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Metal–Support Interaction Effects of Silver Catalysts during Ethylene Oxidation

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The role of metal–support interaction has been systematically investigated for the epoxidation of ethylene over silver, supported on doped aluminas of different electronic properties. The supports were prepared by doping α-alumina with germanium oxide and magnesium oxide, thereby transforming them into *n*-type or *p*-type semiconductors, respectively. It was found that catalysts which were supported on *p*-type semiconducting carriers (magnesium oxide-doped) exhibit enhanced activity and selectivity to ethylene oxide formation. The opposite behavior is caused by doping with germanium oxide. The results are explained in terms of electronic interactions between the silver crystallites and the support which alter the work function of electrons at the surface of the metal. In the light of theories concerning the mechanism of silver-catalyzed ethylene-oxidation reactions, these results are consistent with the rate-controlling step as a surface reaction which involves electron transfer from the intermediate complex to the catalyst surface.

1. INTRODUCTION

The role of the support in the performance of supported metal catalysts is often presumed to be physical in nature, its most important function often being to disperse the metal as small crystallites over its surface. Such dispersion provides a large active surface area relative to the amount of metal used, and is especially favorable when precious metals are employed. In addition, the support stabilizes the highly dispersed metal by retarding growth of small metallic crystallites, a sintering process which may occur at high reaction temperatures. The support can also help dissipate the heat of reaction and increase the resistance of the catalyst to poisoning. In addition to the physical effects of the support, a chemical or electronic type of interaction between it and the metal has been reported to influence the intrinsic catalytic activity or selectivity of the metal (*1*, *2*). In such cases, the metal is thought to have its chemical or electronic properties changed by contact with the support (*2–4*).

According to the metal–semiconductor boundary-layer theory, when a metal contacts a semiconductor (the support in this case) at thermodynamic equilibrium, the Fermi level of electrons of the metal must equal that of the electrons of the semiconductor at the interface (*5*, *6*). In cases where the work function of electrons of the metal is larger than the work function of electrons of the semiconductor, electrons will flow from the semiconductor to the metal until the Fermi level of electrons at the interface is the same in each solid. The converse is, of course, also true.

According to electronic theory, the Fermi level and the density of electronic states of a catalyst are related to its catalytic activity, because both catalytic processes (e.g., chemisorption of the reactants on the catalyst and surface reactions) involve redistribution of electrons between the catalyst and the reacting system (*7*). An electronic interaction between the metal

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and the support, therefore, would be expected to influence the performance of the catalyst in terms of its activity and/or selectivity.

Studies of metal–support interaction have been reported for the hydrogenolysis of ethane over supported nickel and cobalt (*8*). The specific catalytic activity of the metal was found to depend on the particular support which was used. Maxted and Akhtar (*9*) also observed metal–support interaction effects on the specific catalytic activity of platinum in the liquid-phase hydrogenation of cyclohexene. Additional evidence for the specific influence of the support in the platinum–silica and platinum–alumina systems comes from studies of the kinetics of ethane hydrogenolysis (*10, 11*). The apparent activation energy of the hydrogenolysis reaction varied considerably with the support, from 54 kcal/mole for the silica to 31 kcal/mole for the alumina support. Baddour and Deibert (*12*) studied the activity of nickel as a function of the electronic properties of its support and concluded that electronic interaction between the support and nickel has a strong promoting effect on the decomposition of formic acid. Finally, Eischens and Pliskin (*13*) showed that the infrared spectrum of carbon monoxide adsorbed on platinum depended on the nature of the support.

More recently, strong metal–support interaction was observed by Vannice (*14*) on alumina-supported palladium catalysts for methane formation from carbon monoxide/hydrogen mixtures and by Tauster *et al.* (*15*) between the Group VIII noble metals and titanium dioxide supports in the adsorption of carbon monoxide and hydrogen on the metals. Moreover, den Otter and Dautzenberg (*16*) reported that the alumina support strongly influenced the chemisorption of hydrogen on platinum.

Several reviews (*5, 7, 17*) of metal–support interaction studies are available. The trend of the conclusions in these compilations is that the electronic properties of the support often influence the specific catalytic activity or selectivity of the metal. That this effect may be ascribed to the electronic interaction between the metal and the support due to different positions of their Fermi level of electrons is the prevailing hypothesis.

