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Crystal Field Effects in Chemisorbed H, N, O, S, F, Cl Atoms

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The crystal field stabilization energy has been calculated for O, S, N, H, F, Cl atoms chemisorbed on third row transition metal oxide catalysts. The stabilization energies obtained decrease in the following order $S > O \approx Cl > F$ with N and H having no stabilization effect at all.

Introduction and Problem Statement

Third row transition metal oxide catalysts have been successfully explained by assuming ionic bonds (*1*). Chemisorption on these catalysts can proceed with or without electron transfer between adsorbate and catalysts. The former case was considered in a previous paper (*2*) in which ligand field theory—or more accurately crystal field theory—was applied to calculate the crystal field stabilization energy of a chemisorbed O^- ion. This crystal field stabilization is caused by an electric field induced by the metal ions as well as the O^{2-} ions of the catalyst.

Considering chemisorption without electron transfer it seems to have been neglected that also chemisorbed neutral atoms are affected by such a crystal field. Crystal field stabilization energy can be partly responsible for the fact that diatomic molecules are often chemisorbed as atoms (*3*).

This paper is an extension of Reference 2, presenting the crystal field stabilization energy of O, S, H, F, Cl, N atoms chemisorbed at third row transition metal oxide catalysts.

Crystal Field Calculations

Table 1 presents the electron structures and the resulting atom terms for O, S, F, Cl, H, N atoms in the ground state and for H and N atoms in the lowest excited state which is not an *S* term. The method used has been outlined in Reference 2. The crystal fields have been assumed to be of C_{4v} symmetry. Lower symmetries like C_{2v} do not differ from the C_{4v} case in respect to the contribution to the stabilization energy caused by any ligand positioned on the main axis, which usually are the most effective ligands. The same is approximately true for any ligand in a C_{2v} structure which can be considered as a distorted C_{4v} structure (Reference 2 has been limited to such structures). However, there are C_{2v} structures where the stabilization energies for the B_1 and B_2 terms differ considerably from each other. The contribution of a given ligand to the stabilization energy in these cases are distinctly different from the results of corresponding C_{4v} cases.

The perturbation treatment has been carried out with the weak field method

TABLE 1
PERTIENT ELECTRON STRUCTURES AND ATOMIC TERMS FOR H, N, O, S, F, Cl ATOMS

H: Ground state	$1s^1 \rightarrow {}^2S$
Excited state	$2p^1 \rightarrow {}^2P$
N: Ground state	$(1s^2,2s^2)2p^3 \rightarrow {}^4S$
Excited state	$(1s^2,2s^2)2p^3 \rightarrow {}^2D$
O: Ground state	$(1s^2,2s^2)2p^4 \rightarrow {}^3P$
S: Ground state	$(1s^2,2s^2,2p^6,3s^2)3p^4 \rightarrow {}^3P$
F: Ground state	$(1s^2,2s^2)2p^5 \rightarrow {}^2P$
Cl: Ground state	$(1^2,2s^2,2p^6,3s^2)3p^5 \rightarrow {}^2P$

(4–6). The formalism has been taken from Condon and Shortley (7).

C_{4v} or C_{2v} ligand fields cause the atomic terms from Table 1 to split according to the following scheme:

$$S \xrightarrow{C_{4v}} A_1; \qquad S \xrightarrow{C_{2v}} A_1 \quad \text{(no splitting or shifting)}$$
$$P \xrightarrow{C_{4v}} A_1 + E; \qquad P \xrightarrow{C_{2v}} A_1 + B_1 + B_2$$
$$D \xrightarrow{C_{4v}} A_1 + B_1 + B_2 + E; \qquad D \xrightarrow{C_{2v}} 2A_1 + A_2 + B_1 + B_2$$

H and N atoms have S terms as ground states. Therefore, these atoms can only show crystal field stabilization if one of the split terms resulting from an excited state has a crystal field stabilization energy exceeding the energy difference between this excited state and the ground state.

In the case of an H atom, the energy difference between the ^2S ground state and the ^2P excited state (Table 1) exceeds 300 kcal/mole which is larger than the crystal field stabilization energy possibly could be. In the case of an N atom, however, the ^4S state differs from the ^2D excited state by about 60 kcal/mole.

