

Poisoning and Promoting Effects of Additives on the Catalytic Behavior of Metal Clusters

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Extended Hückel calculations are used to explain the mechanisms by which additives such as Cu, Ag, Cl, and S affect the catalytic behavior of Pt or Ag clusters. The complete oxidation of ethylene over Pt/Al₂O₃, the oxidation of CO over Pt/Al₂O₃, and the ethylene epoxidation over supported silver catalysts are used as examples. It is found that Cu or Ag, unlike S, change mainly the net atomic population (the localized electrons around each atom) and very slightly the bond population among the atoms of the Pt clusters. The increased electron density at the surface of Pt clusters due to the electron transfer from Cu or Ag facilitates the electron transfer from the cluster to the π^* antibonding MO of adsorbed O₂. As a result, the dissociative chemisorption of O₂ over Cu- or Ag-treated Pt catalyst is enhanced and the reaction rates for the complete oxidation of C₂H₄ and the oxidation of CO are increased. The electronic effect of Cu on the electron redistribution in the clusters is stronger than that of Ag. Sulfur inhibits these reactions because it is a strong electron acceptor and the competition for electrons, as well as the destabilization of the MOs of the cluster, reduces the dissociative chemisorption of O₂. The inhibition effect of sulfur overcomes the promoting effect of Cu or Ag. Two forms of chemisorbed O₂ molecule, normal and parallel to the surface of a Ag (111) cluster, have been assumed in the calculations. For both forms, the coadsorption of chlorine results in a significant energy shift of the O₂ dissociation curves toward higher energies, thus inhibiting the chemisorption of O₂ and its dissociation. As a consequence, a loss in overall activity occurs, while the selectivity for epoxidation is higher. In the presence of chlorine, the O₂ adsorbed normal to the surface seems to be more stable than the O₂ adsorbed parallel to the surface. In the absence of chlorine, the former form becomes less stable than the latter if the elongation of the O-O bond is larger than 1.4 Å.

INTRODUCTION

This paper is concerned with the mechanisms by which certain additives, such as Cu, Ag, Cl, and S affect the catalytic behavior of metal clusters. For illustrative purposes, we consider the oxidation over supported platinum of both ethylene to CO₂ and H₂O, and of CO to CO₂, and the ethylene epoxidation over supported silver catalysts. The extended Hückel method is employed in the investigation.

A copper-treated Pt/Al₂O₃ catalyst (that is used in the pollution abatement of automobile exhausts), prereduced in a H₂ atmosphere to avoid the presence of oxides, leads to a significant increase in the activity

for CO oxidation and to a more moderate increase in the activity for ethylene oxidation (*I*) in comparison with a copper-free catalyst. The addition of Ag, instead of Cu, has a similar, but less strong, effect. The presence of sulfur in the feed decreases the activity of the Pt/Al₂O₃ catalyst both for the oxidation of CO and for the oxidation of ethylene (*I*). The addition of Cu to the Pt/Al₂O₃ catalyst compensates in part for the negative effects of sulfur.

The first objective of the present paper is to explain the mechanisms by which these promoting and inhibiting effects take place and in particular, to understand why the inhibition effect of S is stronger than the promoting effects of Cu or Ag. Effects similar to those described above have been observed in the epoxidation of ethylene over Ag/Al₂O₃ catalysts, when the substrate was

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TABLE I
Parameters Used in the Calculations

Pt	Ag	Cu	S	Cl	O
$\mu(6s) = 2.554^a$	$\mu(5s) = 2.244$	$\mu(4s) = 1.98$	$\mu(3s) = 1.817$	$\mu(3s) = 2.033$	$\mu(2s) = 2.275$
$\mu(6p) = 2.535$	$\mu(5p) = 2.244$	$\mu(4p) = 1.20$	$\mu(3p) = 1.817$	$\mu(3p) = 2.033$	$\mu(2p) = 2.275$
$\mu_1(5d) = 6.013$	$\mu_1(4d) = 6.07$	$\mu_1(3d) = 5.95$	$\mu(3d) = 1.5$		
$\mu_2(5d) = 2.696$	$\mu_2(4d) = 2.663$	$\mu_2(3d) = 2.10$			
$C_1(5d) = 0.633^b$	$C_1(4d) = 0.589$	$C_1(3d) = 0.58$			
$C_2(5d) = 0.551$	$C_2(4d) = 0.637$	$C_2(3d) = 0.62$			
$H_{II}(6s) = -8.091 \text{ eV}^c$	$H_{II}(5s) = -7.56 \text{ eV}$	$H_{II}(4s) = -7.66 \text{ eV}$	$H_{II}(3s) = -20.00 \text{ eV}$	$H_{II}(3s) = -30.00 \text{ eV}$	$H_{II}(2s) = -32.3 \text{ eV}$
$H_{II}(6p) = -6.36 \text{ eV}$	$H_{II}(5p) = -3.83 \text{ eV}$	$H_{II}(4p) = -3.96 \text{ eV}$	$H_{II}(3p) = -13.30 \text{ eV}$	$H_{II}(3p) = -15.00 \text{ eV}$	$H_{II}(2p) = -14.8 \text{ eV}$
$H_{II}(5d) = -10.989 \text{ eV}$	$H_{II}(4d) = -11.58 \text{ eV}$	$H_{II}(3d) = -10.62 \text{ eV}$	$H_{II}(3d) = -8.00 \text{ eV}$		

^a μ is the orbital exponent.

^b C_1 and C_2 are the coefficients of the double-zeta orbitals.

^c H_{II} is the ionization potential.

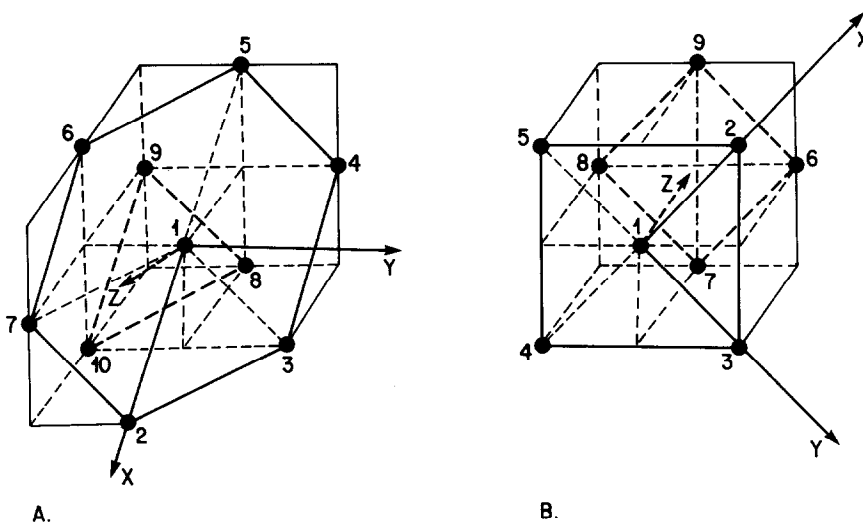


FIG. 1. Clusters used in the calculations.

doped with germanium oxide or magnesium oxide (2). The overall activity and the selectivity for epoxidation are enhanced when the catalyst is doped with magnesium oxide, which is a p-type semiconductor, but are decreased when germanium oxide, which is an n-type semiconductor, is used. The same authors observe that the addition of chlorine to the feed promotes the selectivity of the catalyst for epoxidation (3). For this reason, as a second objective, we examine the two types of adsorption of O_2 on the clusters (normal and parallel to the surface) and the effect of chlorine on their dissociative chemisorption. In essence, we are interested in investigating how the electronic properties of the clusters change under the action of preadsorbed gases, or by the addition of a second metal, and what are the effects of these changes on the activity and selectivity of the cluster catalysts.