2. METHODS AND TECHNIQUES

The electronic interactions between the metal and the support were investigated by preparing and testing catalysts supported on α-alumina carriers which had been doped with germanium oxide or magnesium oxide at various concentrations. Alcoa's partially hydrated alumina, Type C-331, was slurried with the dopant and small amounts of water and nitric acid and then compressed into pellets. The pellets were dried, dehydrated, and sintered in air at 1350°C for approximately 3 days. That α-alumina can be doped with germanium oxide or magnesium oxide to form an *n*-type or a *p*-type semiconductor, respectively, has been established by Schwab (*17, 30*).

The catalysts used in this study were prepared by impregnation of the doped supports in an excess silver nitrate solution with vigorous stirring while the temperature was controlled at 80°C. After decanting the impregnating solution, the catalysts were dried slowly at 50°C, washed with deionized water, slowly dried again, and then reduced in flowing hydrogen at 200°C for approximately 3 days.

The catalysts were characterized as to total surface area by argon adsorption at liquid-nitrogen temperature, and as to free metallic silver surface area by selective chemisorption of oxygen at 200°C and pressures ranging between 0.1 and 10 mm Hg. Further details concerning the chemisorption experiments have been reported elsewhere (*18, 32*). The average size of the silver crystallites was obtained from the chemisorption data, assuming spherical particles, and by X-ray diffraction line broadening. Details of the X-ray diffraction experiments can also be found in Refs.

TABLE 1

Laboratory-Prepared Supports and Their Properties

Support	Dopant	Percentage dopant	Sg (m^2/g)	Catalyst series
GA-331-3	GeO_2	3.0	2.78	600
GA-331-1	GeO_2	1.0	2.99	700
GA-331-0.5	GeO_2	0.5	2.45	800
GA-331-0.3	GeO_2	0.3	2.63	900
MA-331-1	MgO	1.0	2.58	1200
MA-331-3	MgO	3.0	2.87	1300
MA-331-5	MgO	5.0	2.93	1400

(*18*, *32*). Specific reaction rates were measured using an isothermal, tubular, continuous, plug-flow reactor operated in the differential mode. The absence of external and internal mass and heat transfer effects or of deviations from plug-flow was confirmed by separate experimentation (*32*). Experiments were conducted at 200 psig pressure and 200°C using a feed consisting of ethylene, oxygen, and nitrogen, of respective molar concentrations of 6, 10, and 84%.

Aluminum oxide was chosen as the support for this study primarily because it has been reported (*19*) that alumina does not exert any catalytic activity toward ethylene oxidation and its chemical and crystal structure does not change during the reaction. In a number of preliminary experiments (blank runs) we also ascertained that the germanium oxide- and the magnesium oxide-doped supports did not catalyze ethylene oxidation.

The characteristics of the supports and catalysts used in this study are summarized in Tables 1 and 2, respectively.

Measured specific rates to ethylene oxide and to carbon dioxide and water were the basis for comparing catalytic activity. It has been argued by Slinkin and Fedorovskaya (*7*) that specific rates offer a more accurate mode of comparing catalytic activities than do activation energies. Specific rates are preferable primarily because it cannot be ascertained that the same kinetic expression applies to all the catalysts tested and because metal–support interactions could influence the preexponential factor as well as the activation energy. In the present work the basis for computing specific rates was the exposed surface area of Ag measured by chemisorption.

3. RESULTS

It is known (*18*, *20*) that the oxidation of ethylene over supported silver catalysts is a structure-sensitive reaction. To distinguish the effects of silver crystallite size from the effects of metal–support interaction, the catalysts were sintered at various temperatures and for various periods of time in order to obtain series of catalysts with different average silver crystallite size. The catalysts which were prepared using germanium oxide-doped supports (series 600, 700, 800, and 900) ranged in average silver crystallite size between approximately 300 and 700 Å. The catalysts which were prepared using magnesium oxide-doped supports (series 1200, 1300, and 1400) ranged in average silver crystallite size between ap-

