JOURNAL OF CATALYSIS 88, 409–417 (1984)

The Oxidation of Ethylene over Silver-Based Alloy Catalysts

I. Silver–Palladium Alloys

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Received December 1, 1983; revised March 5, 1984

Silver–palladium alloy catalysts were prepared by impregnation of α-alumina supports with silver nitrate and tetraammine palladious nitrate, followed by drying and reduction in flowing hydrogen at 400°C. They were characterized in terms of degree of alloying achieved, total metallic surface area, and surface composition, employing X-ray diffraction and selective chemisorption techniques. Specific rates, per exposed silver atom, were determined under ethylene oxidation conditions. The specific rate of the epoxidation reaction and the selectivity were found to decrease with increasing palladium content of the surface. The opposite trend was observed in the specific rate of the combustion reaction. The activation energies of both reactions were found not to be affected by alloying. These results are related to geometric and electronic considerations of the alloy surfaces and it is concluded that electronic influences of the palladium atoms on the silver atoms via near-neighbor interactions are responsible for their observation.

INTRODUCTION

A revival of interest in catalysis by bimetallic and alloy catalysts has been observed in recent years. This phenomenon is primarily due to the fact that certain bimetallic systems are superior to monometallic ones in reactions of industrial importance, exhibiting higher selectivity for desired products, high activity and stability as well as resistance to poisoning (*1*, *2*). In studies of fundamental concepts, alloy catalysts have been used to investigate the effects of the geometric and electronic structure of the surface on chemisorptive and kinetic parameters. Alloying a catalytically active metal with an inactive one results in dilution of the active atom surface matrix, while the number of surface atom "ensembles" required for chemisorption and surface reaction changes. Simultaneously, the electronic characteristics of the active metal atoms are altered to some degree by near-neighbor interactions with atoms of different electronic configuration. Thus, the shape of the orbitals, the position of the energy levels and their degree of occupation are modified by alloying. These concepts are discussed in detail in a few review articles (*3–6*).

In the present investigation, geometric and electronic effects in alloy catalysis are investigated employing silver-based alloys under ethylene oxidation conditions. The oxidation of ethylene over silver catalysts has been shown to be a structure-sensitive reaction (*7–9*), i.e., activity and selectivity depend on the details of surface structure. The structure sensitivity can be explained by the mechanism proposed by Kilty *et al.* (*10*) according to which molecular oxygen adsorbed on one silver atom participates in the epoxidation reaction while atomic oxygen adsorbed on an ensemble of four silver atoms participates in the combustion reaction. If the ratio of adsorbed diatomic to monatomic oxygen species defines selectivity, then, this parameter must also be sensitive to the electronic structure of the surface since the adsorption of oxygen on silver involves transfer of one electron from silver to oxygen to produce an adsorbed molecular oxygen, or transfer of two electrons to produce adsorbed atomic oxygen.

0021-9517/84 $3.00

It would be expected, then, that changes in the local energy density of states and in the local electron density of states, brought about by alloying, would influence activity and selectivity of silver catalysts.

Studies of ethylene oxidation using alloy catalysts have been limited to alloys of silver with gold (*11*) and palladium (*12, 13*) only, apparently because silver forms continuous series of solid solutions with these metals. Flank and Beachel (*11*) observed that selectivity almost doubled when Ag–Au alloys were used with gold content of 5–25%, decreasing rapidly in alloys of higher gold content. Contradictory results have been reported by Geenen *et al.* (*20*) who observed selectivity to decrease monotonically with increasing gold content of the alloys. Moss and his co-workers (*12, 13*) using Ag–Pd alloy-evaporated films observed that the rate of the epoxidation reaction decreased monotonically with increasing Pd content and dropped to zero over alloys with Pd content greater than 40%. The rate of the combustion reaction was found to be constant over the composition range 0–80% Pd.