METHOD OF CALCULATION AND STRUCTURE OF THE CLUSTERS

The familiar Extended Hückel Method (EHM) (4) is employed in the computations. The method accurately predicts trends (and eventually values) for some quantities which are significant in catalysis.

Although the method is not as sophisticated as other quantum-chemical methods (CNDO, X_{α} , ab initio), its application is useful, if one is interested in trends and not in precise calculated values. Mulliken's expressions (5) are used to calculate the bond population and the atomic charges of the system. The parameters used in the calculations are listed in Table 1. The ionization potentials of Pt are taken from Ref. (6) and those for Cu and Ag from Ref. (7). The exponents of the Slater orbitals for the double-zeta-type orbitals are taken from Ref. (8). All the parameters for sulfur, oxygen, and chlorine are from Quantum Chemistry Program Exchange N344.

The calculations have been carried out for clusters containing 10 or 9 platinum or silver atoms. The 10 atoms are arranged as in the (111) fcc plane (Fig. 1A) and the 9 atoms as in the (100) fcc plane (Fig. 1B).³ The numbering of the atoms is indicated in the figure. The plane in which atom 1 lies will be referred to as the first layer for both crystallographic structures and the plane below, formed by the 3 (Fig. 1A) or 4 (Fig.

³ The coordinate systems shown in Figs. 1A and B are connected with the calculations and not with the crystallographic orientation of the clusters.

1B) metal atoms, constitutes the second distance in the bulk metals (2.775 Å for layer. The distance between the metal platinum and 2.984 Å for silver). The distance between the cluster and the adsorbed atoms in the clusters is taken equal to the distance between the cluster and the adsorbed

TABLE 2

Bond Population Matrices and Charge Distribution in Pt (111) Cluster after Adsorption of Single Cu, Ag, or S Atoms

System	Atom	Bond population matrix			Atomic charges
		1	2	8	
Ten Pt atoms in (111) plane without adsorbed species	1	9.4788	0.1825	0.1735	-0.28662
	2	0.1825	9.6092	0.0041	-0.00642
	3	0.1825	0.2076	0.2018	-0.00642
	4	0.1825	0.0005	0.2018	-0.00642
	5	0.1825	0.0001	0.0041	-0.00642
	6	0.1825	0.0005	0.0005	-0.00642
	7	0.1825	0.1969	0.0005	-0.00642
	8	0.1735	0.0041	9.3894	0.10838
	9	0.1735	0.0005	0.2091	0.10838
	10	0.1735	0.2018	0.2091	0.10838
Ten Pt atoms in (111) plane and a Cu atom adsorbed above the central Pt atom 1	1	8.9917	0.1877	0.1805	0.01420
	2	0.1877	9.7909	0.0036	-0.18631
	3	0.1877	0.2004	0.1958	-0.18631
	4	0.1877	0.0005	0.1958	-0.18631
	5	0.1877	0.0001	0.0036	-0.18631
	6	0.1877	0.0005	0.0004	-0.18631
	7	0.1877	0.1906	0.0004	-0.18631
	8	0.1805	0.0036	9.7096	-0.18814
	9	0.1805	0.0004	0.1888	-0.18814
	10	0.1805	0.1958	0.1888	-0.18814
	11	0.3208	0.0112	-0.0008	1.66810
Ten Pt atoms in (111) plane and a Cu atom adsorbed above the gap formed by the three Pt atoms of the second layer	1	9.4303	0.1821	0.1753	-0.23847
	2	0.1821	9.7088	0.0039	-0.09870
	3	0.1821	0.2031	0.1964	-0.09870
	4	0.1821	0.0004	0.1964	-0.09870
	5	0.1821	0.0001	0.0039	-0.09870
	6	0.1821	0.0004	0.0005	-0.09870
	7	0.1821	0.1925	0.0005	-0.09870
	8	0.1753	0.0039	9.5211	-0.06012
	9	0.1753	0.0005	0.1947	-0.06012
	10	0.1753	0.1964	0.1947	-0.06012
	11	-0.0023	0.0003	0.1117	1.01106
Ten Pt atoms in (111) plane and a Ag atom adsorbed above the central Pt atom 1	1	9.3354	0.1823	0.1729	-0.26187
	2	0.1823	9.6972	0.0037	-0.08910
	3	0.1823	0.2030	0.1962	-0.08910
	4	0.1823	0.0005	0.1962	-0.08910
	5	0.1823	0.0001	0.0037	-0.08910
	6	0.1823	0.0005	0.0005	-0.08910
	7	0.1823	0.1923	0.0005	-0.08910
	8	0.1729	0.0037	9.5517	-0.03747
	9	0.1729	0.0005	0.1988	-0.03747
	10	0.1729	0.1962	0.1988	-0.03747
	11	0.2405	0.0047	0.0004	0.90885

TABLE 2—Continued

System	Atom	Bond population matrix			Atomic charges
		1	2	8	
Ten Pt atoms in (111) plane and a Ag atom adsorbed above the gap formed by the three Pt atoms of the second layer	1	9.4338	0.1818	0.1742	-0.24067
	2	0.1818	9.7046	0.0039	-0.09348
	3	0.1818	0.2029	0.1956	-0.09348
	4	0.1818	0.0004	0.1956	-0.09348
	5	0.1818	0.0001	0.0039	-0.09348
	6	0.1818	0.0004	0.0005	-0.09348
	7	0.1818	0.1920	0.0005	-0.09348
	8	0.1742	0.0039	9.5196	-0.04355
	9	0.1742	0.0005	0.1976	-0.04355
	10	0.1742	0.1956	0.1976	-0.04355
	11	0.0002	0.0001	0.0784	0.93218
Ten Pt atoms in (111) plane and a S atom adsorbed above the central Pt atom 1	1	7.8495	0.1583	0.1695	0.77995
	2	0.1583	9.5186	0.0032	0.09134
	3	0.1583	0.1970	0.1991	0.09134
	4	0.1583	0.0003	0.1991	0.09134
	5	0.1583	0.0001	0.0032	0.09134
	6	0.1583	0.0003	0.0004	0.09134
	7	0.1583	0.1866	0.0004	0.09134
	8	0.1695	0.0032	9.2554	0.26069
	9	0.1695	0.0004	0.1967	0.26069
	10	0.1695	0.1991	0.1967	0.26069
	11	1.2832	0.0349	-0.0004	-2.11004
Ten Pt atoms in (111) plane and a S atom adsorbed above the gap formed by the three Pt atoms of the second layer	1	8.6886	0.1837	0.1779	0.49442
	2	0.1837	9.5602	0.0027	0.04581
	3	0.1837	0.2041	0.2000	0.04581
	4	0.1837	0.0004	0.2000	0.04581
	5	0.1837	0.0001	0.0027	0.04581
	6	0.1837	0.0004	0.0003	0.04581
	7	0.1837	0.1959	0.0003	0.04581
	8	0.1779	0.0027	8.9102	0.40617
	9	0.1779	0.0003	0.1418	0.40617
	10	0.1779	0.2000	0.1418	0.40617
	11	-0.0021	0.0000	0.4997	-1.98781

atom is assumed equal to the sum of their atomic radii. The dissociation energy of O₂ over the Pt or Ag catalysts is calculated keeping the metal-oxygen distance constant and then allowing the O-O distance to elongate. The adsorption sites considered in the calculations are indicated in the tables containing the numerical results.

