Photodesorption from a Nickel Oxide Surface

Among the various techniques employed to investigate surface phenomena, photodesorption methods with visible or ultraviolet radiation play an important role. These methods are principally applied to semiconducting oxides, such as ZnO, and the results are explained by the electronic band structure of these solids.

Recently Stone and Haber (*1,2*) have extended the scope of this interesting technique to include consideration of the individual adsorption sites of nickel oxide. They report that illumination of a nearly stoichiometric nickel oxide carrying adsorbed oxygen gives rise to oxygen desorption. The part of the visible spectrum that is active is reported to be confined to wavelengths between 650 and 900 mμ.

In their explanation of the phenomena observed, Stone and Haber suggest a mechanism which is based on the transition ${}^3A_{2g} \rightarrow {}^3T_{1g}$ of an octahedrally surrounded nickel ion. This transition has its spectral absorption centered around 650 mμ.

In this letter, we wish to make some remarks on both experimental and theoretical aspects of the work quoted.

We did very similar experiments, using samples of nickel oxide prepared in the same way (*2*). Our light source was a slide projector with a 500 watt incandescent tungsten lamp. Spectral bands were isolated by combinations of high- and low-pass filters, as described by Shcherbov (*3*), and a thermopile instrument was used to measure light intensities, incident on the sample. The half-width of the filters amounted to approximately 100 mμ.

Our results, like those of Stone and Haber, could be expressed by the kinetic equations:

$$dp/dt = k_{\mathrm{des}}I_\nu - k_{\mathrm{ads}}(p - p_0) \tag{1}$$

$$(p - p_0) = (p_\infty - p_0)[1 - \exp(-k_{\mathrm{ads}}t)] \tag{2}$$

$$p_\infty - p_0 = (k_{\mathrm{des}}/k_{\mathrm{ads}})I_\nu \tag{3}$$

Here p_0 is the pressure in the sample container after the preadsorption equilibrium has been established; illumination is started at $t = 0$; p_∞ stands for the steady state pressure under illumination of intensity I_ν quanta/sec, with frequency ν.

From Eq. (3) we can derive a quantity η', proportional to the quantum efficiency of the photodesorption:

$$\eta' = (p_\infty - p_0)/I_\nu \tag{4}$$

or

$$\eta'' = (p_\infty - p_0)/I\bar{\lambda} \tag{5}$$

In Eq. (5), I stands for the millivolt reading of the thermopile, and $\bar{\lambda}$ for the wavelength at which transmission of the light filter is maximum.

Our results are in good agreement with those in the work quoted (*2*), as regards the total magnitudes of the desorption effects, and the rate constant k_{ads}. Our interpretation of the dependence of the photodesorption effects on wavelength, however, is different: From our results for η'', which are plotted in Fig. 1, we conclude, even though the experimental values are rather inaccurate, that there is no pronounced specific activity of light with wavelengths around 650 mμ.

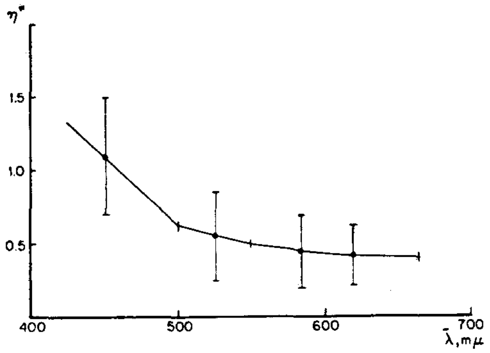

FIG. 1. Quantum efficiency of photodesorption in arbitrary units.

In their theoretical model of the adsorption site behavior, Stone and Haber concentrate on nickel ions in [1,1,0] faces of the nickel oxide surface. If this surface is bare, the nickel ions are supposed to be tetrahedrally surrounded by oxygen ions. By adsorption of two oxygen atoms, the configuration of the nickel ion can become octahedral.

The reason why only [1,1,0] faces are considered is that nickel ions at these faces experience the largest "crystal-field stabilization" upon adsorption. These sites are therefore assumed to be preferentially occupied.

In this model photodesorption starts with an excitation of the nickel ion from its octahedral $^3A_{2g}$ state to the $^3T_{1g}$ level. It is further supposed that, besides by its normal relaxation processes, the nickel ion relaxes partially in another way, *viz.* by desorption of two oxygen ligands. The nickel ion thus returns to its tetrahedral coordination.

The excitation to $^3T_{1g}$ is considered effective, since the $^3T_{1g}$ orbits already possess the symmetry required for the tetrahedral ground state.

In our opinion this relaxation process is impossible, for the following reasons:

Firstly, it seems impossible to have a continuous transition from O_h to T_d symmetry during which the $^3T_{1g}$ wave function conserves its symmetry.

Secondly, the model fails to allow for charge transfer and valence changes of the nickel ion since neutral oxygen is desorbed. Finally, the tetrahedral ground state should be lower in energy than the octahedral $^3T_{1g}$ state. In other words, the difference between the two coordinations in the spherically symmetrical part of the crystal field potential should be small compared with the crystal field splitting energies of the ^3F octahedral ground term.

There is no *a priori* justification for this assumption, since the coordination number changes from six to four. As a consequence "crystal field stabilizations" might be small contributions to complex stabilities.

We conclude that photodesorption of oxygen from nickel oxide of the type discussed is not related to a *d–d* transition of nickel in an octahedral crystal field. The effects observed are presumably due to thermal effects.

In order to obtain the desired description of individual adsorption sites, a more complete method, i.e. a molecular orbital treatment, would seem required.

REFERENCES

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