In our investigation we are attempting to distinguish the effects of the geometric factor from those of the electronic factor by a careful selection of alloying metals. Furthermore, particular emphasis has been placed in the determination of the alloy surface composition which can vary significantly from the bulk composition. In the present paper we report results of ethylene oxidation using supported silver–palladium alloy catalysts.

EXPERIMENTAL

Supported Ag–Pd alloy catalysts were prepared following the method of Cormack *et al.* (*13*). High purity α-alumina was used as support and a 5% total metal loading was obtained for all catalysts. The preparation method involved the following steps: (1) Impregnation of the support with weighed amounts of mixed silver nirate and tetraammine palladious nitrate solutions of appropriate concentrations. (2) Drying of the impregnated support at approximately 50°C in an oven overnight. (3) Reduction of the dried and impregnated support at 400°C in flowing hydrogen for 18 h.

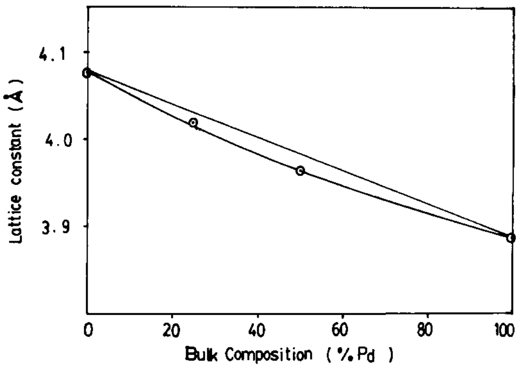

FIG. 1. Lattice constants of silver–palladium alloy catalysts as a function of alloy bulk composition.

All catalysts were examined with respect to the extent of alloying achieved by X-ray diffraction using a General Electric counter diffractometer, employing Cu*K*α radiation. Scanning was performed between 30 and 80° (2θ). Diffraction peaks from a number of crystal planes of the alloy were recorded and lattice constants, a_0, were found by extrapolation to $\theta = 90°$. Lattice constants measured in alloy catalysts were compared with values reported in the literature and an excellent agreement was observed. Figure 1, which shows lattice constants as a function of bulk alloy composition, indicates that only monophasic alloys were formed under the present preparation procedure. The symmetry of the X-ray diffraction profiles is an additional indicator of alloy homogeneity.

The total surface area of the catalysts 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 alloy surface were determined by selective chemisorption of oxygen and carbon monoxide. 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 and at oxygen pressures of up to 60 mm Hg. Since oxygen chemisorbs on both silver and palladium, these experiments led to the determination of the sum of the surface atoms of the two metals. The CO chemisorption experiments were carried out at room temperature and since CO chemisorbs on Pd only, the results led to the determination of surface Pd atoms. The total surface area of the catalysts was very close to that of the carrier, which was found to be 0.5 m^2/g. The exposed metallic area was determined to be around 0.3 m^2/g while the average crystallite size was larger than 1,000 Å in all cases. All catalysts had a metal content of approximately 5%.

Specific reaction rates were obtained in an apparatus consisting of a tubular, plug flow reactor, immersed in a fluidized constant-temperature sand bath. The reactor was operated in the differential mode by maintaining total conversions less than 5%. Feed flow rates were measured and controlled by thermal mass flowmeters and control valves. In preliminary experiments, catalyst particle size and feed flow rates were determined so as to eliminate intraparticle and interparticle diffusion effects. Analysis of the product mixture was carried out by a gas chromatograph (HP5730 A) equipped with a thermal conductivity detector operated at 150°C and a reporting integrator (HP3390 A). The column used was packed with 80–100 mesh Porapak Q and was operated isothermally at 90°C for 2 min, following which, the temperature was raised to 150°C at a rate of 16°C/min.

The experiments were conducted at three temperatures between 200 and 240°C, at a pressure of 15 atm. The feed stream consisted of 3.0% ethylene, 3.3% oxygen, and 93.7% nitrogen for all runs. The oxygen concentration was kept at low levels so as to avoid phase separation of the alloy catalysts during reaction.

