Crystal Field Effects in a Chemisorbed O⁻ Ion

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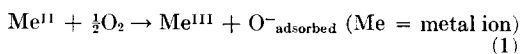
The crystal field stabilization energy has been calculated for an O⁻ ion chemisorbed on third row transition metal oxide catalysts. This stabilization energy can reach values up to 70 kcal/mole for certain geometric arrangements of the transition metal oxides.

INTRODUCTION AND PROBLEM STATEMENT

Recently, ligand field theory has been applied to explain the activity of transition metal oxide catalysts. For simplicity, most authors have assumed that the metal oxides display only ionic bonds, which seems fairly well justified for transition metals with $3d$ valence electrons. This assumption permits the use of the simpler crystal field theory. The crystal field effects on the third row transition metal ions in inorganic complex ions have been extensively worked out in numerous publications. These results have been used to explain the catalytic activity pattern of transition metal oxides. However, there is not only the crystal field affecting the metal ion but there is also a crystal field affecting the chemisorbed reactant; i.e., on one hand, the chemisorbed reactant induces a field affecting the metal ion, on the other hand, the catalyst ions induce a field affecting the reactant. Because of the lack of data, the crystal field effects on the chemisorbed reactant seem to have been unjustifiably neglected.

Klier (*1*) has incorporated crystal field stabilization of the pertinent metal ions to calculate the activity of various transition metal oxide catalysts for oxidation–reduction reactions. In his treatment, the chemisorbed oxygen ion, O⁻, plays a very important role. He has related the chemisorption energy to the reaction enthalpy of the following reaction:

$$\text{Me}^{II} + \tfrac{1}{2}\text{O}_2 \rightarrow \text{Me}^{III} + \text{O}^-_{\text{adsorbed}} \quad (\text{Me} = \text{metal ion})$$
$$(1)$$

The crystal field stabilization of the O⁻ ion should amount to a considerable part of the chemisorption energy.

In H_2–O_2 or hydrocarbon–O_2 fuel cells, a chemisorbed O⁻ ion occurs at a decisive state. According to the peroxide mechanism, the slowest step seems to be the decomposition of the peroxide, Eq. (A3), (see Appendix).

This paper presents the crystal field stabilization energy of an O⁻ ion chemisorbed on transition metal oxide catalysts with various geometric arrangements.

CRYSTAL FIELD CALCULATIONS

An O⁻ ion has a $(1s^2, 2s^2)\, 2p^5$ electron structure. According to Hund's rule (*2*), the resulting ^2P term is ground term.

Under the influence of an electric field, the ^2P term can split into three or fewer split terms. An ideal cubic lattice, for example, would induce a C_{4v} field effecting the chemisorbed O⁻ ion. The most distorted lattice, on the other hand, would induce a C_1 field. As a compromise C_{2v} symmetry has been assumed. It has been found that for all pertinent symmetries, a given ligand in a given position contributes approximately the same energy shifting of the lowest split term; i.e., it contributes about the same amount to the crystal field stabilization energy.

The contribution of the dipole moments of any surface metal or surface oxygen ion to the ligand field is at least one order of magnitude smaller than the contribution of an electric charge. Therefore, no attention has been paid to those parts of the ligand field

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TABLE 1
EIGENFUNCTIONS FOR THE $^2A_1$, $^2B_1$, $^2B_2$ SPLIT TERMS

Free ion	C_{2v} field	Linear combination of atom eigenfunctions	Linear combination of antisymmetrized products of one-electron eigenfunctions
^2P	$^2A_1$	$\Psi(\frac{1}{2}\ 1\frac{1}{2}\ 0)$	$-\phi(1^+1^-0^+ - 1^+ - 1^-)$
	$^2B_1$	$\Psi(\frac{1}{2}\ 1\frac{1}{2}\ 1)$	$\phi(1^+1^-0^+0^- - 1^+)$
	$^2B_2$	$\Psi(\frac{1}{2}\ 1\frac{1}{2}\ -1)$	$-\phi(1^+0^+0^- - 1^+ - 1^-)$

which were induced by dipole moments of the catalyst, of other reactants, or of any possible solvents wetting the catalyst.

A C_{2v} field causes a P term to split into an A_1, B_1, and B_2 term. A perturbation treatment covering the influence of the crystal field has been used to determine the exact energetic position of the three split terms. Let ΔE be the energy difference between the resulting split term and the original term. Then the crystal field stabilization is equal to the ΔE of the lowest split term. The perturbation treatment has been carried out with the weak field method (2, 3, 4). The formalism has been taken from Condon and Shortley (5). Slater's eigenfunctions have been used.