RESULTS

1. Adsorption of Cu, Ag, Ag and S, or Cu and S Atoms on the Pt (111) Plane

In this section, the results for adsorption

of a single Ag or Cu atom are compared to those obtained when simultaneous adsorption of Ag and S or Cu and S atoms occurs. Table 2 contains the bond population matrices (the electron density between the atoms) and the atomic charges of the cluster atoms (charges of each individual atom) after adsorption of a single Cu, Ag, or S atom on different adsorption sites. The values of the charges in Table 2 are probably higher than the real ones because of the approximations involved in the method. There is a great difference in the effect of sulfur as compared with the effect of Ag or

Cu. The numerical values show that the effect of sulfur on the cluster is opposite to that of copper or silver atoms. Sulfur decreases considerably the bond population among the atoms of the cluster. In addition, the diagonal elements of the bond population matrix which provide the localized electron density around each atom (Mulliken's net atomic population) also decrease considerably. In contrast, the effect of copper or silver atom on the bond population is negligible and the shift toward lower energies of the cluster-adsorbate MOs dominated by the AOs of Pt is negligible. The electron redistribution in the latter case affects mainly the net atomic populations. Copper has a more pronounced effect on the electronic properties of the cluster than silver.

Calculations have also been carried out for simultaneous adsorption of Cu and S or Ag and S atoms. Several adsorption sites have been considered. Table 3 contains the computed charges of all atoms. For comparison, the results for adsorption of single Cu, Ag, or S atoms on the peripheral atoms of the cluster are also included in the table. It is obvious that for any of the considered adsorption sites, sulfur largely (but not totally) compensates the negative charges caused by copper. The negative charges of the platinum atoms for the simultaneous copper-sulfur adsorption are larger than those of the pure platinum clusters. We will return to this point when we discuss the inhibition by sulfur.

The situation is somewhat different when the preadsorbed metal is silver. Sulfur overcomes in this case the electron donor effect of silver and thus generates positive or negative charges (but less negative than in a pure cluster) on different Pt atoms.

2. Adsorption of Cu, Ag, Ag and S, or Cu and S Atoms on the Pt (100) Plane

The trends observed for the Pt (111) plane are preserved for the Pt (100) plane as well. The calculated results are presented

TABLE 3
Atomic Charge Distribution after Simultaneous Copper-Sulfur or Silver-Sulfur Adsorption on Pt (111) Plane

Cu over Pt atom 2	S over Pt atom 2		S over Pt atom 1		S over Pt atom 2		S over Pt atom 1		S over Pt atom 2		S over Pt atom 1		S over Pt atom 2		S over Pt atom 1	
	Pt 1	Pt 2	Pt 1	Pt 2	Pt 1	Pt 2	Pt 1	Pt 2	Pt 1	Pt 2	Pt 1	Pt 2	Pt 1	Pt 2	Pt 1	Pt 2
Pt 1	-0.25977	0.39730	0.75955	0.57056	-0.12189	-0.27555	0.79657	0.19304	0.73608	0.19304	0.73608	0.19304	0.73608	0.19304	0.73608	0.19304
Pt 2	-0.02426	0.86187	0.18012	0.33969	-0.41485	-0.07531	0.07281	0.72180	0.73608	0.72180	0.73608	0.72180	0.73608	0.72180	0.73608	0.72180
Pt 3	-0.13532	0.02380	-0.05814	-0.16121	-0.07724	-0.08705	-0.00657	-0.03107	-0.02170	-0.03107	-0.02170	-0.03107	-0.02170	-0.03107	-0.02170	-0.03107
Pt 4	-0.15751	0.07647	-0.08799	-0.18356	-0.12734	-0.09769	-0.02377	0.01396	0.00048	0.01396	0.00048	0.01396	0.00048	0.01396	0.00048	0.01396
Pt 5	-0.16723	0.06424	-0.10315	-0.20425	0.40694	-0.10155	-0.01673	-0.03208	0.04793	-0.03208	0.04793	-0.03208	0.04793	-0.03208	0.04793	-0.03208
Pt 6	-0.16424	0.8410	-0.09196	-0.17759	-0.10504	-0.10079	-0.02923	0.00301	0.00139	-0.02923	0.00301	-0.02923	0.00301	-0.02923	0.00301	-0.02923
Pt 7	-0.13199	0.17053	-0.07016	-0.15651	-0.09472	-0.08781	-0.00462	0.08682	0.04928	-0.00462	0.08682	-0.00462	0.08682	-0.00462	0.08682	-0.00462
Pt 8	-0.14895	0.14265	-0.04431	-0.12045	-0.10005	-0.05230	0.07099	0.03727	0.04794	-0.05230	0.07099	-0.05230	0.07099	-0.05230	0.07099	-0.05230
Pt 9	-0.16070	0.15571	-0.04008	-0.10154	-0.02525	-0.05538	0.08203	0.05683	0.06990	0.08203	0.05683	0.08203	0.05683	0.08203	0.05683	0.08203
Pt 10	-0.08553	0.15843	-0.05315	-0.05881	0.00211	-0.03339	0.12399	0.12292	0.13844	0.12399	0.12292	0.12399	0.12292	0.12399	0.12292	0.12399
Cu 11	1.43550	-2.13511	-2.00257	-2.04297	-2.17599	0.96680	-2.02246	-2.08411	-2.14213	-2.02246	-2.08411	-2.02246	-2.08411	-2.02246	-2.08411	-2.02246
Cu 12			1.50552	2.29673	2.00361		0.95705	0.91162	0.96915	0.95705	0.91162	0.95705	0.91162	0.95705	0.91162	0.95705

in Tables 4 and 5. Sulfur again decreases considerably both the bond population among the Pt atoms and their net atomic charges. Copper again causes a greater electron redistribution than silver. As in the previous case, sulfur compensates largely the electron donor effect of copper, but the negative charge of the Pt atoms for simultaneous copper-sulfur adsorption is greater than that without adsorbed species. The coadsorption of silver and sulfur results in positive or negative (but less negative than in a pure cluster) charges on different Pt atoms. Since from a qualitative point of view, the results for the (100) plane do not differ from those for the (111) plane, they are no longer discussed in what follows.

3. Dissociation of O_2 over Pt Clusters

The dissociation of O_2 over Pt (111) clusters in the presence or absence of adsorbed Cu or Ag atoms was investigated by keeping the Pt-O distance constant and increasing the O-O distance. The binding energies for O_2 adsorbed normal to the surface above Pt atom 2 in the presence and absence of a Cu atom (adsorbed above the central Pt atom 1) are shown in Fig. 2. In the presence of Cu the energy curve is shifted by about 0.1 eV, toward the lower energies. The energy shift between the two curves increases with the O-O distance. The same relationship is obtained for the bond population between the oxygen atoms in the presence of Cu.⁴ In this case the oxygen-oxygen bond population values are smaller than those which exist in the absence of copper. Obviously the Cu atom enhances the dissociative chemisorption of O_2 over Pt clusters.

Calculations have also been carried out for other adsorption sites, such as: Cu above Pt atom 2 and O_2 above Pt atom 1,

⁴ For example, the O-O bond population for an O_2 molecule is 0.6780, for O_2 adsorbed above Pt 2 it is 0.4366, for O_2 above Pt 2 and Cu above Pt 1 it is 0.4299, and for O_2 above Pt 2 and Cu above Pt 5 it is 0.4291. The above values are calculated before any elongation of the O-O bond takes place.