RESULTS AND DISCUSSION

(*a*) *Alloy Surface Composition*

It is well known that the surface composition of alloy particles can vary substantially from that of the bulk. In catalytic applications, the surface composition of the alloy catalysts must be experimentally determined in order to obtain meaningful results. In the present study, the total number of exposed silver and palladium atoms was determined by selective oxygen chemisorption. This technique was verified in preliminary experiments employing selective oxygen chemisorption and physical adsorption of argon on pure Ag–Pd alloy powders. The exposed surface area of the same sample was determined using these two methods. A very good agreement was obtained, indicating that, under the present experimental conditions, no bulk oxidation of the alloy was taking place during oxygen chemisorption. Results of these and other preliminary adsorption experiments which were conducted to develop techniques for the determination of surface composition of the alloy catalysts are shown in Table 1.

The number of exposed Pd atoms in the alloy catalysts was determined by selective chemisorption of CO which does not adsorb on alumina or on silver. Comparison of results obtained from BET and CO chemisorption experiments on pure Pd powders indicated a stoichiometric carbon monoxide-to-palladium ratio of 1/1.43. This ratio compares favorably with the ratio of 1/1.5 proposed by Scholten and van Montfoort (*14*) based on the observation that 50% of the CO is present in the linear and 50% in the bridged form on pure palladium surfaces. Nevertheless, it would be expected that the amount of CO adsorbed in the bridged form decreases as the surface of Pd is diluted with Ag atoms. Indeed, infrared studies (*1*, *15*) reveal that the bridged form of CO decreases as Pd is alloyed with Ag and that on Ag-rich alloys most of the CO molecules are linearly adsorbed. Thus, in the present study, since all the alloys

TABLE 1

Comparative Results of Preliminary Adsorption Experiments

Catalyst	Adsorbate	Temp. (°C)	Volume adsorbed at monolayer (ml/g cat)	Exposed area (m^2/g)
Pd, powder	Ar	−196	0.578	2.14
Pd, powder	CO	25	0.665	2.12
Pd/Al_2O_3	CO	25	0.040	0.12
Pd/Al_2O_3	O_2	200	0.037	0.15
Ag/Pd(75:25), powder	Ar	−196	0.125	0.46
Ag/Pd(75:25), powder	O_2	200	0.075	0.57
Ag/Pd(50:50), powder	Ar	−196	0.217	0.60
Ag/Pd(50:50), powder	O_2	200	0.090	0.59

were rich in Ag, a stoichiometric ratio of 1/1 was assumed.

The surface composition of Ag–Pd alloy catalysts versus bulk composition is shown in Fig. 2. In this figure we have also included results obtained from catalysts which had not been exposed to reaction conditions based on a CO chemisorption stoichiometry of 1/1.5. Since the alloys used in this study are Ag-rich, the surface composition is shown to be a weak function of the assumed stoichiometric ratio. Enrichment of the surface with Ag atoms which increases after the catalyst has been exposed to reaction conditions is shown on Fig. 2. However, the enrichment is not of the degree predicted by the theoretical model of Williams and Nason (*16*) based on pure element vaporization enthalpies, heat of mixing, and alloy solution activity coefficients.

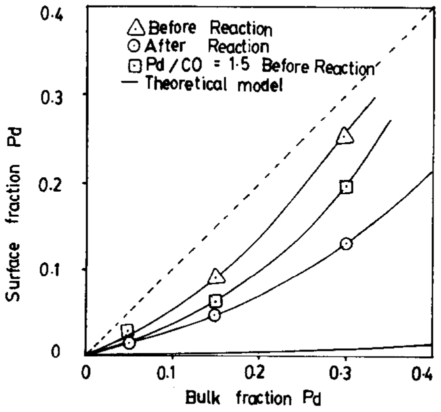

FIG. 2. Surface composition as a function of bulk composition of alloy catalysts.

