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X-RAY PHOTOELECTRON SPECTROSCOPIC STUDY OF THE SURFACE OF CARBON DOPED WITH POTASSIUM CARBONATE

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The X-ray photoelectron spectra of K and O peaks of the carbon impregnated with potassium carbonate were dramatically decreased by evacuation at 650 ℃. When oxygen was introduced onto this surface, remarkable growth of these peaks was observed at room temperature, however, in case of contact with carbon dioxide, temperature as high as 650 ℃ was required to cause the same effect. These results support the reaction mechanism of a redox cycle of catalyst for the reduction of carbon dioxide with carbon.

The gasification of carbon or coal is an urgent problem in the present age of an effective use of carbon resources. Alkali metal compounds have been known as good catalysts for the gasification of carbon, however, the detail of their catalytic action has not been elucidated. The reaction mechanism of carbon gasification proposed so far may be classified into two categories1), the electron-transfer mechanism2∼4) and oxygen-transfer mechanism5,6) but the decisive proof has not been available.

We have recently examined7) the reduction of carbon dioxide with carbon doped with alkali metal carbonates and have found that the activity is proportional to the amount of oxygen taken up during reaction irrespective of the sort of alkali metal.

In this paper, a direct evidence of a redox process of potassium oxide on carbon surface was obtained by XPS. Amorphous carbon of high pure grade with 10∿30 mesh (Kishida Chem. Co., Ltd.) was used. Ash impurity was less than 650 ppm. The sample containing 11.7 wt% of potassium carbonate was prepared by immersing carbon in an aqueous solution of the salt. The surface area measured by the BET method was 78.3 m^2/g. X-ray photoelectron spectra were taken with a VG ESCA-3 Photoelectron Spectrometer using Al Kα (1486.6 eV) radiation. Samples were mounted on gold mesh net attached to the sample holder. Spectra were observed at room temperature after the samples were pre-treated in the chamber. The electron binding energies of respective photoelectron peaks were calibrated with reference to C 1s (283 eV) of bulk carbon. Figure 1 shows the X-ray photoelectron spectra of C, K and O of the sample.

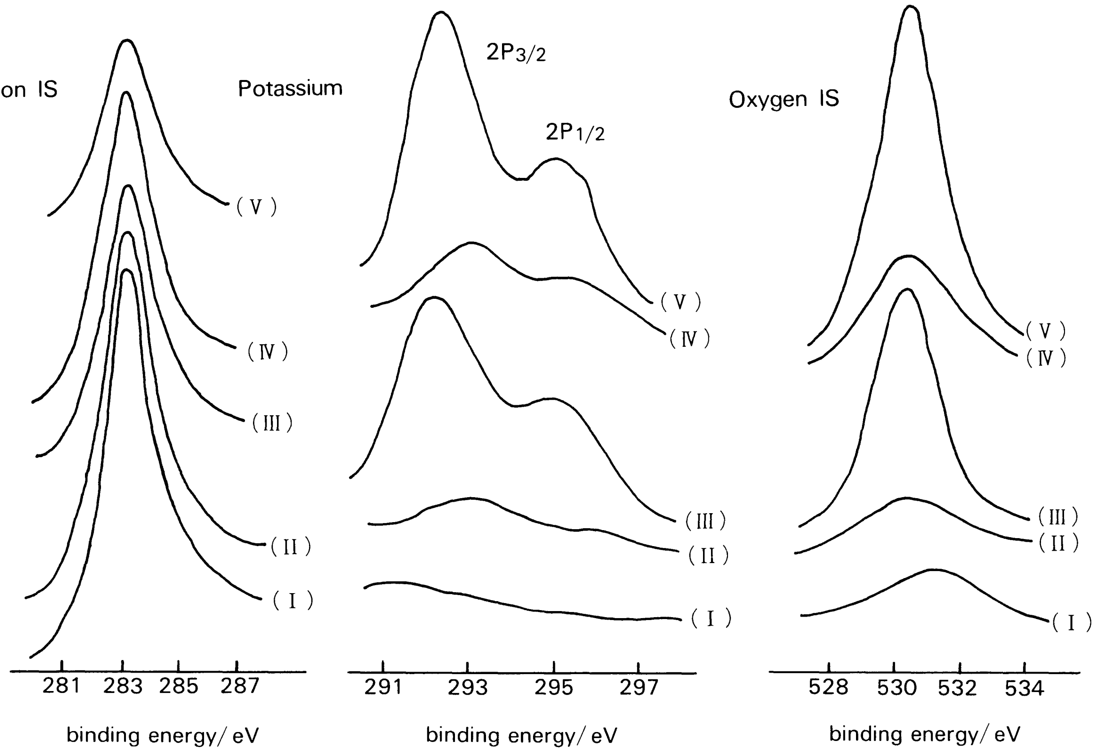

Fig. 1 Carbon (1s), potassium ($2p_{3/2}$, $2p_{1/2}$) and oxygen (1s) XPS spectra. (I) untreated K_2CO_3 11.7 wt%-carbon, (II) after evacuation at 650 ℃ for 2 h, (III) after contact with CO_2 of 0.4 torr at 650 ℃ for 30 min during which about 10 % of CO_2 was converted to CO, (IV) after additional evacuation at 650 ℃ for 2 h, and (V) after the same treatment as (III).