Cu above Pt atom 2 and O_2 above Pt atom 5. Even though in the latter case there are no direct interactions between O_2 and Cu, there are indirect interactions between them via the cluster. The results of these calculations confirmed that the dissociation of O_2 takes place easier in the presence of Cu. The calculations carried out in the present paper allow one to propose the following explanation: The molecular orbitals of O_2 before adsorption have much lower energy levels than the molecular orbitals of the Cu-containing Pt clusters. For this reason after the adsorption one can distinguish the group of low-energy orbitals in which the weight of the atomic orbitals of oxygen is dominant and the group of high energies which are dominated by the Pt and/or Cu atomic orbitals. The adsorption shifts slightly the low-energy levels to even lower ones (stabilizes these orbitals). Because of the complex mixing of atomic orbitals, with close energies, in the group dominated by Pt and Cu, some of the high-energy molecular orbitals are slightly stabilized while others are slightly destabilized. While it is difficult to identify all the stabilization and destabilization details of these high-energy orbitals, the overall effect of the low and high occupied MOs is a stabilization of the system. This produces a shift of the dissociation energy curve toward lower (more negative) energies in comparison with Cu-free Pt clusters and enhances the dissociation of O_2 .

The main process behind this energetic description is the electron transfer from the cluster to the π^* antibonding orbital of O_2 which decreases the strength of the O-O bond. The mechanism of this electron transfer can be described as follows: The adsorption of Cu results in a charge transfer from the s and d_{z^2} orbitals of copper (and to a lesser extent from the d_{xz} and d_{yz} orbitals) mainly to the d_{z^2} atomic orbitals of the Pt atoms of the first layer surrounding the central Pt atom, above which the Cu atom is adsorbed. The atomic-orbital occupation values for the occupied MOs (Table 6)

show that after the adsorption of O₂ the main electron transfer takes place from the electron-enriched (enriched because of the presence of Cu) *d*_{z²} (and to a lesser extent from) *d*_{xy}, *d*_{yz}, and *d*_{xz} atomic orbitals of the Pt atom above which O₂ is adsorbed, to the

other Pt atoms and to the antibonding π* MO of O₂. (For the latter they are not coming from *d*_{z²} because of symmetry considerations.) The main electron density changes occur on the Pt atom above which the adsorption takes place and its immediate

TABLE 4

Bond Population Matrices and Charge Distribution in Pt (100) Cluster after Adsorption of Single Cu, Ag, or S atoms

System	Atom	Bond population matrix			Atomic charge
		1	2	6	
Nine Pt atoms in (100) plane without adsorbed atoms	1	9.5668	0.1930	0.1770	-0.30814
	2	0.1936	9.7337	0.2023	-0.03823
	3	0.1936	0.0048	0.2023	-0.03823
	4	0.1936	0.0001	0.0006	-0.03823
	5	0.1936	0.0048	0.0006	-0.03823
	6	0.1770	0.2023	9.3789	0.11527
	7	0.1770	0.0006	0.2118	0.11527
	8	0.1770	0.0006	0.0053	0.11527
	9	0.1770	0.2023	0.2118	0.11527
Nine Pt atoms in (100) plane and a Cu atom adsorbed above the central Pt atom 1	1	9.0133	0.2009	0.1874	0.03854
	2	0.2009	9.8830	0.1976	-0.19392
	3	0.2009	0.0045	0.1976	-0.19392
	4	0.2009	0.0001	0.0005	-0.19392
	5	0.2009	0.0045	0.0005	-0.19392
	6	0.1874	0.1976	9.7441	-0.23217
	7	0.1874	0.0005	0.1949	-0.23217
	8	0.1874	0.0005	0.0038	-0.23217
	9	0.1874	0.1976	0.1949	-0.23217
	10	0.3431	0.0155	-0.0011	1.66585
Nine Pt atoms in (100) plane and a Cu atom adsorbed above the gap formed by the four Pt atoms in the second layer	1	9.5577	0.1917	0.1759	-0.29133
	2	0.1917	9.8185	0.1961	-0.11534
	3	0.1917	0.0043	0.1961	-0.11534
	4	0.1917	0.0001	0.0005	-0.11534
	5	0.1917	0.0043	0.0005	-0.11534
	6	0.1759	0.1961	9.5315	-0.05679
	7	0.1759	0.0005	0.1994	-0.05679
	8	0.1759	0.0005	0.0041	-0.05679
	9	0.1759	0.1961	0.1994	-0.05679
	10	-0.0032	-0.0001	0.0785	0.97987
Nine Pt atoms in (100) plane and a Ag atom adsorbed above the central Pt atom 1	1	9.3985	0.1947	0.1777	-0.26640
	2	0.1947	9.8100	0.1976	0.11299
	3	0.1947	0.0047	0.1976	-0.11299
	4	0.1947	0.0001	0.0006	-0.11299
	5	0.1947	0.0047	0.0006	-0.11299
	6	0.1777	0.1976	9.5567	-0.04822
	7	0.1777	0.0006	0.2020	-0.04822
	8	0.1777	0.0006	0.0046	-0.04822
	9	0.1777	0.1976	0.2020	-0.04822
	10	0.2460	0.0055	0.0004	0.91126

TABLE 4—Continued

System	Atom	Bond population matrix			Atomic charge
		1	2	6	
Nine Pt atoms in (100) plane and a Ag atom adsorbed above the gap formed by the four Pt atoms in the second layer	1	9.5510	0.1917	0.1757	-0.28606
	2	0.1917	9.8189	0.1960	-0.11582
	3	0.1917	0.0044	0.1960	-0.11582
	4	0.1917	0.0001	0.0006	-0.11582
	5	0.1917	0.0044	0.0006	-0.11582
	6	0.1757	0.1960	9.5271	-0.04039
	7	0.1757	0.0006	0.2009	-0.04039
	8	0.1757	0.0006	0.0047	-0.04039
	9	0.1757	0.1960	0.2009	-0.04039
	10	0.0004	0.0001	0.0512	0.91092
Nine Pt atoms in (100) plane and a S atom adsorbed above Pt atom 1	1	7.9190	0.1758	0.1736	0.73221
	2	0.1758	9.5917	0.1978	0.09925
	3	0.1758	0.0034	0.1978	0.09925
	4	0.1758	0.0001	0.0004	0.09925
	5	0.1758	0.0034	0.0004	0.09925
	6	0.1736	0.1978	9.2730	0.23746
	7	0.1736	0.0004	0.2026	0.23746
	8	0.1736	0.0004	0.0046	0.23746
	9	0.1736	0.1978	0.2026	0.23746
	10	1.3003	0.0390	-0.0007	-2.07904
Nine Pt atoms in (100) plane and a S atom adsorbed above the gap formed by the four Pt atoms in the second layer	1	9.2776	0.1781	0.1571	0.05145
	2	0.1781	9.6788	0.1835	0.04561
	3	0.1781	0.0029	0.1835	0.04561
	4	0.1781	0.0001	0.0002	0.04561
	5	0.1781	0.0029	0.0002	0.04561
	6	0.1571	0.1835	8.9842	0.43401
	7	0.1571	0.0002	0.1606	0.43401
	8	0.1571	0.0002	-0.0033	0.43401
	9	0.1571	0.1835	0.1606	0.43401
	10	0.0011	-0.0001	0.3212	-1.96993

neighbors. This justifies the assumption on which all cluster model calculations are based, namely, that the chemical interactions during adsorption are largely localized to a small number of atoms. One should note that, in the presence of O_2 , the electron transfer from Cu to the Pt cluster is somewhat reduced compared to the transfer in the absence of O_2 .

The atomic orbitals involved in the charge transfer, when the adsorbed metal is Ag, are the same as those for Cu. However, the interactions among orbitals are weaker and the electron transfer from the silver atom to the cluster and from the cluster to the O_2 molecule is reduced in comparison

with Cu. As a result, the effect of silver on the dissociative chemisorption of O_2 is weaker than that of copper. The shift toward lower energies of the dissociation energy curve of O_2 in the presence of Ag, is about half of that obtained in the presence of Cu.