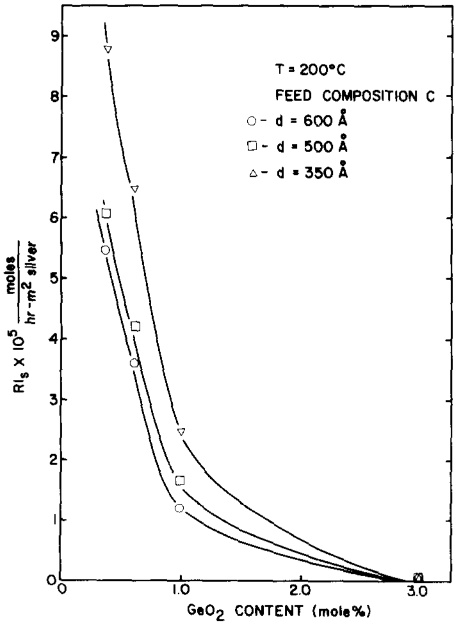


FIG. 1. Effects of germanium oxide content of the support on the specific rate to ethylene oxide.

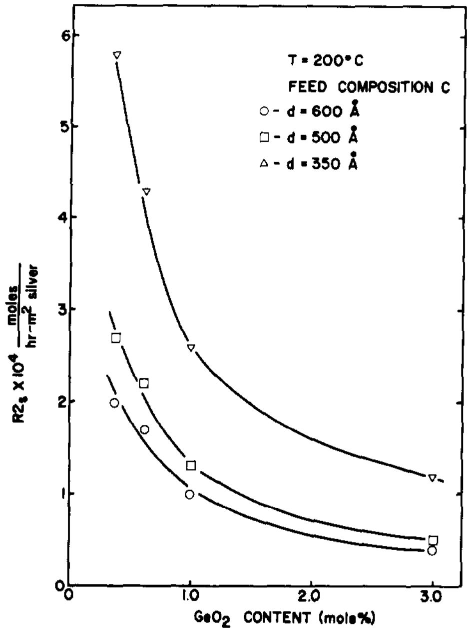


FIG. 2. Effects of germanium oxide content of the support on the specific rate to carbon dioxide and water.

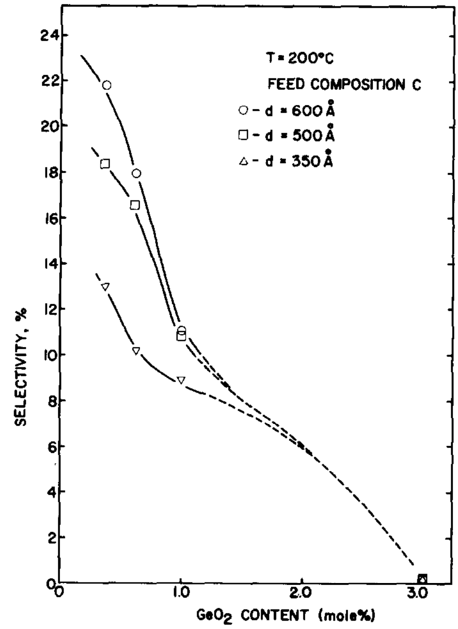


FIG. 3. Effects of germanium oxide content of the support on selectivity.

proximately 350 and 650 Å. The performance of these catalysts, compared at the same average silver crystallite size, is shown in Figs. 1–6.

Specific rates at 200°C to ethylene oxide and to carbon dioxide and water are plotted in Figs. 1 and 2, respectively, versus the mole percentage dopant content of the support for average silver crystallite sizes of 350, 500, and 600 Å. Both specific rates decrease with increasing germanium oxide content of the support. The specific rate to ethylene oxide decreases more rapidly, however, and becomes zero at a dopant content of 3.0 mole%. The result of the different rates of decrease of the specific rates is that the selectivity for epoxidation decreases with increasing germanium oxide content of the support as shown in Fig. 3 for average silver crystallite sizes of 350, 500, and 600 Å. Similar results were obtained at a reaction temperature of 240°C (*32*).

Doping the support with MgO causes just the opposite behavior as shown by Figs. 4 and 5. In contrast to the effect of germanium oxide, doping with magnesium oxide causes an increase in both specific rates.

