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RELATION BETWEEN ELECTRICAL CONDUCTIVITY AND THERMAL DESORPTION SPECTRA FOR COBALT PHTHALOCYANINE-OXIDATIVE GAS SYSTEM

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In the thermal desorption spectra of β-CoPc-NO_2 system two peaks appeared. The first and second peaks were assigned to the desorption of the NO_2 on the pseudoaromatic rings and on the Co ions, respectively. The electrical conductance was enhanced mainly by the interaction of the pseudoaromatic ring with NO_2.

In the previous paper we have reported that the electrical conductivity of phthalocyanine thin films is very sensitive to oxidative gases and that the sensitivity of gas detection is in the order of $NO_2 > NO > O_2$[1]. Although several papers have been published concerning the gas adsorption on phthalocyanines,[2-4] adsorption states and binding energies have hardly been clarified. The present work aims at elucidating interaction between cobalt phthalocyanine(CoPc) and O_2, NO and NO_2 by means of a thermal desorption technique and electrical conductivity measurement.

Metal phthalocyanines were purified by sublimation under vacuum. For electrical measurements, cells of surface type were prepared by depositing polycrystalline phthalocyanines over glass substrates with two evaporated gold electrodes(0.05 cm in width and 200 μm in separation) on it. The α-phthalocyanine films thus prepared were converted into the polycrystalline film of β-form by heating to 300 °C for 20 min or more in N_2 atmosphere.[1] Thermal desorption spectra were obtained for β-phthalocyanine powder. After heat-treatment under evacuation β-phthalocyanine loaded in a sample tube exposed to O_2, NO or NO_2 gas(ca. 8×10^3 Pa) at elevated temperature followed by spontaneous cooling to room temperature(RT). After evacuating to ca. 4 Pa or below at room temperature the sample was then heated up to ca. 350 °C at constant rates under evacuation. Gas desorption was manifolded by use of a Pirani vacuum gauge and a quadrupole mass analyzer. In the latter case, a part of the desorbed gas was introduced into the analyzer through a capillary tube.

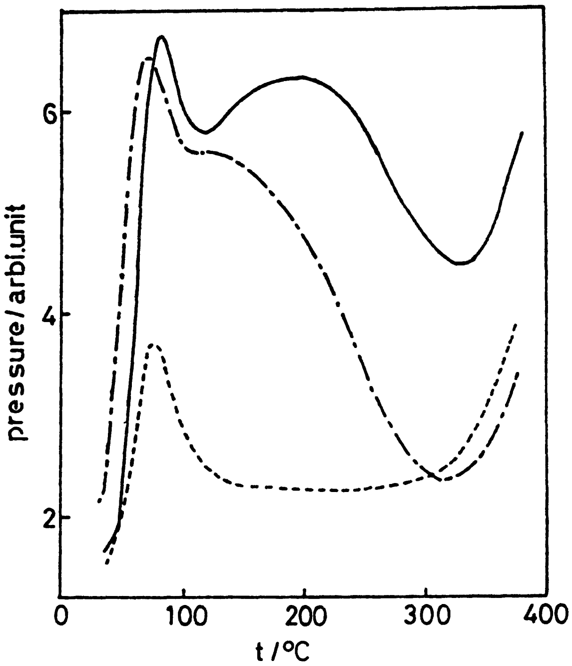

Fig.1 Desorption spectra of CoPc on which oxidative gas had been adsorbed
Heating rate; 10 °C/min.
Adsorbate:(——)NO_2,(-·-·)NO,(----)O_2.

The thermal desorption spectra of O_2, NO and NO_2 are shown in Fig. 1. The desorption of these gases were indicated by the appearance of peaks below 300 °C. The ascents above 300 °C, which appeared even without gas adsorption, were attributed to the thermal decomposition of phthalocyanine samples. As seen in the figure, the CoPc-O_2 system gives a single desorption peak in the temperature range 40-100 °C, while CoPc-NO and -NO_2 show desorption in two steps, the first at 50-100 °C and the second at 100-300 °C. The desorbed gas was subjected to mass analysis continuously. The change of the signal intensity of O_2, NO or NO_2 reproduced essentially the same spectra as above, though some minor complication occured in the CoPc-NO_2 system. In the CoPc-NO_2 systems, the mass spectra showed the presence of NO(m/e 30), the amount of which was larger than expected from the craking of NO_2. It is likely that a part of adsorbed NO_2 reacts with a trace of adsorbed H_2O to produce NO.

In the separate experiments, it was found that the thermal desorption of O_2, NO or NO_2 from CuPc and H_2Pc took place in a single desorption peak at 40-120 °C. This fact indicates that the desorption below 100 °C is common to any of the phthalocyanines, while the second desorption peak(above 100 °C) of NO or NO_2 is specific to CoPc. An estimation follows that the adsorbates responsible for the lower temperature desorption are adsorbed on the phthalocyanine ring while the NO or NO_2 adsorbed on Co ions is responsible for the second desorption peak. This estimation was supported from the measurements of the binding energy of adsorbates as well as from the measurements of electrical conductivity as described below.