Figure 2 also contains the calculated energy curve for the dissociation of O_2 adsorbed normal to the surface of a Pt (111) cluster above Pt atom 2, in the presence of a S atom adsorbed above Pt atom 1. As can be seen, the dissociative chemisorption of O_2 is inhibited by the presence of sulfur, since the curve is shifted toward higher energies by about 0.3 eV. This shift is larger

TABLE 5

Atomic Charge Distribution after Simultaneous Copper-Sulfur or Silver-Sulfur Adsorption on Pt (100) Plane

Cu over Pt atom 2	S over Pt atom 2		S over Pt atom 1		S over Pt atom 2		S over Pt atom 4		S over Pt atom 2		S over Pt atom 1		S over Pt atom 2		S over Pt atom 2	
	Pt 1	Pt 2	Pt 1	Pt 2	Pt 1	Pt 2	Pt 1	Pt 2	Pt 1	Pt 2	Pt 1	Pt 2	Pt 1	Pt 2	Pt 1	Pt 2
Pt 1	-0.29230	0.25026	0.67082	0.63449	-0.05953	-0.29621	0.74111	0.32964	0.74111	0.32964	0.74111	0.32964	0.74111	0.32964	0.74111	0.32964
Pt 2	-0.05029	0.71988	0.23315	0.13407	0.46546	-0.08971	0.06792	0.61567	0.06792	0.61567	0.06792	0.61567	0.06792	0.61567	0.06792	0.61567
Pt 3	-0.18306	0.05060	-0.07143	-0.15680	-0.17258	-0.12982	0.00509	-0.01701	-0.12982	0.00509	-0.01701	-0.12982	0.00509	-0.01701	-0.12982	0.00509
Pt 4	-0.18569	0.08150	-0.10247	-0.18882	0.20785	-0.12298	0.00509	-0.00705	-0.12298	0.00509	-0.00705	-0.12298	0.00509	-0.00705	-0.12298	0.00509
Pt 5	-0.18306	0.05060	-0.07143	-0.15680	-0.17258	-0.12982	0.00509	-0.01701	-0.12982	0.00509	-0.01701	-0.12982	0.00509	-0.01701	-0.12982	0.00509
Pt 6	-0.10170	0.22904	-0.00248	-0.11087	0.09681	-0.05704	0.04273	0.06701	-0.05704	0.04273	0.06701	-0.05704	0.04273	0.06701	-0.05704	0.04273
Pt 7	-0.16776	0.22760	-0.09823	-0.16652	-0.10863	-0.05704	0.04273	0.07068	-0.05704	0.04273	0.07068	-0.05704	0.04273	0.07068	-0.05704	0.04273
Pt 8	-0.16776	0.22760	-0.09823	-0.16652	-0.10863	-0.05704	0.04273	0.07068	-0.05704	0.04273	0.07068	-0.05704	0.04273	0.07068	-0.05704	0.04273
Pt 9	-0.10170	0.22904	-0.00248	-0.11087	0.09681	-0.05704	0.04273	0.06701	-0.05704	0.04273	0.06701	-0.05704	0.04273	0.06701	-0.05704	0.04273
Cu 10	1.43331	-2.06615	-1.99160	-2.03857	-2.15991	0.97156	-1.99944	-2.05908	0.97156	-1.99944	-2.05908	0.97156	-1.99944	-2.05908	0.97156	-1.99944
			Cu II	2.32722	Cu II	2.32722	Ag 11	0.94549	Ag 11	0.94549	Ag 11	0.94549	Ag 11	0.94549	Ag 11	0.94549

TABLE 6

Atomic-Orbital Population on Pt (111) Cluster in the Presence or Absence of Adsorbed Species

Orbital	O ₂ above Pt 2						Cu above Pt 1						Cu above Pt 1 and O ₂ above Pt 2						S above Pt 1						S above Pt 1 and O ₂ above Pt 2											
	Pt 1	Pt 2	O 1	O 2	Pt 1	Pt 2	Cu	Pt 1	Pt 2	Cu	O 1	O 2	Pt 1	Pt 2	Cu	O 1	O 2	Pt 1	Pt 2	S	Pt 1	Pt 2	S	Pt 1	Pt 2	S	O 1	O 2								
s	0.55323	0.30177	0.53215	0.36106	1.66839	1.82368	0.58931	0.31464	0.16824	0.56760	0.36147	0.20885	1.66975	1.81869	0.51246	0.27924	1.74479	0.50176	0.33606	1.74805	1.66816	1.82147	1.74805	1.66816	1.82147	1.74805	1.66816	1.82147	1.74805	1.66816	1.82147					
p _x	0.17539	0.09149	0.17833	0.11989	1.90312	1.99012	0.20531	0.08721	0.01563	0.19327	0.11762	-0.02698	1.94188	1.98530	0.20671	0.08118	1.86452	0.20878	0.11372	1.85793	1.88048	1.98254	1.85793	1.88048	1.98254	1.85793	1.88048	1.98254	1.85793	1.88048	1.98254					
p _y	0.17539	0.09149	0.17833	0.11989	1.90312	1.99012	0.20531	0.08721	0.01563	0.19327	0.11762	-0.02698	1.94188	1.98530	0.20671	0.08118	1.86452	0.20878	0.11372	1.85793	1.88048	1.98254	1.85793	1.88048	1.98254	1.85793	1.88048	1.98254	1.85793	1.88048	1.98254					
p _z	0.10310	0.05150	0.10264	0.25224	0.924	1.23048	0.17847	0.05662	-0.00876	0.16661	0.28717	0.00592	0.92955	1.22454	0.34805	0.04985	1.70464	0.35334	0.24383	1.70475	0.92619	1.22930	1.70475	0.92619	1.22930	1.70475	0.92619	1.22930	1.70475	0.92619	1.22930					
d _{x²-y²}	1.81214	1.86461	1.58314	1.81303	1.81417	1.90832	1.99721	1.77252	1.90677	1.99802	1.81417	1.90832	1.99721	1.77252	1.90677	1.99802	1.81417	1.90832	1.99721	1.77252	1.90677	1.99802	1.81417	1.90832	1.99721	1.77252	1.90677	1.99802	1.81417	1.90832	1.99721	1.77252	1.90677	1.99802		
d _{xy}	1.82650	1.83612	1.79822	0.99599	1.47183	1.92002	1.43771	1.39923	0.99838	1.38738	1.47183	1.92002	1.43771	1.39923	0.99838	1.38738	1.47183	1.92002	1.43771	1.39923	0.99838	1.38738	1.47183	1.92002	1.43771	1.39923	0.99838	1.38738	1.47183	1.92002	1.43771	1.39923	0.99838	1.38738		
d _{yz}	1.81214	1.86513	1.74394	1.83943	1.81417	1.87931	1.99721	1.81939	1.85944	1.99888	1.81417	1.87931	1.99721	1.81939	1.85944	1.99888	1.81417	1.87931	1.99721	1.81939	1.85944	1.99888	1.81417	1.87931	1.99721	1.81939	1.85944	1.99888	1.81417	1.87931	1.99721	1.81939	1.85944	1.99888		
d _{zx}	1.91437	1.94945	1.86400	1.49220	1.85362	1.94874	1.85452	1.87050	1.92113	1.95079	1.85362	1.94874	1.85452	1.87050	1.92113	1.95079	1.85362	1.94874	1.85452	1.87050	1.92113	1.95079	1.85362	1.94874	1.85452	1.87050	1.92113	1.95079	1.85362	1.94874	1.85452	1.87050	1.92113	1.95079		
d _{zz}	1.91437	1.96025	1.91082	1.68877	1.85362	1.97613	1.85452	1.88063	1.92113	1.93333	1.85362	1.97613	1.85452	1.88063	1.92113	1.93333	1.85452	1.88063	1.92113	1.93333	1.85452	1.88063	1.92113	1.93333	1.85452	1.88063	1.92113	1.93333	1.85452	1.88063	1.92113	1.93333	1.85452	1.88063	1.92113	1.93333

Note. Pt 1 and Pt 2 are the platinum atoms 1 and 2 while O 1 and O 2 are the oxygen atoms which is adsorbed and the second atom, respectively.