Following the method outlined in Reference 2, the eigenfunctions belonging to the proper irreducible representations have been expressed in linear combinations of antisymmetrized products of one-electron eigenfunctions. Integrals over products of one-electron eigenfunctions can be reduced to one-electron integrals as shown by Condon and Shortley (7). The perturbation energy can finally be expressed in sums of one-electron integrals:

O, S atoms

$$^3A_1: \quad \Delta E = -\tfrac{1}{3}\textstyle\int 1^*V_s1\,d\tau + \tfrac{2}{3}\int 0^*V_s0\,d\tau - \tfrac{1}{3}\int -1^*V_s -1\,d\tau$$
$$^3E: \quad \begin{cases} \Delta E = \tfrac{2}{3}\int 1^*V_s1\,d\tau - \tfrac{1}{3}\int 0^*V_s0\,d\tau - \tfrac{1}{3}\int -1^*V_s -1\,d\tau \\ \Delta E = -\tfrac{1}{3}\int 1^*V_s1\,d\tau - \tfrac{1}{3}\int 0^*V_s0\,d\tau + \tfrac{2}{3}\int -1^*V_s -1\,d\tau \end{cases}$$

F, Cl atoms

$$^2A_1: \quad \Delta E = \tfrac{1}{3}\textstyle\int 1^*V_s1\,d\tau - \tfrac{2}{3}\int 0^*V_s0\,d\tau + \tfrac{1}{3}\int -1^*V_s -1\,d\tau$$
$$^2E: \quad \begin{cases} \Delta E = \tfrac{1}{3}\int 1^*V_s1\,d\tau + \tfrac{1}{3}\int 0^*V_s0\,d\tau - \tfrac{2}{3}\int -1^*V_s -1\,d\tau \\ \Delta E = -\tfrac{2}{3}\int 1^*V_s1\,d\tau + \tfrac{1}{3}\int 0^*V_s0\,d\tau + \tfrac{1}{3}\int -1^*V_s -1\,d\tau \end{cases}$$

N atom

$$\Delta E = 0 + 60 \text{ kcal/mole,}$$

where $1, 0, -1$ = Slater's one-electron eigenfunctions (see appendix)

V_s = perturbation operator representing the ligand field affecting one electron (see Reference 2)

$\int \ldots d\tau$ = integration over the whole space

All second-order effects like configurational interaction have been neglected. The result on the N atom indicates that an N atom is not stabilized by any C_{4v} crystal field.

The final evaluation of these integrals leads to the following expressions for the crystal field stabilization caused by the jth ligand (in atomic units, a.u.):

$$\text{O:} \quad \Delta E_j(^3A_1) = +0.869n_j\left(\cos^2\vartheta_j - \frac{1}{3}\right)\frac{1}{R_j^3}$$
$$\Delta E_j(^3E) = -0.435n_j\left(\cos^2\vartheta_j - \frac{1}{3}\right)\frac{1}{R_j^3}$$
$$\text{S:} \quad \Delta E_j(^3A_1) = +2.54n_j\left(\cos^2\vartheta_j - \frac{1}{3}\right)\frac{1}{R_j^3}$$
$$\Delta E_j(^3E) = -1.27n_j\left(\cos^2\vartheta_j - \frac{1}{3}\right)\frac{1}{R_j^3}$$
$$\text{F:} \quad \Delta E_j(^2A_1) = -0.666n_j\left(\cos^2\vartheta_j - \frac{1}{3}\right)\frac{1}{R_j^3}$$
$$\Delta E_j(^2E) = +0.333n_j\left(\cos^2\vartheta_j - \frac{1}{3}\right)\frac{1}{R_j^3}$$
$$\text{Cl:} \quad \Delta E_j(^2A_1) = -2.04n_j\left(\cos^2\vartheta_j - \frac{1}{3}\right)\frac{1}{R_j^3}$$

$$\Delta E_j(^2E) = +1.02 n_j \left(\cos^2 \vartheta_j - \frac{1}{3}\right) \frac{1}{R_j^3}$$

where ϑ_j = angle formed by the main axis and the shortest connection between the jth ligand and the chemisorbed atom
n_j = number of elementary charges of the jth ligand
R_j = distance between the jth ligand and the chemisorbed atom