For each irreducible representation, the application of the operator rules by Ufford and Shortley (6, 7) and by Condon and Shortley (5) have been applied to determine the proper linear combinations of atom eigenfunctions, $\Psi(S\ L\ M_s\ M_L)$, where S is the spin momentum quantum number, L is the orbital momentum quantum number, M_s is the spin momentum quantum number in direction of the Z axis, and M_L is the magnetic momentum quantum number. These atom eigenfunctions can be replaced by antisymmetrized products of one-electron eigenfunctions $\phi(m_{l_1}^+ m_{l_2}^- \ldots)$, where m_l is the magnetic quantum number of the electron; the suffix $+$ or $-$ refers to spin quantum number $+\frac{1}{2}$ or $-\frac{1}{2}$. The results are given in Table 1.

Equation (2) provides the perturbation energy for the $^2A_1$ term

$$\Delta E_{2_{A_1}} = \int \phi^*(1^+1^-0^+ - 1^+ - 1^-)$$

$$\sum_{i=1}^{5} V_{si}\ \phi(1^+1^-0^+ - 1^+ - 1^-)\ d\tau + 5\epsilon \quad (2)$$

$$V_{si} = \sum_j \frac{n_j e^2}{r_{ij}}$$

where the asterisk refers to the conjugated complex nature of the first $\phi(\cdots)$; the operator V_{si} represents the ligand field affecting the ith electron of the O^- ion; n_j is the number of elementary charges, e; r_{ij} is the distance of the ith electron from the jth ligand; $\int \cdots d\tau$ indicates the integration over the whole space; and ϵ is the constant amount of shifting per one-electron integral inherent in this method (2).

Similar equations are valid for the perturbation energies of the other split terms. Such integrals can be replaced by sums of one-electron integrals (5).

In order to evaluate ϵ, an O^{2-} ion has been submitted to the same perturbation treatment as used for the O^- ion. Since the ^1S ground term of an O^{2-} ion is not affected by any ligand field, ϵ can be determined in terms of one-electron integrals.

The perturbation energies for the $^2A_1$, $^2B_1$, $^2B_2$ split terms of an O^- ion can now be expressed in terms of one-electron integrals:

$$\Delta E_{2_{A_1}} = \frac{1}{3}\int 1^*V_s\ 1\ d\tau - \frac{2}{3}\int 0^*V_s\ 0\ d\tau$$
$$+ \frac{1}{3}\int -1^*V_s -1\ d\tau \quad (3a)$$

$$\Delta E_{2_{B_1}} = \frac{1}{3}\int 1^*V_s\ 1\ d\tau + \frac{1}{3}\int 0^*V_s\ 0\ d\tau$$
$$- \frac{2}{3}\int -1^*V_s -1\ d\tau \quad (3b)$$

$$\Delta E_{2_{B_2}} = -\frac{2}{3}\int 1^*V_s\ 1\ d\tau + \frac{1}{3}\int 0^*V_s\ 0\ d\tau$$
$$+ \frac{1}{3}\int -1^*V_s -1\ d\tau \quad (3c)$$

The complex Slater one-electron eigenfunctions have been replaced by real Slater one-electron eigenfunctions. Using Slater's rule (8) for the O^- ion, the screening constant

in these real one-electron eigenfunctions has been evaluated to $\sigma = 3.8$ a.u. (atomic units). The evaluation of these integrals leads to the following equality:

$$\Delta E_{^2B_1} = \Delta E_{^2B_2} \qquad (4)$$

(i.e., the split terms $^2B_1$ and $^2B_2$ are accidently degenerate). For the final results, the expression $1/r_{ij}$ has been developed into spherical harmonics. The ΔE caused by a single ligand is considered in the following equations:

$$\Delta E_j(^2A_1) = 1.02 n_j e \ (\cos^2 \vartheta_j - \tfrac{1}{3})(1/R_j^3) \qquad (5a)$$

$$\Delta E_j(^2B_1) = -0.51 n_j e \ (\cos^2 \vartheta_j - \tfrac{1}{3})(1/R_j^3) \qquad (5b)$$

where ϑ_j is the angle formed by the main axis and the shortest connection between the O^- ion and the jth ligand; and R_j is the distance between the jth ligand and the O^- ion.

The charges and the positions of the involved ligands determine which split term is the lower one.

CALCULATIONS ON AN O^{2-} ION

Since the ^1S ground term of an O^{2-} ion is not affected by any ligand field, there is no crystal field stabilization of the ground state. The first excited state is a ^3P term resulting from the electron structure $(1s^2, 2s^2) \ 2p^5, 3s$. This ^3P term lies approximately 150 kcal/mole above the ^1S ground term. The splitting of the ^3P term of the O^{2-} ion exactly follows the equations derived for the ^2P term of the

O^- ion. In general, the crystal field stabilization for the O^{2-} ion is smaller than the corresponding one for the O^- ion due to the difference in ion radius. Therefore, it seems unlikely that any pertinent catalyst configuration induces a crystal field stabilization exceeding 150 kcal/mole.