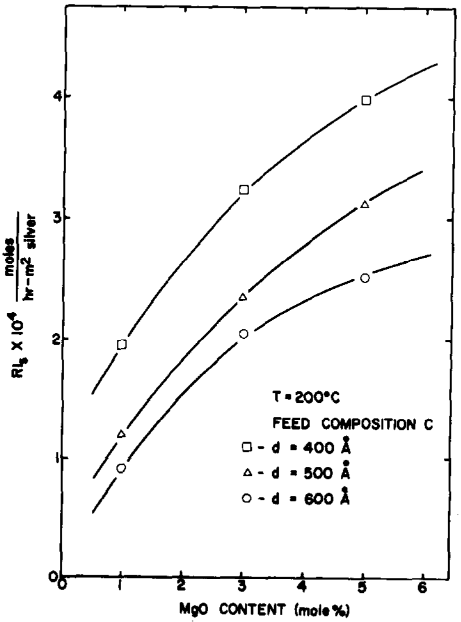


FIG. 4. Effects of the magnesium oxide content of the support on the specific rate to ethylene oxide.

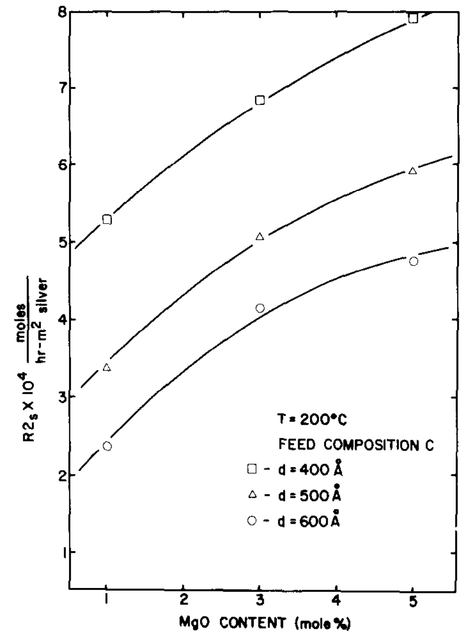


FIG. 5. Effects of the magnesium oxide content of the support on the specific rate to carbon dioxide and water.

Epoxidation selectivity also increases with increasing magnesium oxide content of the support as shown in Fig. 6 for average silver crystallite sizes of 400 and 600 Å.

4. DISCUSSION AND CONCLUSIONS

To provide reasonable certainty that the observed effects may be attributed only to the presence of the dopants identical methods of preparation and activation were used to control total surface areas and crystallite sizes. Increasing the germanium content of the Al_2O_3 support is expected to increase the concentration of electrons in the alumina and also in the supported silver because the Fermi level of electrons of the semiconductor support must equal that of the electrons of the metal at the interface. The opposite effect is expected from doping alumina with magnesium.

a. Activity Considerations

If the rate-determining step of a reaction involves electron transfer *from* a reactant or an intermediate *to* the metal, then a higher Fermi level of electrons of the metal (or a lower work function) should increase the activation energy and decrease the rate of the reaction. Lowering the Fermi level in the metal catalyst should have the opposite effect. Just such effects were observed; doping with Ge (higher Fermi level) caused decreased specific rates, whereas doping with Mg (lower Fermi level) increased specific rates. Adsorption of oxygen on silver involves electron transfer in the opposite direction, viz., *from* silver *to* oxygen, according to the reaction: $O_2 + e \rightarrow O_2^-$ and $O_2^- + e \rightarrow 2O^-$. Observed results suggest then that adsorption of oxygen is at equilibrium during the reaction and *not* rate controlling. Whether ethylene participates directly from the gas phase or from the adsorbed state is controversial (*31*). It seems to be generally conceded, however, that ethylene adsorption is weak and not rate controlling. The viewpoint that surface reaction is the rate-determining step, independent of adsorption or desorption rates, agrees with kinetic studies by other investigators (*31*).