Table I Values of binding energy Q

	Q/eV		
	O_2	NO	NO_2
CuPc	1.0_0	0.9_8	1.0_0
CoPc(first peak)	1.0_0	1.0_2	1.0_4
(second peak)		1.1_8	1.3_5

The binding energy was determined on the basis of the simple kinetic theory given by Brehmer et al.[5] who correlated the binding energy Q with the temperature T_m at d^2(desorption rate)/dt^2 = 0 under constant heating rate β(K/S) by the following equation

$$Q = kT_m(\ln T_m/\beta - 26.3) \qquad (1)$$

where k is the Boltzmann constant. The mean values of Q obtained under several heating rates are listed in Table I. The binding energies of O_2, NO and NO_2 obtained from the first peak for CoPc were almost the same as those for CuPc. These are also close to those reported for carotene-O_2[5] and activated carbon-NO_2[6]. In contract, binding energies of NO and NO_2 corresponding to the second peak are considerably larger than the above values: Q is larger for NO_2 than for NO, in agreement with the order of the electron affinities of the gases ($NO_2 > NO > O_2$).

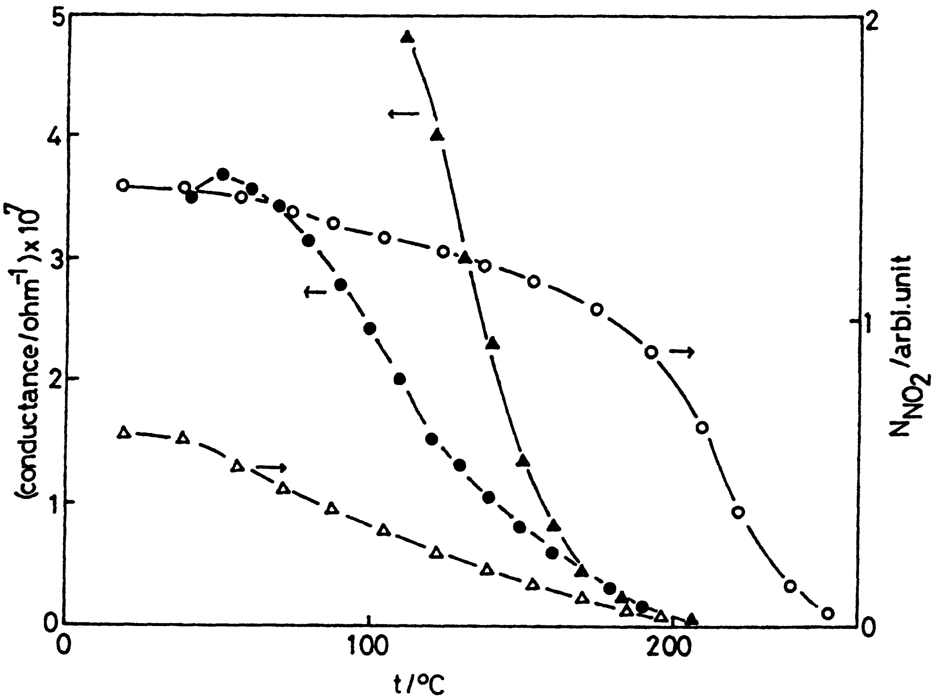

Fig. 2 Temperature dependence of electrical conductance and the amount* of residual NO_2(in arbitrary unit)on phthalocyanines Heating rate; 10 °C/min, (△,▲)CuPc,(○,●)CoPc.

* The amount of residual NO_2 were calculated by means of integration of pressure between 300 °C and the corresponding temperature.

The phthalocyanine films were preadsorbed with the gases in the same way as above and were subjected to the electrical measurement during the gas desorption. The results for CoPc and CuPc films are shown in Fig. 2. At room temperature, the electrical conductance of the films exposed to NO_2 is larger than that of the films unexposed or exposed to NO or O_2 by a factor of 10^3 or more. With raising temperature at a constant rate, the electrical conductance decreased rapidly becoming very low at 200 °C. Apparently the decreases in conductance resulted from the thermal desorption of NO_2. The amounts of residual gas on the films were estimated from the desorption spectra and plotted in the same figures. The comparison of the behaviour of electric conductance and the amount of residual gas shows that the rapid decrease in electrical conductance for CoPc-NO_2 is associated with the NO_2 desorption at lower temperature(first desorption peak). This is consistent with that the electrical conductance of CuPc film decreases in the same temperature. It follows that the electrical conductance increases when NO_2 adsorbs on the pseudoaromatic ring of the phthalocyanines, while the NO_2 adsorption on Co ion does not affect the conductance. In addition, the enhancement of electrical conductance by the NO_2 adsorption is in the order of CuPc $>$ CoPc, which is in agreement with the order of facility of ligand oxidation of phthalocyanines.[7]

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