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XPS Studies of Nitrosyl Metal (Fe, Co, and Mn) Phthalocyanines

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Interest in the chemistry of nitrosyl compounds of transition metal [1] has recently been amplified in connection with the catalytic elimination of NO_x from exhausted gas. The coordination of NO to transition metals to form nitrosyl compounds can be regarded as a model of non-dissociative chemisorption of NO molecule to the surface of catalyst, in which the nature of the bonding is often ambiguous because of the complex properties of the surface, *i.e.*, structure, composition, *etc.* In this letter we will report on the bonding between NO and the central metal in some nitrosyl metal phthalocyanines [2] as revealed by X-ray photoelectron spectroscopy (XPS). The following properties of nitrosyl metal phthalocyanines make them especially interesting as a model system for NO chemisorption on catalysts. The coordination of NO to the central metal is considered to cause no appreciable changes in the phthalocyanine skeleton, so that we can concentrate our attention onto the electronic state of the metal–NO system and its changes upon the formation of nitrosyl complex. The chemical state of oxygen in the nitrosyl groups will manifest itself in the oxygen XPS spectrum without interference from the other oxygen species which often causes the analysis of oxygen spectra to be difficult with the nitrosyl complexes containing oxygen in the ligands other than nitrosyl groups and with NO chemisorbed on metal oxides. Finally, but not of the least importance, some metal phthalocyanines have recently been demonstrated to be active in the catalytic reduction of NO [3], which renders them interesting more than as a mere model system.

Metal phthalocyanines (M-Pc's) were synthesized according to the known procedures [4], and were purified by sublimation. Samples of NO·M-Pc for XPS measurements were prepared as follows: M-Pc was sublimed onto an aluminum plate, then the sublimed M-Pc was brought into contact with nitrogen oxide (~20 cmHg) for more than 30 hours at room temperature. After nitrogen oxide was removed, the NO coordinated M-Pc was loaded into the sample chamber of XPS without contact of air by use of a nitrogen dry box. The binding energies of XPS peaks were determined by taking Au $4f_{7/2}$ = 83.7 eV. The changes in the XPS peak intensities (especially O 1s for NO) were not observed during the measurements, which shows that the nitrosyl complexes are stable during the XPS measurements.

The Fe 2p and 3s XPS spectra of Fe-Pc·NO and Fe-Pc are shown in Fig. 1. The binding energies of Fe $2p_{3/2}$ shifted from 708.4 eV for Fe-Pc to 709.7 eV for Fe-Pc·NO. The shift corresponds to the change from ferrous to ferric state [5]. The significant changes of full width at half maximum (FWHM) of Fe $2p_{3/2}$ peak and of the shape of Fe 3s spectrum were also observed. By coordination of NO to Fe-Pc, Fe $2p_{3/2}$ peak was sharpened, and the intensity of the high binding energy shoulder of Fe 3s peak was reduced to make the line shape more symmetric. These changes in Fe $2p_{3/2}$ and 3s spectra are considered to be due to the decrease of spin magnetic moment from S = 1 (Fe^{2+}) in Fe-Pc to S = 1/2 (Fe^{3+}) in Fe-Pc·NO [6]. The resulting decrease in the exchange splitting brings about the observed changes in the 2p and 3s spectra. With Co-Pc, similar results indicating the increase in the valence of Co from Co^{2+} (S = 1/2) in Co-Pc to Co^{3+} (S = 0) in Co-Pc·NO were obtained, although the changes in Co 2p and Co 3s peaks were not so distinct as in the case of Fe-Pc mentioned above. Accordingly, the electron transfer from Fe or Co to NO is suggested to occur upon the formation of the nitrosyl complex.

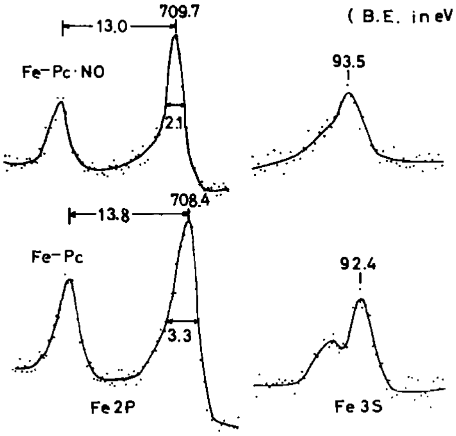

Fig. 1. Fe 2P and 3S XPS spectra of Fe-Pc and Fe-Pc·NO.