Electron transfer from an intermediate complex to the catalyst implies that one or more oxygen–silver bonds are broken dur-

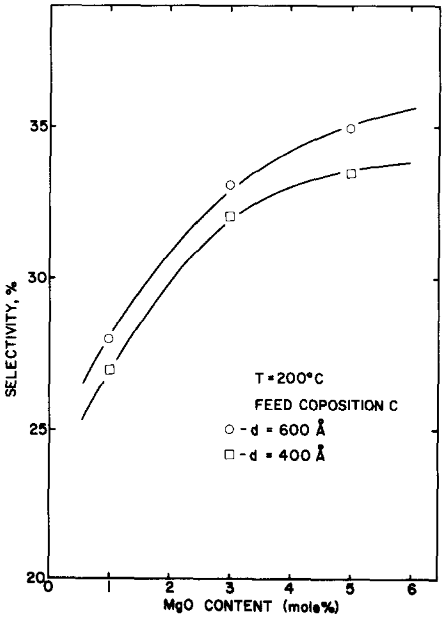


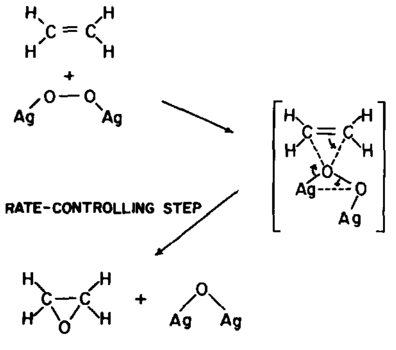
FIG. 6. Effects of the magnesium oxide content of the support on selectivity.

TABLE 2

Catalysts Prepared on Doped Supports and Their Properties

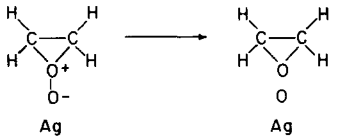
Catalyst No.	Sintering		Silver (wt%)	Sg (m^2/g cat)	Sm (m^2 Ag/g cat)	dc (Å)	dx (Å)
	Temp. (°C)	Time (hr)					
600	—	—	6.37	2.51	0.85	427	407
601	430	6	6.37	2.51	0.76	480	492
602	610	24	6.37	2.51	0.60	604	583
700	—	—	2.55	2.73	0.45	323	341
701	420	6	2.55	2.73	0.29	500	495
702	630	27	2.55	2.73	0.25	594	584
800	—	—	4.71	2.22	0.64	420	402
801	420	6	4.71	2.22	0.52	522	539
802	600	27	4.71	2.22	0.41	654	680
900	—	—	4.20	2.47	0.57	418	436
901	415	6	4.20	2.47	0.42	566	549
902	600	24	4.20	2.47	0.35	689	701
1200	—	—	6.01	2.29	0.83	412	397
1201	400	6	6.01	2.29	0.64	538	542
1202	590	24	6.01	2.29	0.55	625	627
1300	—	—	6.31	2.55	0.79	457	467
1301	410	6	6.31	2.55	0.67	532	516
1302	600	24	6.31	2.55	0.55	657	681
1400	—	—	4.56	2.69	0.69	379	383
1401	415	6	4.56	2.69	0.54	482	467
1402	605	24	4.56	2.69	0.43	609	583

ing the rate-determining process. In the mechanism proposed by Kenson and Lapkin (*21*), and independently by Ionov *et al.* (*22*), gaseous ethylene reacts with a complex of *molecular* oxygen and silver to form an intermediate which decomposes to ethylene oxide and an adsorbed oxygen atom:



Breaking an oxygen–silver bond with simultaneous electron transfer *from* the intermediate complex *to* the surface of the catalyst is the slow step. Positive charge at the silver surface would speed up such a rate-determining step, in accord with our experimental observations that reaction rates are enhanced by electron-deficient silver supported on a *p*-type semiconductor (magnesium oxide-doped alumina). According to Kenson and Lapkin (*21*), ethylene can also react with adsorbed *atomic* oxygen to form chemisorbed ethylene oxide which reacts further to carbon dioxide and water.

