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ACTIVE SPECIES FOR THE FORMATION OF ETHYLCHLORIDE FROM ETHANOL ON POLY(4-VINYLPYRIDINE)-CHLORANIL EDA COMPLEX STUDIED BY MEANS OF X-RAY PHOTOELECTRON SPECTROSCOPY

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The effect of pretreatment on the reactivity of electron donor acceptor (EDA) complexes between poly(4-vinylpyridine) and chloranil was studied by means of X-ray photoelectron spectroscopy (XPS). The active species for the formation of ethylchloride from ethanol was revealed to be the negatively charged chlorine of chloranil in the EDA complex.

X-ray photoelectron spectroscopy (XPS) is an effective technique for studying electron donor acceptor (EDA) complexes formed between organic components, because it can give information on the charge distribution in the complex without destroying the sample. In this communication, we will report on the XPS studies of the marked effects of pretreatment on the reactivity of the EDA complexes between poly(4-vinylpyridine) (denote as 4-PVP hereafter) and chloranil.

4-PVP was prepared by polymerizing 4-vinylpyridine in a sealed tube, as reported previously.[1] Chloranil was purified by sublimation in vacuo. EDA complexes were prepared by mixing ethanol solution of 4-PVP and benzene solution of chloranil in the absence of air. It was found that trace of ethylchloride was formed during the preparation. After evaporating the solvent, the complex was washed with benzene repeatedly in the air and pretreated in the following two ways: (1) evacuated at room temperature (complex I), (2) evacuated at 140°C (complex II). Ethanol vapor was introduced onto the complexes at room temperature. It is interesting to note that complex I exhibited a marked reactivity with ethanol vapor to form ethylchloride readily. On the other hand, such reaction did not proceed at all on complex II; however, it exhibited a photocatalytic activity for oxidation of alcohols to form corresponding aldehydes and CO_2 and complex I did not have such a photocatalytic activity, which will be reported elsewhere in detail.$^{2)}$ It was confirmed separately that no reaction proceed between ethanol and chloranil under the similar conditions. The elemental analyses of these complexes gave the following compositions; for complex I, $C_{11}H_{14}N_1Cl_1O_4$, which is consistent with a 4:1 complex of the pyridine unit of 4-PVP and chloranil, for complex II, $C_9H_{11}N_1Cl_{0.6}O_2$, suggesting a 7:1 complex. The binding energies of photoelectrons appeared in the XPS were measured with a McPherson ESCA 36 electron spectrometer, which are summarized in the table. For calibrating the binding energies, Au 4f 7/2 (83.7eV) was used as a reference.

The XPS spectra of N1s for complex I gave two different values of binding energies; 398.4eV and 401.0eV, the former corresponding to that of 4-PVP (398.8eV) as is shown in the table. The latter peak can be assigned to a positively charged nitrogen of pyridinium cation in comparison with the binding energies of N1s of 4-PVP hydrochloride listed in the table. On the other hand, Cl2p also exhibited two peaks at binding energies of 196.5eV and 200.2eV, the latter corresponding to that of chloranil (200.2eV) itself.$^{3)}$ The former chlorine at 196.5eV can be due to a chloranil having a negative charge, comparing to the Cl2p peaks at binding energies of 196.9eV in 4-PVP-HCl. However, no absorption band due to a N-H streching was observed in the ir spectra of complex I. Consequently, the formation of N^+-Cl^- bond in complex I is most likely as has been demonstrated by Hercules et al. for pyridine-chloranil EDA complex.$^{4)}$ When gaseous ethanol was introduced onto

Table. Binding Energies of XPS Pesks for Complexes and Related Compounds.
(unit: eV)