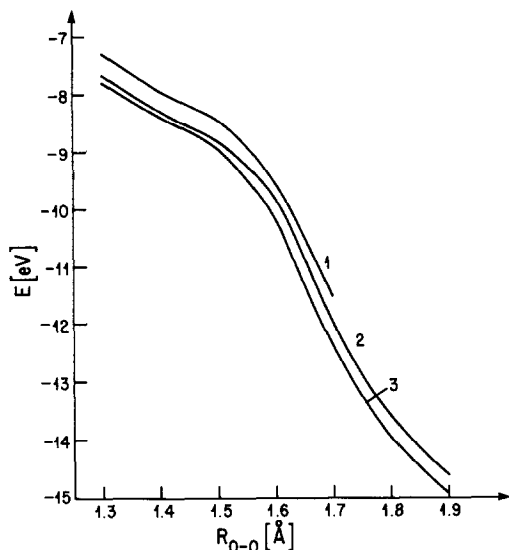


FIG. 2. Potential energy curves for the dissociation of O_2 adsorbed normal to the surface of a Pt (111) cluster above Pt atom 2 vs the bond lengths R_{O-O} : (1) dissociation of O_2 in the presence of S adsorbed above Pt atom 1; (2) dissociation of O_2 over a pure cluster; (3) dissociation of O_2 in the presence of Cu adsorbed above Pt atom 1.

than the shift in the opposite direction caused by the presence of a Cu or Ag atom. Therefore, one might expect that the inhibiting effect caused by a single S atom prevails over the promoting one caused by a single Cu or Ag atom. This has been, indeed, observed experimentally (1).

4. Dissociation of O_2 over Ag Clusters in the Presence and Absence of Chlorine

Calculations have been carried out to investigate the effect of adsorbed Cl on the ability of silver (111) clusters to dissociate adsorbed oxygen molecules. The d orbital functions of chlorine have been used in some of the calculations, but led to unrealistically high charge numbers and very high occupation numbers for these orbitals. For this reason, in the calculations presented here, the basis set of wavefunctions does not include d orbitals. Two configurations of the O_2 molecule have been assumed in the computation: (a) O_2 is adsorbed normal to the cluster surface and above silver atom

2; (b) the O_2 molecule is adsorbed parallel to the cluster surface and is parallel to and above the bond between silver atoms 5 and 6. These two possibilities have been chosen because they are often discussed in literature. Kilty and Sachtler (9) favor the former, while Kenson and Lapkin (10) prefer the latter configuration.

It is generally accepted that the nondissociatively adsorbed O_2 is responsible for the epoxidation reaction and therefore, if the presence of Cl in the feed improves the selectivity of the catalyst, this means that Cl should decrease the rate of dissociation of O_2 . The dissociation energy curves for the parallel adsorption of O_2 are plotted in Fig. 3, which show that the presence of Cl adsorbed above Ag atom 1, shifts the curve toward higher energies by about 1.5 eV. The change of the oxygen-oxygen bond population value follows the same trend, e.g., they are slightly larger than those in the absence of Cl. Obviously, chlorine

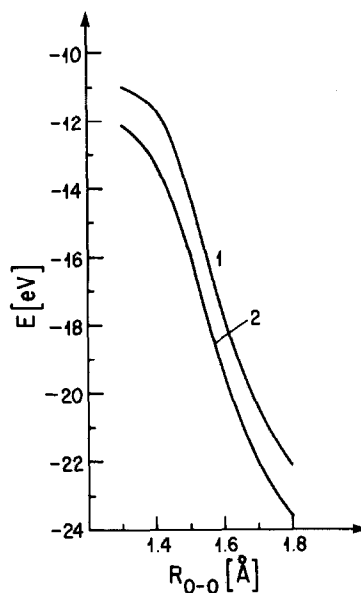


FIG. 3. Potential energy curve for the dissociation of O_2 adsorbed parallel to the surface of a Ag (111) cluster above the bond between Ag atom 5 and Ag atom 6: (1) dissociation of O_2 in the presence of Cl adsorbed above Ag atom 1; (2) dissociation of O_2 over a pure cluster.

makes both the adsorption and dissociation of O_2 more unfavorable.

The present calculations allow us to suggest the following explanation for the effect of chlorine. The s orbitals of silver are the main orbitals that interact with the O_2 molecule. Electrons from the s orbitals are transferred to the π^* antibonding MO of adsorbed O_2 . Chlorine interacts with the silver cluster in a similar way, electrons being transferred mainly from the silver s orbitals to the p orbitals of chlorine. Because of the competition for electrons between O_2 and Cl, the electron transfer from the cluster to the oxygen molecule is reduced. As a consequence, the bond strength between the oxygen atoms is increased and the dissociation rate of adsorbed O_2 is decreased. In addition, the molecular orbitals of oxygen are stabilized by the interaction with the orbitals of Ag and Cl, while the molecular orbitals of the cluster are destabilized. However, the de-

stabilization overcomes the stabilization and leads to a lower heat of adsorption of O_2 in the presence of chlorine, reducing the amount which is adsorbed. For the above reasons, the overall activity is reduced while the selectivity for epoxidation is increased.

The results of the calculations for the adsorption of O_2 normal to the surface are shown in Fig. 4. The results are similar to those for the parallel adsorption. However, the effect of Cl adsorbed above Ag atom 1 is now weaker, since the energy shift of the potential energy curve is about 0.9 eV instead of 1.5 eV. Calculations have also been carried out with O_2 adsorbed normal to the surface above Ag atom 2 and Cl adsorbed above Ag atom 5. They show that, in this case, there is no direct interaction between O_2 and Cl. They interact, however, via the cluster atoms. The results are similar to those obtained for the other adsorption sites.

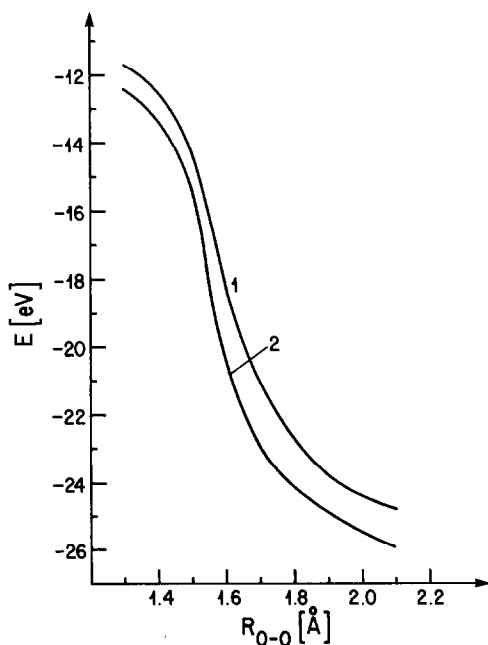


FIG. 4. Potential energy curves for the dissociation of O_2 adsorbed normal to the surface of a Ag (111) cluster above Ag atom 2: (1) dissociation of O_2 in the presence of Cl adsorbed above Ag atom 1; (2) dissociation of O_2 over a pure cluster.