RESULTS AND DISCUSSION

Table 2 presents the contribution of a single ligand to the crystal field stabilization of a chemisorbed O^- ion where Me^{III}, Me^{II}, and O^{2-} are the ligands at various positions relative to the main axis. The distance used between the O^- ion and the ligand are discussed in the appendix. For formal consistency, these distances in Table 2 should be altered by infinitesimal amounts so that the ligand field reduces from C_{4v} to C_{2v} symmetry

A negative ΔE_j implies stabilization of the O^- ion. The highest stabilization energy of almost 70 kcal/mole occurs when the O^- ion is chemisorbed in a "whole" type configuration, where the O^- is surrounded by four Me^{III} ions with $\vartheta = 90°$ and by one O^{2-} ion with $\vartheta = 0°$. Due to the relatively small contribution of any ion with $\vartheta = 45°$, the planes 100 and 110 in a cubic lattice should be relatively similar. Since all pertinent metal ions have very similar ion radii, no distinction in activity can be deduced from the O^- stabilization. However, an Me^{II} shows about half the stabilization energy of an Me^{III} which supports the model of a red-ox couple. Any unstable higher oxida-
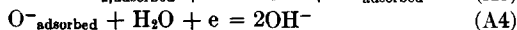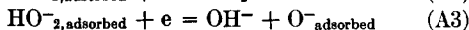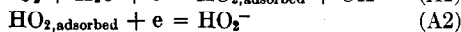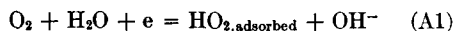
TABLE 2

PART OF THE CRYSTAL FIELD STABILIZATION OF CHEMISORBED O^- ION DUE TO A SINGLE LIGAND

j	n_j	R_j (a.u.)	ϑ_j	$\Delta E_j(^2A_1)$ (kcal/mole)	$\Delta E_j(^2B_1)$ (kcal/mole)
Me^{III}	-3	3.5	$0°$	$+30$	-15
Me^{II}	-2	3.8	$0°$	$+15.7$	-7.8
O^{2-}	$+2$	5.0	$0°$	-7	$+3.5$
Me^{III}	-3	$3.5 \times \sqrt{2}$	$45°$	$+2.5$	-1.3
Me^{II}	-2	$3.8 \times \sqrt{2}$	$45°$	$+1.3$	-0.7
O^{2-}	$+2$	$5.0 \times \sqrt{2}$	$45°$	-0.7	$+0.4$
Me^{III}	-3	3.5	$90°$	-15	$+7.5$
Me^{II}	-2	3.8	$90°$	-7.8	$+3.9$
O^{2-}	$+2$	5.0	$90°$	$+3.5$	-1.8

tion state of the considered transition metal
ions would cause a stabilization energy much
more pronounced than the corresponding
Me^{III} ion. Such high oxidation states have
been found catalytically very active. Gen-
erally, the crystal field stabilization energy
of a reactant with an incomplete outer elec-
tron shell is of the same order of magnitude
as the stabilization of a transition metal ion.

APPENDIX

(1) The mechanism of the oxygen reaction
of a base compact type fuel cell can be seen
in the following scheme:

$$O_2 + H_2O + e = HO_{2,adsorbed} + OH^- \quad (A1)$$
$$HO_{2,adsorbed} + e = HO_2^- \quad (A2)$$
$$HO^-_{2,adsorbed} + e = OH^- + O^-_{adsorbed} \quad (A3)$$
$$O^-_{adsorbed} + H_2O + e = 2OH^- \quad (A4)$$

(In an acid cell, H_2O might be replaced by
H^+, and HO_2^- reacts to H_2O_2.)

(2) Pauling (9) reports the following ion
radii:

$$r = 0.69 \text{ Å for } Cr^{3+}$$
$$r = 0.63 \text{ Å for } Co^{3+}$$
$$r = 0.62 \text{ Å for } Ni^{3+}$$
$$r = 1.40 \text{ Å for } O^{2-}$$

The radius of O^- has here been assumed to be
0.15 Å smaller than the one of O^{2-}. For illus-
tration, the following values have been
taken:

$$R_1 = 1.25 \text{ Å} + 0.63 \text{ Å} = 1.88 \text{ Å} = 3.5 \text{ a.u.}$$
$$R_2 = 1.25 \text{ Å} + 0.77 \text{ Å} = 2.02 \text{ Å} = 3.8 \text{ a.u.}$$
$$R_3 = 1.25 \text{ Å} + 1.40 \text{ Å} = 2.65 \text{ Å} = 5.0 \text{ a.u.}$$

where R_1 is the distance between O^- and
Me^{III}, R_2 is the distance between O^- and
Me^{II}, and R_3 is the distance between O^-
and O^{2-}.

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