The enrichment of the alloy surface with Ag atoms occurs in two stages, during the preparation of the alloy, and during reaction. It is well known that the surface is enriched with the element with the lower heat of vaporization if in equilibrium with vacuum or a nonadsorbing gas. Since silver has lower heat of vaporization than palladium, we would expect surface enrichment with silver. Nevertheless, the catalysts were reduced in an atmosphere of hydrogen which adsorbs strongly on palladium. Since the surface tends to be enriched with the metal forming the strongest chemisorption bonds with the gas, the surface would tend to be enriched with Pd atoms in the presence of hydrogen. Clearly we have two opposing phenomena: surface enrichment with silver due to thermodynamic factors and enrichment with palladium due to strong chemisorption bonds. The thermodynamic forces dominate and lead to enrichment with Ag. Because of the opposing factors stated above, the enrichment of the surface with silver is weaker than theoretical models predict.

When the alloy catalysts are exposed to reaction conditions, ethylene and oxygen, further enrichment of the surface with Ag occurs as Fig. 2 indicates. This phenomenon is due to the fact that the adsorption free energy of oxygen on silver is higher than on palladium and thus diffusion of Ag atoms from the bulk to the surface occurs at reaction temperatures. Since the concentration of oxygen in the reaction mixture was deliberately maintained at low levels, the surface enrichment during reaction is a weak one. Silver enrichment of the surface under reaction conditions can also be attributed to carbonate formation from adsorbed oxygen and CO_2 which is present in the reaction mixture.

The results obtained in this study are in agreement with those obtained by Wood and Wise (*17*) and Kuijers and Ponec (*18*) who used Auger Electron Spectroscopy to examine surfaces of Ag–Pd alloys. In both studies, the surface was found to be enriched in silver relative to the bulk. The degree of enrichment was found to depend upon the atmosphere under which the alloy exists. Kuijers and Ponec (*18*) observed a higher degree of silver enrichment under vacuum compared to a CO atmosphere. Our results show surface enrichment with Ag in an atmosphere of hydrogen and an increase in the degree of Ag-enrichment during reaction conditions where the alloy catalyst is exposed to oxygen at low concentrations.

The possibility of gross separation of the alloys toward their components during reaction was also considered. X-Ray diffraction profiles of all the alloy catalysts before and after reaction were obtained. No phase shift, nor split in the profiles was observed indicating that no phase separation occurred during reaction. There is also no evidence of oxide formation in which case the (111) peak would drastically change its position. The absence of oxide formation can be explained by the low oxygen level (approximately 3%) in the reaction mixture.

(b) Specific Reaction Rates

Specific reaction rates per exposed silver atom (turnover frequencies) were determined from kinetic experiments, utilizing the alloy surface compositions obtained from the selective chemisorption experiments. Since palladium itself is a good oxidizing catalyst, its independent catalytic role during the reaction had to be determined before analysis of the data on alloy catalysts could proceed. For this purpose, supported palladium catalysts were prepared, characterized in terms of exposed metallic surface area per unit weight of catalyst, and tested under reaction conditions identical to those used with the alloy catalysts. As was expected, palladium was found to catalyze the combustion reaction at a very high rate while it did not catalyze the epoxidation reaction to any measurable degree. Other partial oxidation products such as acetic acid, acetic anhydride, or acetaldehyde, which have been observed by other investigators (*21*), were not detected under the present experimental conditions probably because of the very low oxygen concentration. Since palladium is a highly active and totally unselective catalyst for ethylene oxidation, it was assumed that its specific reaction rate is independent of the details of surface structure. Thus the specific rate per exposed palladium atom obtained from supported palladium catalysts is assumed to be the same as that obtained from Ag–Pd catalysts. Alternatively, alloying was assumed not to affect the performance of palladium under ethylene oxidation conditions.