5. Effect of cluster Size

Previous calculations based on the EHM (17) carried out for Ag and Pd clusters indicate a dependence of the ionization potential, IP [identified with the highest occupied MO (HOMO)], and of the electron affinity, EA [identified with the lowest unoccupied MO (LUMO)], on the size of the cluster. These two quantities affect the charge transfer from or to the cluster. They have practically identical values for bulk metals, but they differ significantly when the number of atoms in the cluster is small. Increasing the number of atoms results in a rapid decrease of the energy gap between them. The above-mentioned calculations (17) show a rapid change of the IP and the EA up to 10–15 atoms and a much slower change for larger sizes. Therefore, the charge transfer to or from the cluster is not expected to differ drastically for clusters between 10 and 20 atoms. Furthermore, EH calculations (18) carried out for the dissociative chemisorption of H_2 on Pd clus-

ters of different sizes show that the adsorption characteristics of H_2 depend insignificantly on the cluster size, but depend on the adsorption site. The latter observation is also confirmed by our calculations. The change of the adsorption site changes, however, only the numerical values, but does not change the observed trend of the effect of the coadsorbed atoms on the dissociation of O_2 . We note, that the increased number of cluster atoms could result in a larger charge transfer from the Cu or Ag atom to the cluster, since the LUMO shifts toward lower energies with the increase of the size of the cluster. This could contribute to an increased compensation of the inhibition effect of S. However, it is difficult to believe that the orbital interaction between the cluster orbitals and the orbitals of Cu and Ag would become so strong with increasing cluster size, that the resulting shift of the dissociation energy curve of O_2 toward lower energy would overcome the opposite shift caused by the strong cluster-sulfur interaction and, thus, change the observed trends.

6. Catalytic Implications

Let us consider first the complete oxidation of C_2H_4 to CO_2 and H_2O . Ethylene is a well-known nucleophilic reagent. Therefore, one might expect that the more positive the surface of the catalyst is, the easier the adsorption of C_2H_4 will take place and the larger the reaction rate will be. If the copper- or silver-treated Pt/Al_2O_3 catalyst is used instead of pure Pt/Al_2O_3 , our calculations indicate that the catalyst surface is more negatively charged. Hence, the catalytic activity should decrease. If, however, the rate-determining step is the interaction between the adsorbed oxygen atoms and the gas-phase ethylene, the reaction rate should increase, since, as our calculations show, the dissociation of oxygen molecules on the more negatively charged surface of the catalyst is easier. The experimental results in (1) seem to support the latter conclusion. This point of view is compati-

ble with the explanation given in Ref. (2), where the decreased selectivity of a Ag catalyst, used for ethylene epoxidation, supported on a germanium oxide- (n-type semiconductor) doped alumina, is explained in terms of electron transfer from the support to the silver clusters. This decreases the fraction of nondissociatively adsorbed oxygen molecules, which are probably responsible for the selective epoxidation, and increases the fraction of dissociatively adsorbed oxygens which participate in the complete oxidation reaction.

The addition of Cu or Ag to the Pt/Al_2O_3 catalyst has similar effects on the reaction rate in the oxidation of CO. According to the Blyholder mechanism (11, 12), the adsorption of CO on the surface of transition metals involves electron transfer from and to the metal surface. The electron transfer to the metal atoms is from the nonbonding orbital of CO. This does not affect the bond strength between the C and O atoms. On the contrary, the electrons coming from the metal fill the antibonding orbitals of CO thus changing its reactivity. Therefore, the increased electron density at the surface of the Cu- or Ag-treated Pt/Al_2O_3 catalyst should increase the catalytic activity in the CO oxidation. In addition, as the curves in Fig. 2 show, the bimetallic catalyst enhances the dissociation of O_2 thus further contributing to the increase of the reaction rate. These theoretical considerations are again supported by the experiments of Ref. (1).

Let us now consider the poisoning effect of sulfur. Somorjai (13) has suggested that the structural change from (111) to (100) planes, which occur on the surface of Pt crystallites after adsorption of sulfur, constitutes the main reason for the inhibition of platinum catalyst by sulfur. The results of Sivasanker and Ravaswamy (14) and Maurel *et al.* (15) show that this interpretation cannot always explain the experimental facts. While it is obvious that any structural change will bring changes in the electronic properties of the catalyst, the ad-

sorption of contaminants can change the electronic properties of the atoms at the surface without causing major structural rearrangements of the surface atoms. Previous quantum-chemical calculations (16) show that structural changes of the (111) and (100) Pt planes can, indeed, occur after adsorption of electron acceptor elements, such as sulfur or chlorine, because of the significant decrease in the bond strength among the atoms of the cluster. However, the same calculations indicate that the inhibiting effect of sulfur is also caused by a change in the electronic properties of the platinum atoms themselves. It should be noted that other mechanisms of the inhibition by sulfur include: the blocking of the active sites and/or its reaction with the reactants to produce undesirable reaction pathways. Without excluding the latter possibilities, we will emphasize the electronic changes brought on the platinum atoms by the adsorption of sulfur.

To explain the inhibiting effect of sulfur, we use the calculated atomic-orbital population values of a Pt (111) cluster (Table 6) in the presence and absence of sulfur. These values suggest that sulfur adsorbed above the central Pt atom 1, accepts electrons, mainly, from the d_{z^2} (and to a lesser extent from the d_{xz} and d_{yz} atomic orbitals) of that atom. Electrons are also taken from the s , d_{z^2} , d_{xz} , and d_{yz} atomic orbitals of the surrounding Pt atoms. Similar results have been obtained (Table 6) when O_2 is absorbed above Pt atom 2 of a sulfur-free Pt (111) cluster. The O_2 molecule accepts electrons, mainly, from the d_{z^2} , d_{xz} , and d_{yz} orbitals of that atom. However, in the presence of sulfur, the electron population of these orbitals is diminished. Hence, the electron transfer to the antibonding MO of the adsorbed O_2 is impeded and the dissociative chemisorption of O_2 is inhibited. The chemisorption of O_2 on a S-free Pt (111) cluster is accompanied by the following energy changes: The low-energy cluster-adsorbate MOs are composed, mainly, of AO of oxygen. These orbitals are, how-

ever, stabilized (shifted toward lower energies) in comparison with the MOs of a free O_2 molecule. The cause of this stabilization is the interaction of the low-energy orbitals of O_2 with the high-energy orbitals of the cluster. The stabilization of these orbitals is accompanied by the destabilization of the higher-energy MOs of the cluster-adsorbate, which are composed, mainly, of Pt AO. Concerning the effect of S, we mention that the ionization potential of the $3s$ AO of S is smaller than that of the $2s$ AO of O, but higher than that of the $5d$ AO of Pt. That is why the simultaneous chemisorption of O_2 and S results in further stabilization of the MOs composed mainly of oxygen AO and further destabilization of the high-energy MOs, composed mainly of Pt AO. This resultant destabilization caused by O_2 and S overcomes the stabilization of the lowest (cluster-adsorbate) MOs and thus decreases the heat of adsorption of O_2 over the sulfur-contaminated cluster by about 0.3 eV (Fig. 2).

It is worth noting that in contrast to the energy curves for the dissociation of O_2 (Fig. 2), the numerical values of the atomic charges of the Pt atoms (Table 3) seem to suggest that the promoting effect of a Cu atom is stronger than the inhibiting effect of a S atom. However, as we have mentioned before, the adsorption of Cu above the Pt cluster results in a major change of the net atomic population, while the bond population values are only slightly affected. This means that even though the charges of the atoms are high, the shifts toward lower energies of the cluster-adsorbate MOs dominated by the AOs of Pt, are small. These shifts, as well as the slight stabilization of the cluster-adsorbate MOs dominated by the AOs of oxygen, contribute to the shift of the O_2 dissociation curve toward lower energies. Sulfur stabilizes slightly the cluster-adsorbate MOs dominated by the AOs of oxygen, but destabilizes the MOs dominated by the AOs of Pt. This destabilization is higher than the stabilization caused by Cu, although the atomic charges generated

in the presence of sulfur are smaller in absolute value than those caused by Cu.

