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NOTES

Ni^{2+} Adsorption Centers on the MgO Lattice

It has been shown in many cases that ions on the surface of a solid are, similarly to ions in a homogeneous phase, responsible for catalytic activity (*1*). Examination of the change in coordination undergone by these ions on adsorption on oxide catalysts for example, and elucidation of the structure of the respective active centers provide a possibility for a more detailed understanding of the mechanism of catalysis. The EPR technic is especially suitable for this purpose (*2*).

The bivalent nickel ion participating in various complexes exhibits a so-called "anomalous" magnetic moment when subjected to a change in its coordination number (*3*). This property has been made use of in the present investigation for identifying the Ni^{2+} adsorption centers on the surface of MgO cubic crystal.

The MgO sample examined containing Ni^{2+} ions in its cubic crystal lattice was prepared by impregnation of analytical grade MgO in a nickel nitrate ammonia complex and heating it subsequently in 1 atm of air at 500°C and before the experiment *in vacuo* at 800°C. The sample prepared in this manner contained 1.5% (by weight) of nickel.

The influence of adsorbed H_2O, HBr, and NH_3 on the spectra of Ni^{2+} placed on the crystal lattice of MgO was examined with the aid of JES-3BS EPR spectrometer.

The sample treated at 800° gives a resonance absorption line characteristic for the Ni^{2+} ion in octahedral surrounding (*4*) with a *g* value of 2.24 and a line width of 280 gauss at 25°. Investigation of such NiO/MgO diluted systems (*5*, *6*) showed that the Ni^{2+} ions are not isolated but grouped in clusters and that there are even microcrystals of NiO; and dipole–dipole interaction between paramagnetic neighbors occurs. The line narrowing observed after heating at 800° has been interpreted to indicate that exchange interaction begins also to take place (*5*).

After evacuation to a pressure of 10^{-6} mm Hg, adsorption of water vapor did not affect the *g* value and practically so the line width, but increased the integral intensity, as evidenced by repeated graphical integration and the use of a standard. This increase is reversible and the effect can be observed by repeating the adsorption–desorption cycles. The increase of the integral intensity was strongly temperature dependent. Adsorption of HBr and NH_3 led to a much smaller increase in the integral intensity than water vapor (Table 1).

TABLE 1
INCREASE OF THE INTEGRAL INTENSITY OF THE EPR SIGNAL OF Ni^{2+} IONS DURING THE ADSORPTION OF H_2O, HBr, AND NH_3[a]

Adsorbed compound	Partial pressure of the adsorbed compound (mm Hg)	Temp at registration of spectra (°C)	Increase of integral intensity (%)
H_2O	20	25	13
	20	−100	17
	20	−170	23
HBr	1	25	6
NH_3	40	25	4

[a] The adsorption of all substances was carried out at 25°C.

Oxygen adsorption at 350 mm Hg had the same effect as water vapor.

The observed increase of the integral intensity is related to the change in the coordination number of the Ni^{2+} ions on the surface during adsorption and can be easily explained from Balhausen and Liehr's view on the "anomalous" magnetic moment of nickel complexes (7).

Prior to adsorption the Ni^{2+} ion on the crystal face (001) is situated in a crystal field with approximately flat square pyramid symmetry (C_{4v}). This adsorbed water molecule occupies the site of the sixth ligand and restores the octahedral coordination (O_h). This change in coordination affects the spin multiplicity of the Ni^{2+} ions. As shown in Fig. 1a an ion in a field of O_h symmetry possesses two unpaired electrons belonging to the e_g doublet. The change to C_{4v} symmetry (desorption of the H_2O ligand from the surface) and a sufficiently high value for Δ yields in the extreme case the diamagnetic complex because of the singlet state ${}^1A_{1g}$, $\psi_1 = (d_{z^2}^{\uparrow})(d_{z^2}^{\downarrow})$.

The observed dependence of the integral intensity on the temperature (Table 1) can be easily explained with Balhausen and Liehr's formula for the magnetic susceptibility:

$$\chi_\alpha = \frac{2g^2N\beta^2}{3kT}\left[1 + \tfrac{1}{3}\exp^{\Delta E/kT}\right]^{-1} + N_\alpha \quad (1)$$

where g is Landé's factor for the state ${}^3B_{1g}$; N, Avogadro number; k, the Boltzman constant; N_α, the temperature independent part of the susceptibility; ΔE, the difference in energy between the singlet ${}^1A_{1g}$ and triplet ${}^1B_{1g}$ $\psi_2 = (d_{z^2}^{\uparrow})(d_{x^2-y^2})$ states. At low temperature the singlet state population increases and so the difference between magnetic susceptibility before and after adsorption increases.