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

Results and Discussion

A cobalt oxide catalyst has been chosen as a concrete example to illustrate the crystal field stabilization effects obtained by this method. Table 2 presents the contribution of a single Co^{3+} ligand to the crystal field stabilization of a chemisorbed O, S, F, Cl atom as a function of the position of the ligand. The distance R_j between catalyst and chemisorbed atom has been assumed to be the sum of the ion radius of the catalyst ion (as taken from ionic crystals) and the atom radius of the chemisorbed atom. To exhibit the dependence of ΔE_j on the distance R_j, the radii of the chemisorbed atoms have been varied between the van der Waal radii and the covalent radii with $\bar{R}_j$ being the arithmetic mean of the two. The numerical values of the radii used have been taken from Pauling (*8*).

In the case of Co^{2+} ligands, all ΔE_j's are about half as large as in the case of Co^{3+}. O^{2-} ligands have ΔE_j values of about a quarter of the ones for Co^{3+} with opposite signs. As mentioned in Reference 2, a negative ΔE_j value means stabilization.

Considering the dependence of ΔE_j on the angle ϑ_j, one finds largest ΔE_j values at $\vartheta_j = 90°$ and at $\vartheta_j = 0°$ while ΔE_j values at $\vartheta_j = 45°$ are considerable smaller. In the case of metal ligands as catalyst ions Cl and F show equal ΔE_j values for $\vartheta_j = 90°$ and $\vartheta_j = 0°$; O and S, on the other hand, show ΔE_j's at $\vartheta_j = 0°$ by far exceeding the ones at $\vartheta_j = 90°$.

As shown in Table 2, the crystal field stabilization energy of such chemisorbed atoms are of significant order of magnitude. It should be added that both atoms of a chemisorbed diatomic molecule can be submitted to these crystal field effects. Depending on the distance, the crystal field stabilization energies obtained possibly exceed the dissociation energy of the diatomic molecules considered. This indicates that the crystal field effects might largely be responsible for diatomic molecules like O_2, S_2, F_2, Cl_2 being chemisorbed as atoms. H_2 and N_2, on the other hand, show no

TABLE 2
Crystal Field Stabilization of Chemisorbed O, S, F, Cl Atoms Due to a Single Co^{3+} Ligand
(in kcal/mole, i.e. in kcal/gram atom)

	O		S		F		Cl	
$\varphi_j = 0°$	$\Delta E_j(^3A_1)$	$\Delta E_j(^3E)$	$\Delta E_j(^3A_1)$	$\Delta E(_j{}^3E)$	$\Delta E_j(^2A_1)$	$\Delta E_j(^2E)$	$\Delta E_j(^2A_1)$	$\Delta E_j(^2E)$
$R_{j\text{v.d.W.}}$	−19.4	+9.7	−30.8	+15.4	+15.8	−7.9	+26.4	−13.2
$\bar{R}_j$	−32.0	+16.0	−51.1	+25.6	+26.3	−13.2	+44.2	−22.1
$R_{j\text{coval.}}$	−62.7	+31.4	−100.6	+50.3	+50.3	−25.2	+89.0	−44.5

	O		S		F		Cl	
$\varphi_j = 90°$	$\Delta E_j(^3A_1)$	$\Delta E_j(^3E)$	$\Delta E_j(^3A_1)$	$\Delta E_j(^3E)$	$\Delta E_j(^2A_1)$	$\Delta E_j(^2E)$	$\Delta E_j(^2A_1)$	$\Delta E_j(^2E)$
$R_{j\text{.v.d.W.}}$	+ 9.7	−4.8	+15.4	−7.7	−7.9	+4.0	−13.2	+6.6
$\bar{R}_j$	+16.0	−8.0	+25.6	−12.8	−13.2	+6.6	−22.1	+11.0
$R_{j\text{coval.}}$	+31.4	−15.7	+50.3	−25.2	−25.2	+12.6	−44.5	+22.2

crystal field stabilization at all. N_2 is rarely chemisorbed on transition metal oxides. Furthermore, N_2 is only chemisorbed as molecule not as atom (*9, 10*). In the case of H_2, the bonding seems to be of more metallic or covalent character. Also, H_2 seems first to reduce such metal oxides at the surface.