	N1s	Cl2p	O1s	C1s
Complex I	401.0 398.4	200.2 196.5	531.2	284.4
Complex II		200.8	532.3	284.4
4-PVP	398.8			284.8
Chloranil$^{3)}$		200.2	531.5	287.7 286.1
4-PVP-HCl	400.8 398.6	196.9		284.5

complex I, ethylchloride was formed, which was confirmed by gas chromatography, ir and mass spectroscopy. The XPS spectra of the complex were examined after the reaction with ethanol. The figure shows the change in the intensity of the N1s and Cl2p peaks in the different runs. The relative intensity of the peaks of nitrogen at 401.0eV and chlorine at 196.5eV to that of the peaks at 398.4eV and 200.2eV respectively decreased gradually as the complex reacted with ethanol. At the fourth run, no ethylchloride was formed any more (1 run: about 4 hours). These results suggest that chlorine which has a negative charge in the complex reacts with ethanol to form ethylchloride, and correspondingly the pyridinium N is reduced to pyridine N. The Cl2p peaks at 196.5eV remained in XPS spectra although the complex had lost its reactivity to form ethylchloride. It is accordingly interpreted that the chloride anion present at the surface of the complex only contributed to the reaction and since the escape depth of photoelectron observed under this experimental condition is considered to be 40-100A,5) chlorine which can not contribute to the reaction was also observed.

On the other hand, when complex II was exposed to ethanol vapor, no ethylchloride was detected in the ambient gas. The XPS spectra of complex II as listed in the table gave only one Cl2p peaks at the binding energy same to that of chloranil (200.2eV). It is interesting to note that the complex II did not exhibit any peak corresponding to the chlorine with a nega-

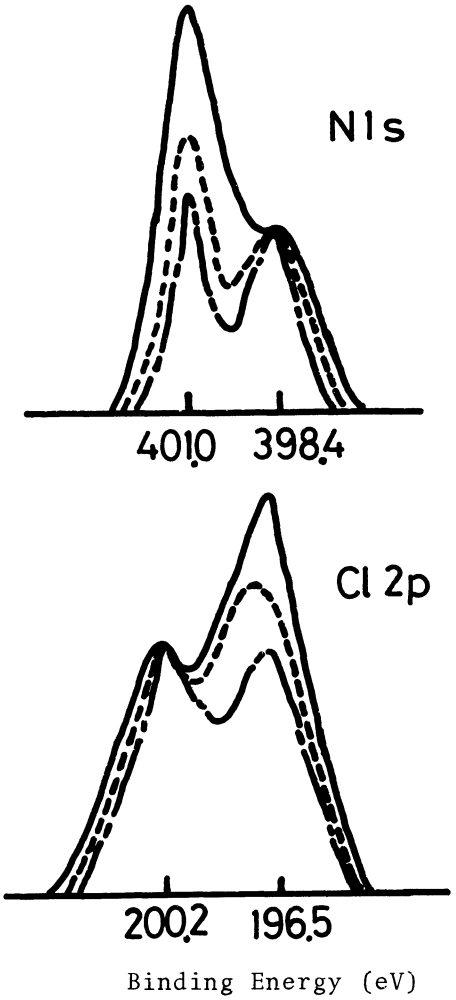

Figure. The change in the relative intensity of the N1s and Cl2p peaks of XPS spectra normalized by 398.4eV for N1s and 200.2eV for Cl2p as standards in the different runs. (before use ——; after 1st run - - - -; after 3rd run —·—·—)

tive charge, which is considered to be an active species for chlorination of ethanol. By the heat treatment at 140°C under vacuum, this anionic chlorine decreased, and the complex became active for the photocatalytic oxidation of ethanol, as mentioned above. The N1s peak was not detected in the XPS spectra of complex II during the whole experiments, although an absorption band due to pyridine ring was observed by infrared absorption measurements. Therefore, pyridine ring of complex II disappeared from the surface layers through the heat treatment at a rather high temperature.

In conclusion, the present report demonstrates that the surface reaction which takes place in the surface of organic EDA complex can be effectively studied by XPS technique and it is revealed that the surface compositions as well as the reactivity are markedly influenced by the heat treatment.

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