The Mn 2p and 3s XPS spectra of Mn-Pc·NO and Mn-Pc are shown in Fig. 2. In this case also it is considered that the magnetic moment of electron spins in Mn decreased by the coordination of NO to Mn-Pc, judging from the FWHM's of Mn $2p_{3/2}$ and the shape of Mn 3s peak. The binding energy of Mn $2p_{3/2}$ shifted to lower energy, whereas the main peak of Mn 3s shifted to the reverse direction apparently. However, when we take the center of gravity of multiplet splitting components, we see the "real" chemical shift of Mn 3s is in the same direc-

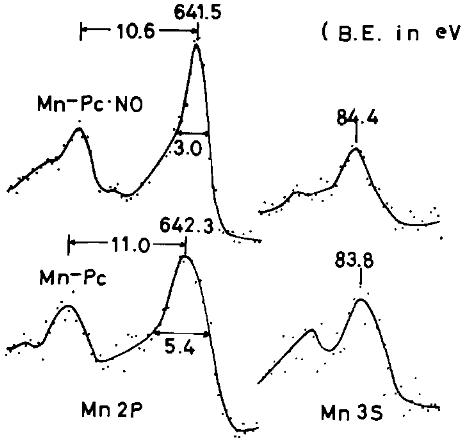

Fig. 2. Mn 2P and 3S XPS spectra of Mn-Pc and Mn-Pc·NO.

tion as that of Mn 2p$_{3/2}$. The chemical shift indicates the net electron transfer from NO to Mn.

Infrared absorption bands due to NO stretching vibration, ν_{NO}, in M-Pc·NO were observed at 1689, 1698, and 1737 cm^{-1} for Fe-, Co-, and Mn-Pc·NO respectively [7]. The trend of the frequency shift is similar to the NO complexes of metal tetraphenylporphine (M-TPP), *i.e.*, 1670, 1689, and 1760 cm^{-1} for Fe- [8], Co- [9], and Mn-TPP·NO [10] respectively. In both cases, ν_{NO}'s for Mn-NO complexes are higher than those for Fe- and Co-NO compounds. Accordingly we assume the M-NO configuration of the M-Pc·NO's to be the same as that of the M-TPP NO's. Then Mn–NO should have linear configuration, while Fe– and Co–NO have the bent configuration [8, 9, 11, 12]. Since the electronic configuration of M^-NO^+ is assigned for the former and that of M^+NO^- for the latter, the observed shifts in the binding energies of metal 2p and 3s spectra are qualitatively consistent with the assumed M-NO configurations.

The binding energies of O 1s for Fe-, Co-, and Mn-Pc·NO were 533.5, 533.6, and 532.7 eV, respectively. The lower binding energy in Mn-Pc·NO is not simply connected with the total electron densities of NO in Mn-Pc·NO, which should be smaller then that in Fe- or Co-Pc·NO according to the above consideration. The more elaborate consideration of the bonding in the nitrosyl complexes as well as the effect of geometry seem to be required. The N 1s peak of Fe-Pc·NO appeared at 398.7 and 400.7 eV. The former agrees with N 1s of Fe-Pc. The latter, appearing as a shoulder, is assigned to the N 1s of NO. As for Co- and Mn-Pc·NO, the shoulder peaks of N 1s of NO were not clearly observed unfortunately, owing to the complex satellite peaks of N 1s of M-Pc's around 400 eV. Although the detailed nature of the metal–NO bonding in M-Pc·NO is still an open question, the above results demonstrate that the XPS offers useful information about the problem.

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7 ν_{NO}'s for sublimed Fe-, Co-, and Mn-Pc in contact with NO were reported as 1685, 1705, and 1763 cm^{-1} respectively by Ercolani *et al.* [2b]. The trend of the frequency shifts is identical with ours, however the frequency on Mn-Pc·NO gives different values. The difference will be considered to be due to the conditions for sublimation.

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