The Rideal–Eley type of mechanism which has been proposed by Kilty and Sachtler (*23*) involves the breaking of an oxygen–oxygen bond, during the rate-controlling step:



Because breaking the oxygen–oxygen bond involves electron transfer *from* the catalyst surface *to* the intermediate complex, a process that ought to be retarded by an electropositive catalyst surface, the present experimental results do not seem to support the Kilty–Sachtler viewpoint. Because the present results also imply that ethylene adsorption is not rate controlling, they do not seem to support previously postulated (*25*, *26*) dual-site mechanisms based on competitive adsorption of oxygen and ethylene.

That ethylene *does not* adsorb on well-reduced, clean silver but *does* adsorb on silver containing preadsorbed oxygen has been observed by many investigators (*31*). By molecular-orbital calculations Beran *et al.* (*24*) have shown that although the interaction of ethylene with silver is not allowed by symmetry, the interaction of ethylene with an electropositive silver surface (Ag^+) is possible. Ethylene adsorption on an electropositive surface is also in accord with the well-recognized nucleophilic character of the ethylene molecule. If preadsorption of oxygen causes electron transfer from silver to oxygen, the resulting electropositive silver should in turn adsorb ethylene. It is not expected that nucleophilic ethylene would adsorb on the preadsorbed oxygen layer which ought to be negatively charged.

b. Selectivity Considerations

The frequently advanced hypothesis that adsorbed molecular oxygen participates in the epoxidation reaction, whereas adsorbed atomic oxygen participates in complete oxidation to carbon dioxide and water, suggests that these respective adsorbed species should govern selectivity. The increased epoxidation selectivity observed for silver supported on magnesium-doped carriers may therefore be ascribed to the higher work function of these catalysts for which the ratio of adsorbed molecular to adsorbed atomic oxygen is higher (*27*). The converse behavior is expected for Ge-doped catalysts. The ratio of adsorbed molecular to adsorbed atomic oxygen would be smaller on germanium-doped catalysts of lower work function. Spath (*27*) has also pointed out that adsorption sites of low work function dissociate adsorbed molecular oxygen into adsorbed atomic oxygen according to the reaction: $O_2^- + e \rightarrow 2O^-$.

Similar reasoning might explain the beneficial effects of adding chlorine to the catalyst or to the feedstock. Chlorine, in small concentrations, enhances (*31*) selectivity for ethylene oxide. Chlorine adsorbed on the surface of silver to form electron-withdrawing chloride (Cl^-) ions could create electron-deficient silver sites which might enhance adsorption of oxygen in the molecular form associated with higher epoxidation selectivity.

Although most of the carbon dioxide and water is produced by the complete oxidation of ethylene, a portion of it is produced by the further oxidation of ethylene oxide (*21*, *28*, *29*) which proceeds by the interaction of an adsorbed ethylene oxide molecule with an adsorbed oxygen atom (*21*). The existence of a high electron concentration at the surface of the catalyst should also enhance adsorption of ethylene oxide on the surface of the catalyst, an electron-acceptor process according to the reaction: $C_2H_4O + e \rightarrow (C_2H_4O)_{ad}$. In contrast, the existence of a positive charge on the surface of silver would retard the adsorption of ethylene oxide and, in turn, the oxidation of ethylene oxide.

c. Magnitude of Electronic Interaction

As the Fermi level of electrons in the support is raised or lowered by doping with ions of different valence, metal–support interaction is thought to occur by electron displacement which alters the 5*s* character of the silver atoms. To obtain significant interaction the metal crystallites should be small and specific interfacial area between metal and support large. Although the catalysts which were used in this study were composed of relatively large silver crystallites, significant metal–support interaction was nevertheless observed for activity and selectivity. The specific rate to carbon dioxide and water changed by as much as a factor of 12 whereas the rate of epoxidation to ethylene oxide fell to nearly zero at a germanium oxide content of 3.0 mole% in the support. A significant change in selectivity of about 70% was also obtained.

Although an electronic interaction between silver and doped alumina supports is strongly suggested by the present results, nevertheless the effects of such interaction on the nature and energy of chemisorption bonds of the reactants and intermediates remain uncertain and speculative. Further investigation might well focus on work function measurements of the surface electrons and precise characterization of the sizes and morphology of the silver crystallites. Beyond shedding additional light on unresolved mechanistic questions, such experiments might also lead to the development of better catalysts for the industrially important epoxidation of ethylene.

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