The specific reaction rate of the epoxidation reaction in units of gram moles of ethylene reacted to ethylene oxide per hour per exposed silver atom of the alloy is given by

$$R_{1s} = R_{1A/Y} \tag{1}$$

where R_{1A} is the rate of the epoxidation reaction per gram of catalyst and Y is the number of exposed silver atoms per gram of

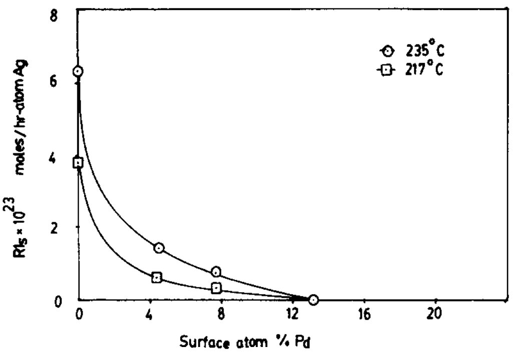

FIG. 3. Effects of palladium content of the surface on the specific rate of silver for the epoxidation reaction.

catalysts. The specific reaction rate of the combustion reaction in units of gram moles of ethylene converted to carbon dioxide and water per hour per exposed silver atom of the alloy is given by

$$R_{2s} = \frac{1}{Y} (R_{2A} - R_{2P} * X) \qquad (2)$$

where R_{2A} is the rate of the combustion reaction per gram of catalyst, R_{2P} is the specific reaction rate of the combustion reaction per exposed palladium atom, and X is the number of surface palladium atoms per gram of catalyst.

Specific reaction rates of the epoxidation and combustion reactions of ethylene over supported silver, palladium, and Ag–Pd alloy catalysts are shown in Figs. 3 and 4 at the temperatures of 217 and 235°C, as a function of alloy surface composition. It is shown in Fig. 3 that the specific rate of the epoxidation reaction is highest over pure silver and decreases monotonically with increasing palladium content of the surface to nearly zero over surfaces with more than 13% Pd. On the other hand, the specific reaction rate of the combustion reaction increases with increasing Pd content of the surfaces. It must be emphasized that these rates are due to silver atoms only, since the contributions of the palladium atoms have been subtracted. In the same figure, specific reactions rates per exposed palladium atom obtained over supported palladium catalysts are shown for comparison. It is apparent that these rates are significantly higher than those obtained over silver.

The trend of the reaction rates shown in Fig. 3 is in general agreement with the results reported by Moss and his co-workers (*3*, *12*, *13*), although a direct comparison cannot be made since these investigators used Ag–Pd alloy evaporated films and did not report specific reaction rates. The same authors observed that the rate of the combustion reaction remained constant in alloys of up to 80% Pd. This is probably due to the fact that they were primarily measuring combustion rates over Pd atoms since the rate over silver atoms is significantly slower than that over palladium. These investigators did not attempt to separate the contributions of the individual metal atoms.

It has been shown in the literature (*10*) that adsorbed molecular oxygen requires an ensemble of one silver atom and it participates in the epoxidation reaction, while adsorbed atomic oxygen requires an ensemble of four adjacent silver atoms and reacts with ethylene to produce carbon dioxide and water. Thus, from a purely geometric view, dilution of the surface silver matrix with palladium atoms will destroy some surface ensembles of four adjacent silver

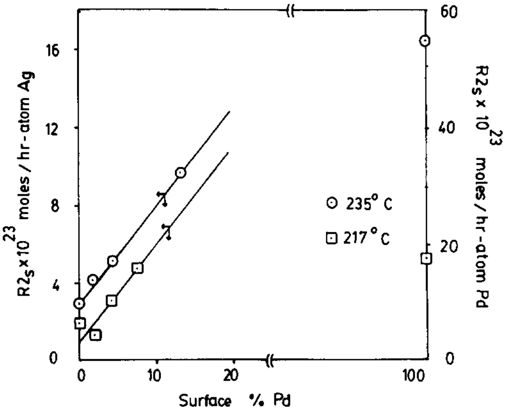

FIG. 4. Effects of palladium content of the surface on the specific rate of silver for the combustion reaction.

atoms thus producing a larger number of ensembles of one silver atom. This process would inhibit the dissociative chemisorption of oxygen and would lead to a higher ratio of adsorbed molecular to adsorbed atomic oxygen. The specific rate of the epoxidation reaction would then be expected to increase as silver is alloyed with palladium while the specific rate of the combustion reaction would be expected to decrease. However, the exact opposite trends are observed in this study.

