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The EPR Observation of O_2^- on Various Supported Metal Surfaces

The molecular anion radical, O_2^-, has been observed to form when oxygen adsorbs on silver metal supported on porous Vycar brand quartz (*1*) and on silica (*2*). The role of the superoxide in silver-catalyzed oxidation still is unclear, although the reactivity of O_2^- is established (*3*). Furthermore, through a lineshape analysis of the EPR spectrum of O_2^- on silver, the usefulness of the superoxide as a molecular probe of the environment of adsorption (*4*), and as a measure of surface mobility (*5*) also has been demonstrated.

Information on the formation of O_2^- on metals other than silver has been scanty. Howe *et al.* (*6*) have reported the formation of O_2^- on tungsten supported on silica, and they observed EPR lineshape changes characteristic of surface mobility. In the course of EPR studies of O_2^- conducted in this laboratory, we have had occasion to observe the formation of O_2^- on a variety of metals other than silver and tungsten. We wish to report these new findings in the hope that they will stimulate interest in investigating the correlation between O_2^- formation and catalytic selectivity for partial oxidation of unsaturated hydrocarbons.

Table 1 lists the metals on which we have observed the EPR spectrum of O_2^- when 0.5 Torr of oxygen at room temperature was allowed to adsorb on metal samples supported on Corning brand porous Vycor quartz, together with the principal g values for the O_2^- signal observed by us and by others. Sample preparations were as follows:

Silver. See Ref. (*3*).

Platinum. Incipient wetness using 0.100 *M* aqueous $H_2PtCl_6 \cdot 6H_2O$, with a reduction under 200 Torr H_2 at 110°C for 12 hr.

Gold. Incipient wetness using 0.10 *M* aqueous $HAuCl_4 \cdot 3H_2O$, with reduction under 200 Torr H_2 at 110°C for 15 hr.

Rhodium. Incipient wetness using saturated hexane solution of $[Rh_2(CO)_4Cl_2]$ under N_2 atmosphere, with reduction under 1 atm H_2 at 125°C for 6 hr.

Electron diffraction studies were made on each of the samples prepared by us to confirm the presence of the metal, and TEM studies showed the disperse nature of the small metal particles formed after reduction. Extent of reduction, based on the sensitivity of electron diffraction to the metal oxides, can be estimated to be greater

TABLE 1

EPR Values for O_2^- on Several Metals

Metal	g_{xx}	g_{yy}	g_{zz}	O_2^- intensity[a]	Reference
Ag	2.0031 ± 0.0002	2.0089 ± 0.0002	2.0311 ± 0.0005	7 × 10^{13} molecules/mg Ag	(*1*)
Ag	2.002 ± 0.001	2.010 ± 0.001	2.040 ± 0.005	(no information)	(*2*)
Au	1.9995	2.0048	2.0316	7 × 10^{12} molecules/mg Au	This work
Rh	1.9978	2.0029	2.0264	Weak	This work
Pt	2.0064	2.0102	2.0366	1 × 10^{13} molecules/mg Pt	This work
W	2.0042	2.0097	2.0266	1 × 10^{15} molecules/mg W[b]	(*6*)

[a] The EPR signal intensity was measured by digitally integrating the O_2^- absorption line and comparing values of the integral thus obtained with a standard sample of Varian Weak Pitch, with a concentration of 1.0 × 10^{13} spins/cm.

[b] Based on loading values presented in Ref. (*6*).

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than 70% ± 20%. Typical particle size distributions were in the diameter range from 30 to 50 Å.

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