylene maintained in the differential reactor. Isomerization of ethylene oxide to acetaldehyde can be discarded on the grounds that no traces of acetaldehyde were detected in the reaction mixture although we explicitly searched for this component.

In order to explain the observed trends in frequency factors and in activation energies, we must examine the mechanism of the reactions and especially the rate-determining step which is generally believed to be a surface reaction step (*2*). Since the activation energies are found to be a function of the surface composition of the alloys, any interaction between cadmium and silver atoms affect the rate-determining step of the reactions. As was stated earlier, electronic interactions between cadmium and silver atoms result in reduction of electron concentrations around the silver atoms. Assuming that this is the factor responsible for reduced activation energies and enhanced frequency factors, the rate-determining step must involve electron transfer from the intermediate complex to the silver atoms. This electron transfer is facilitated by the fact that the silver atoms have become more electropositive via their interaction with the cadmium atoms. A possible rate-controlling step involving electron transfer from the intermediate complex to silver atoms is one in which oxygen–silver bonds are broken. Mechanisms involving such rate-controlling steps have been proposed by Kenson and Lapkin (*13*), Ionov *et al.* (*14*), and other investigators.

The results which were obtained in this study have been interpreted mostly in terms of electronic interactions between cadmium and silver atoms, which influence the rate-controlling step of the reactions. Nevertheless, in most probability, these interactions also influence the mode of oxygen adsorption on silver atoms which, in turn, affects the observed frequency factors. Geometric factors, related to the spacial arrangement of the silver atoms on the surface, might also be contributing, but their contribution is not considered to be very strong. It must be added that, according to the generally accepted schemes of ethylene epoxidation on silver, all these factors point toward the same direction, which is increased selectivity of ethylene oxide formation.

SUMMARY AND CONCLUSIONS

Supported silver–cadmium alloy catalysts were prepared by impregnation of α-alumina with mixed silver nitrate and cadmium nitrate solutions. The catalysts were characterized in terms of degree of alloying achieved, exposed metallic area, and surface composition. The surface composition was found to be drastically different than that of the bulk, being enriched in cadmium. The degree of enrichment with cadmium was found to increase after the catalysts had been exposed to reaction conditions.

Turnover frequencies per exposed silver atom, and activation energies, of the epoxidation and combustion reactions of ethylene were determined as a function of the surface composition of the alloy catalysts. Turnover frequencies of the epoxidation reaction were found to increase with increasing cadmium content of the surface while those of the combustion reaction were found to either remain constant or slightly increase. Activation energies of both reactions were found to decrease and selectivity to increase with increasing cadmium content.

These results were discussed in terms of geometric and electronic alterations on the catalytic surface, brought about by alloying. Geometric and electronic factors can influence the mode of oxygen adsorption on silver while electronic factors can influence the rate of the rate-controlling step and subsequently of the reaction. Although both of these factors might be contributing in the observed results, electronic interactions affecting surface reaction steps are mostly responsible for their observation.

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