In order to explain the results of this study, the modes of oxygen chemisorption on silver must be examined in terms of the electron requirements associated with them. The dissociative adsorption requires the transfer of two electrons from the silver atoms to oxygen according to $O_2 + 2e \rightarrow 2O^-$. On the other hand, the nondissociative adsorption requires transfer of only one electron from the silver atom according to $O_2 + e \rightarrow O_2^-$. Alloying silver atoms with the more electronegative palladium atoms affects the electronic structure of the silver atoms by near-neighbor interactions and makes them "richer" in electrons. Thus, the probability of oxygen adsorbing in the dissociative state by accepting two electrons from an electron-rich ensemble is higher at the expense of oxygen adsorbing in the molecular state. Assuming that adsorbed molecular oxygen leads to ethylene oxide while adsorbed atomic oxygen leads to the combustion products, the specific rate of the epoxidation reaction would be expected to decrease while that of the combustion reaction to increase. These are indeed the trends which were observed in this study as shown in Figs. 3 and 4.

Although the results of this study can be explained in terms of electron requirements for the various modes of oxygen adsorption, geometric factors are also contributing in these results. Geometric and electronic factors are simultaneously present. However, in the present case they influence specific reaction rates in opposite directions. The geometric alteration of the surface is thought to favor ethylene oxide formation while the electronic alteration of the surface in the direction of becoming more electronegative favors the combustion reaction. In addition to the geometric and electronic considerations described above, another factor contributing to the results obtained in this study, must be considered. Oxygen can adsorb dissociatively on palladium atoms and transfer to silver atoms in the ensemble. This phenomenon would tend to reduce the selectivity of silver atoms. However, the contribution of this phenomenon is probably very small in view of the very rapid rates of reaction over palladium atoms and the fact that the chemisorption of oxygen is the rate-controlling step in ethylene oxidation over palladium (*21*).

The activation energies of the epoxidation and combustion reactions over the alloy catalysts were determined and found to be independent of the surface composition of the alloys. The activation energy of the epoxidation reaction was found to be equal to 22.4 ± 0.5 kcal/mole and the activation energy of the combustion reaction was determined to be 26.8 ± 1.0 kcal/mole. These values are in good agreement with those reported in the literature, obtained over pure silver catalysts (*19*). The fact that alloying silver with palladium does not change the activation energies exhibited by the former indicates that alloying does not alter the rate-controlling step of either reaction. The rate-controlling step of both, the epoxidation and combustion reaction, is generally thought to be a surface reaction step (*19*). Then the changes in the specific reaction rates brought about by alloying must be sought in the alteration of the chemisorption characteristics of oxygen on silver, which influence the frequency factors of the reactions. Indeed, the frequency factor of the epoxidation reaction was observed to decrease with increasing palladium content of the surface while the opposite trend was observed with the frequency factor of the combustion reaction. Changes in the modes of oxygen chemisorption on silver, due to

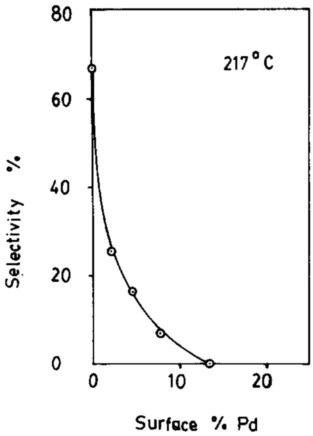

FIG. 5. Effects of alloy surface composition on the selectivity of silver atoms for ethylene oxide formation.

alloying with palladium, were discussed earlier.

The effects of alloying silver with palladium on the selectivity of the former toward ethylene oxide formation are shown in Fig. 5 at the temperature of 217°C. The selectivity of ethylene oxide was found to be highest on pure silver, decreasing sharply with increasing Pd content to nearly zero over surfaces with more than 13% palladium. The observed decrease of selectivity with increasing palladium content of the catalysts is due to the fact that the specific rate of the epoxidation reaction decreases while that of the combustion reaction increases with increasing palladium content of the alloy.