The very high stabilization energy of chemisorbed S atoms can lead to a very large chemisorption strength so that sulfur becomes a pronounced catalyst poison.

A chemisorbed Cl atom is more stabilized than an F atom. This might explain why the reaction

$$CH_3X + H_2 \rightarrow CH_4 + HX \quad \text{over Ni catalysts}$$

goes much faster in the case of $X = Cl$ than in the case $X = F$ (*9*).

Bond (*9*) proposed an intermediate adsorption, so called *C*-adsorption, at a catalyst-adsorbate distance somewhere in the middle between the physical adsorption distance and the chemisorption distance. This mechanism results in a considerable decrease of the activation energy for the chemisorption. Effectively, the crystal field stabilization also lowers the activation energy of the chemisorption (here mainly the dissociation energy). Contrary to the *C*-adsorption model, the crystal field stabilization takes place at any distance R_j.

Since the resulting stabilization energy is linearly proportional to the charge of the catalyst ion, unstable high oxidation states of the transition metal ion produce extremely high crystal field effects (*2, 10*). The present model can be applied to all ionic catalysts. In the case of catalysts with only partly ionic characters, the simple crystal field theory has to be replaced by the much more complicated ligand field theory. As a rough qualitative picture, one can assume a certain portion of the crystal field stabilization to be still effective.

References

1. Klier, K., *J. Catalysis* **8,** 14 (1967).
2. Kollrack, R., *J. Catalysis* **12,** 321 (1968).
3. Ehrlich, G., Proc. 3rd International Congress on Catalysis, Amsterdam, 1964, p. 113.
4. Ballhausen, C. J., Introduction to Ligand Field Theory, McGraw-Hill, New York, 1962.
5. Hartmann, H., "Theorie der chem. Bindung," Springer-Verlag, Berlin, 1954.
6. *Internationale Ferienkurse über theoret. Chem.*, Konstanz, W. Germany, Sept. 1962.
7. Condon, E. U., and Shortley, G. H., "The Theory of Atomic Spectra," Cambridge University Press, London, 1953.
8. Pauling, L., "The Nature of the Chem. Bond," Cornell University Press, Ithaca, New York, 1960.
9. Bond, G. C., "Catalysis by Metals," Academic Press, Inc., New York, 1962.
10. Roginskii, S. Z., "Scientific Selection of Catalysts," S. Monson, Jerusulem (Israel) 1968.

Appendix

Slater's complex $2p$ and $3p$ one-electron eigenfunctions:

$$0_{2p} = \sqrt{\frac{3}{2}} \cos\vartheta \frac{1}{\sqrt{2\pi}} \sqrt{\frac{4}{3}f^5}\, re^{-fr}$$

$$0_{3p} = \sqrt{\frac{3}{2}} \cos\vartheta \frac{1}{\sqrt{2\pi}} \sqrt{\frac{8}{45}f^7}\, r^2e^{-fr}$$

$$1_{2p} = \sqrt{\frac{3}{4}} \sin\vartheta \frac{1}{\sqrt{2\pi}} e^{i\varphi} \sqrt{\frac{4}{3}f^5}\, re^{-fr}$$

$$1_{3p} = \sqrt{\frac{3}{4}} \sin\vartheta \frac{1}{\sqrt{2\pi}} e^{i\varphi} \sqrt{\frac{8}{45}f^7}\, r^2e^{-fr}$$

$$-1_{2p} = \sqrt{\frac{3}{4}} \sin\vartheta \frac{1}{\sqrt{2\pi}} e^{-i\varphi} \sqrt{\frac{4}{3}f^5}\, re^{-fr}$$

$$-1_{3p} = \sqrt{\frac{3}{4}} \sin\vartheta \frac{1}{\sqrt{2\pi}} e^{-i\varphi} \sqrt{\frac{8}{45}f^7}\, r^2e^{-fr}$$

In the case of O and F, one uses $2p$ electrons, in the case of S and Cl $3p$ electrons. The f values have been calculated using Slater's rule in (atomic units):

$$f_O = 2.275 \qquad f_S = 1.820$$
$$f_F = 2.600 \qquad f_{Cl} = 2.033$$