The promoting effect of small amounts of chlorine on the selectivity of the silver catalysts in the reaction of ethylene epoxidation (3) can be explained in a similar way. As the calculations indicate, chlorine adsorption increases the probability for nondissociative chemisorption of O_2 molecules adsorbed in any of the two adsorption forms and decreases the heat of adsorption of O_2 . Concerning the two chemisorbed forms of oxygen molecules, it seems that in the absence of chlorine and at a bond length between the oxygen atoms equal to that in the free molecule, the form adsorbed normal to the surface is favored energetically. Indeed, in this case, this form has a heat of adsorption about 0.25 eV larger than that of form b, adsorbed parallel to the surface. However, the distance between the dissociation curves decreases with the elongation of the O_2 molecule and they cross one another at an oxygen-oxygen distance of about 1.4 Å (Fig. 5). Therefore, one can tentatively conclude that during the dissoci-

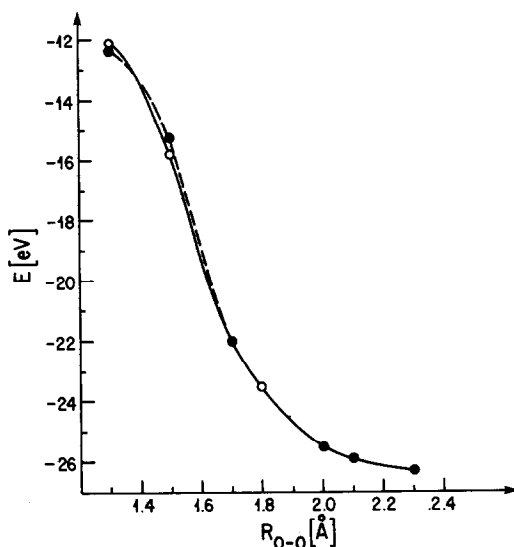


FIG. 5. Potential energy curves for the dissociation of O_2 over a pure Ag (111) cluster: (●) O_2 adsorbed normal to the cluster above Ag atom 2; (○) O_2 adsorbed parallel to the cluster above the bond between Ag atom 5 and Ag atom 6.

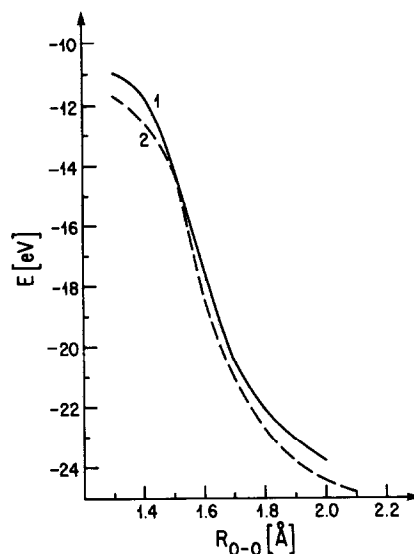


FIG. 6. Potential energy curves for the dissociation of O_2 over a Ag (111) cluster in the presence of Cl adsorbed above Ag atom 1: (1) O_2 adsorbed parallel to the cluster above the bond between Ag atom 5 and Ag atom 6; (2) O_2 adsorbed normal to the cluster above Ag atom 2.

ation process form a may transform into form b before the breaking of the oxygen-oxygen bond, which takes place at a bond length of about 1.5 Å for both adsorption forms. It seems that in the absence of Cl, the two forms may exist. In the presence of Cl, the two curves (Fig. 6) meet at a bond length of about 1.5 Å without crossing one another. This means that in the presence of Cl, the adsorbed form a is favored energetically to form b. It is difficult to conclude whether one of the two adsorption forms, or both of them, take part in the epoxidation reaction since ethylene itself may play a part in this choice. Most probably both forms exist simultaneously, even though the normal configuration seems to be slightly prevailing energetically.

CONCLUSIONS

The EH method has been applied to study the promoter and poisoning effects of different additives to Pt and Ag cluster catalysts and the calculated results have been correlated with the catalytic activity for

ethylene oxidation, CO oxidation, and ethylene epoxidation. Additives such as Cu or Ag cause a shift toward lower energies of the O₂ dissociation curve and slightly increase the population of the π^* antibonding MO of O₂. These effects favor the dissociative chemisorption of O₂ and constitute the main reason for the increased catalytic activity in reactions such as CO oxidation and the complete oxidation of ethylene. For the latter reaction, the computations favor a mechanism in which C₂H₄ from the gas phase interacts with adsorbed O atoms. The inhibition by sulfur for the above reactions is due to the shift of the dissociation curve of O₂ toward higher energies and the decrease of the population of the π^* antibonding MO of O₂. Since sulfur affects both the adsorption of CO and the dissociation of O₂, the reaction of CO oxidation is more sensitive to sulfur poisoning than the complete oxidation of C₂H₄. The poisoning effect of sulfur is stronger than the promoter effect of Cu or Ag, because the electronic changes of the catalyst caused by sulfur are much greater than those caused by Cu or Ag.

The effect of Cl on the dissociation of O₂ over Ag clusters is similar to the effect of S on Pt clusters and the origin of this effect is the same for both cases. Concerning the epoxidation reaction, Cl increases the selectivity because it inhibits the dissociative chemisorption and decreases the overall activity since it decreases the heat of adsorption.

Our calculations suggest that most probably two types of O₂ chemisorbed on Ag may exist—normal to the surface and parallel to it. The normal form eventually transforms into the parallel one with the elongation of the O–O bond before the dissociation occurs. The presence of Cl changes this behavior favoring, under all conditions, the normal configuration.

REFERENCES

1. Kummer, J. T., *J. Catal.* **38**, 166 (1975).
2. Verikios, X. E., Stein, F. P., and Coughlin, R. W., *J. Catal.* **66**, 147 (1980).
3. Verikios, X. E., Stein, F. P., and Coughlin, R. W., *Catal. Rev. Sci. Eng.* **22**(2), 1987 (1980).
4. Hoffman, R., *J. Chem. Phys.* **39**, 1397 (1963).
5. Mulliken, R. S., *J. Chem. Phys.* **23**, 1833 (1955).
6. Lu, C. C., Carlson, T. A., Malik, F. B., Tucker, T. C., and Nestor, C. W., *At. Data* **3**, 1–131 (1971).
7. Moore, C. E., *Natl. Bur. Stand. (U.S.) Circ.*, 1–3 (1949).
8. Basch, H., and Gray, H. B., *Theor. Chim. Acta* **4**, 367 (1966).
9. Kilty, P. A., and Sachtler, W. M. H., *Catal. Rev. Sci. Eng.* **10**(1), 1 (1974).
10. Kenson, R. E., and Lapkin, M., *J. Phys. Chem.* **74**, 1493 (1970).
11. Blyholder, G., *J. Phys. Chem.* **68**, 2772 (1974).
12. Doyen, G., and Ertl, G., *Surf. Sci.* **43**, 197 (1974).
13. Somorjai, G. A., *J. Catal.* **27**, 453 (1972).
14. Sivasanker, S., and Ravaswamy, A. V., *J. Catal.* **37**, 553 (1975).
15. Maurel, R., Leclercq, G., and Barbier, J., *J. Catal.* **37**, 324 (1975).
16. Halachev, T., and Ruckenstein, E., *Surf. Sci.* **108**, 292 (1981).
17. Baetzold, R., *Surf. Sci.* **51**, 1 (1975).
18. Baetzold, R., *J. Catal.* **29**, 129 (1973).