SUMMARY AND CONCLUSIONS

Supported silver–palladium alloy catalysts were prepared and characterized in terms of degree of alloying achieved, total exposed metallic area, and alloy surface composition. It was found that under the current preparation procedure, the surface composition of the alloys differs drastically from that of the bulk, being enriched in silver. The degree of silver enrichment is not of the magnitude which theoretical models predict and it increases after the catalysts have been exposed to reaction conditions.

The oxidation of ethylene was investigated using silver–palladium alloy catalysts. The specific rate to ethylene oxide per exposed silver atom was observed to decrease sharply with increasing palladium content of the surface. The opposite trend was observed for the specific rate of the combustion reaction. As a result, the selectivity of the alloy catalysts was found to decrease with increasing Pd content. These results were related to geometric and electronic alterations of the catalytic surfaces brought about by alloying. Oxygen chemisorption characteristics indicate that, although geometric effects might be present, these are overshadowed by electronic effects.

Work is currently in progress which will assist in distinguishing the geometric from the electronic effects in silver-based alloy catalysts. The modes of oxygen chemisorption on alloy catalysts is also investigated in connection with mechanistic studies of the oxidation of ethylene.

ACKNOWLEDGMENT

The instruments used in conducting this research were obtained by grants from NSF under Award Nos. CPE-8023192 and TFI-8021109.

REFERENCES

1. Sachtler, W. M. H., *Catal. Rev.-Sci. Eng.* **14**(2), 193 (1976).
2. Ponec, V., *Surf. Sci.* **80,** 352 (1979).
3. Moss, R. L., and Whaley, L., *Adv. Catal.* **22,** 115 (1972).
4. Clarke, J. K. A., *Chem. Rev.* **75,** 291 (1975).
5. Ponec, V., *Catal. Rev.-Sci. Eng.* **11**(1), 41 (1975).
6. Sachtler, W. M. H., and van Saten, R. A., "Advances in Catalysis," Vol. 26, p. 69. Academic Press, New York, 1977.
7. Presland, A. E. B., Price, G. L., and Trimm, D. L., *J. Catal.* **26,** 313 (1972).
8. Wu, J. C., and Harriott, P., *J. Catal.* **39,** 395 (1975).
9. Verykios, X. E., Stein, F. P., and Coughlin, R. W., *J. Catal.* **66,** 368 (1980).
10. Kilty, P. A., and Rol, N. C., and Sachtler, W. M. H., "Proceedings, 5th International Congress on Catalysis," Vol. 2, p. 929. 1973.
11. Flank, W. H., and Beachell, H. C., *J. Catal.* **8,** 316 (1967).

12. Moss, R. L., and Thomas, D. H., *J. Catal.* **8,** 151, 162 (1967).
13. Cormack, D., Thomas, D. H., and Moss, R. L., *J. Catal.* **32,** 492 (1974).
14. Scholten, J. J. F., and Van Montfoort, A., *J. Catal.* **1,** 85 (1962).
15. Soma-Nato, Y., and Sachtler, W. M. H., *J. Catal.* **32,** 315 (1974).
16. Williams, F. L., and Nason, D., *Surf. Sci.* **45,** 337 (1974).
17. Wood, B. J., and Wise, H., *Surf. Sci.* **52,** 151 (1975).
18. Kuijers, F. J., and Ponec, V., *J. Catal.* **60,** 100 (1979).
19. Verykios, X. E., Stein, F. P., and Coughlin, R. W., *Catal. Rev.-Sci. Eng.* **22**(2), 197 (1980).
20. Geenen, P. V., Boss, H. J., and Pott, G. T., *J. Catal.* **77,** 499 (1982).
21. Gerberich, H. R., Gant, N. W., and Hall, W. K., *J. Catal.* **16,** 204 (1970).