As already mentioned, there is no considerable line width change during adsorption. The reason for no noticeable influence of field distortion on the line width change during adsorption can be explained by dipole–dipole interaction obscuring the line narrowing. As can be estimated no more than 25% of all nickel ions are on the surface and half of them are in singlet state at room temperature giving no resonance absorption at all. Most of the ions in the

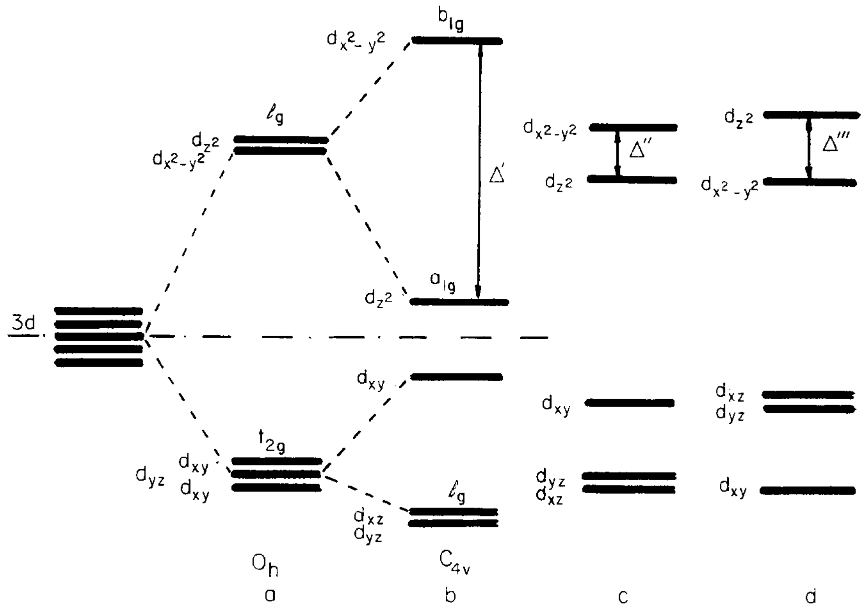

FIG. 1. Diagramatic representation of the d-orbitals in fields of different symmetries: (a) octahedral (O_h); (b) flat square piramidal (C_{4v}); (c) octahedral, distorted with one weaker ligand; (d) octahedral, distorted with one stronger ligand.

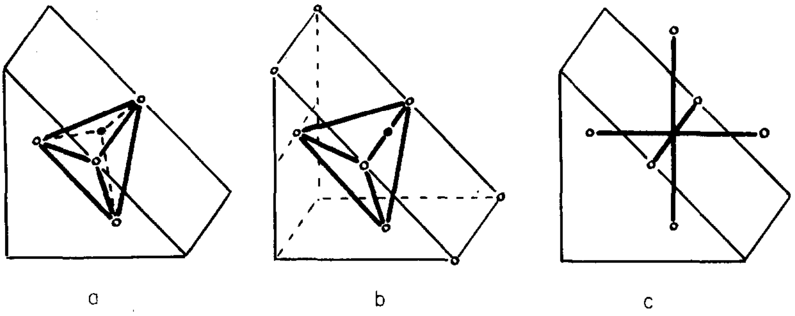

FIG. 2. Ni^{2+} adsorption center on the (110) face: (a) relaxation form; (b) ideal (110) face; (c) after adsorption of two ligands.

bulk of the crystal are not subject to any symmetry change.

The Ni^{2+} on the crystal face (110) provides another type of adsorption center (Fig. 2). The relaxation form of the surface center is Ni^{2+} in tetrahedral coordination. The nickel ion adopts octahedral coordination on adsorption of two molecules of water. The energy diagram for the tetrahedral configuration is almost identical with that for the flat square pyramid. Thus, the mentioned changed in spin multiplicity occurs in this case too. Such adsorption centers were used by Haber and Stone (*8*) to explain the photodesorption of oxygen from NiO lattice.

The adsorbed ligand H_2O is of the same strength as the O^{2-} ligands of the lattice, this is supported by the same values for D_q obtained from spectroscopic data i.e., $D_q^{NiO} = 850\ cm^{-1}$ (*9*) and $D_q^{Ni(H_2O)^{2+}} = 860\ cm^{-1}$ (*10*). The ligands under consideration in the present work can be arranged according to their strength in the following manner:

$$Br^- < H_2O < NH_3$$

The octahedral complex arising from the adsorption of Br^- (a weaker ligand than O^{2-}) on the (001) face leads to a diagram of the type shown in Fig. 1c, while the adsorption of NH_3 results in a diagram as the one depicted in Fig. 1d. As shown, the adsorption of these compounds leads to the creation of a triplet state mixed with a singlet state, this being the result of Δ'', $\Delta''' < \Delta'$. Obviously, in this case a slight change in magnetic susceptibility is to be expected, which has also been observed experimentally.

The study of the changes of EPR spectra of Ni^{2+} ions in a MgO crystal lattice caused by the adsorption of H_2O, HBr, and NH_3 molecules indicate the existence of Ni^{2+} adsorption centers with a definite coordination on the surface.

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