It is clear from the Figure that the peaks of potassium and oxygen decreased dramatically by evacuation at 650 ℃ and repeatedly recovered by the contact with CO_2 at the same temperature. Accompanying with the decrease of peak intensities of K and O, the peak of K was shifted to higher energies by ca. 1 eV[8], suggesting the change of state of K and O. By evacuation of carbon doped with potassium carbonate at 650 ℃, a part of potassium carbonate was decomposed to K_2O and CO_2[9]. The present results with XPS may be consistently explained with the kinetical finding described above. Potassium oxide formed by the decomposition of K_2CO_3 is reduced by carbon to potassium, and sinks into bulk carbon. The growth of peaks of K and O by the contact with CO_2 can be attributed to the accumulation on the surface of K_2O formed by the oxidation of potassium embedded in bulk carbon.

If this mechanism is correct, the growth of the K peak is expected to be more efficient by the use of O_2 instead of CO_2. Figure 2 shows the change of X-ray photoelectron spectra caused by the contact with O_2 at room temperature.

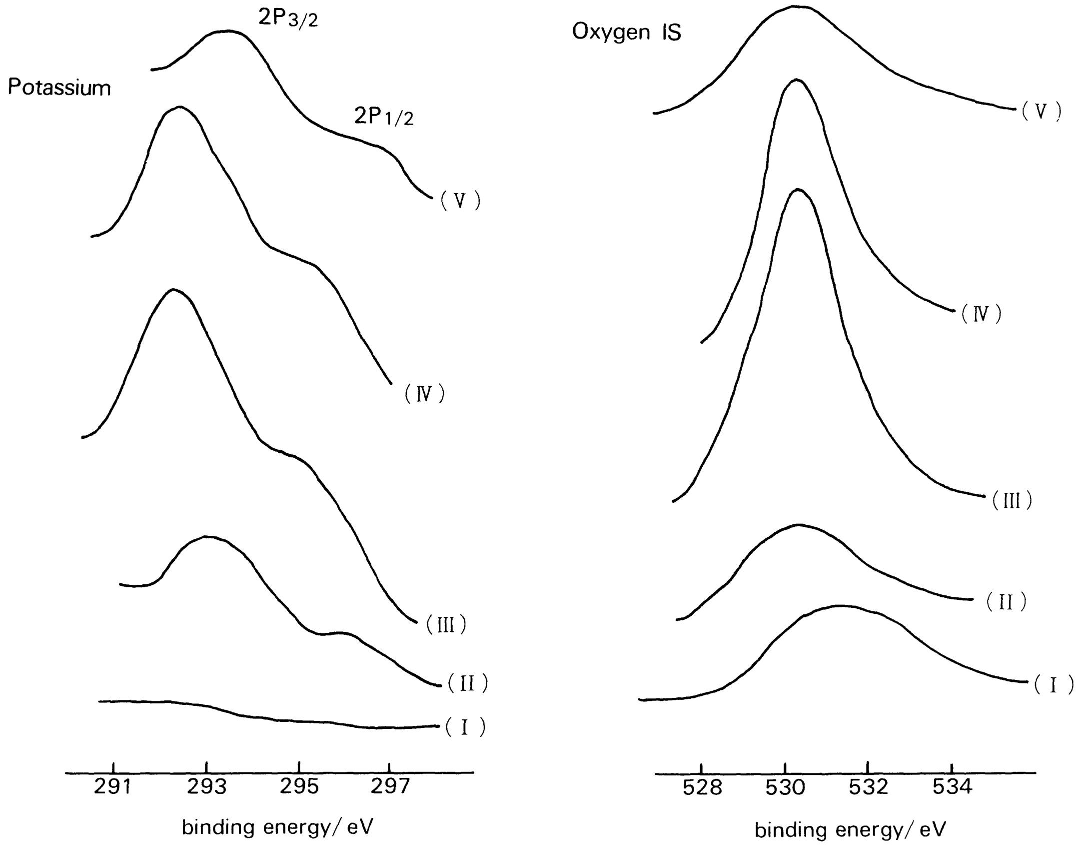

Fig. 2 Potassium ($2p_{3/2}$, $2p_{1/2}$) and oxygen (1s) XPS spectra.
(I) untreated K_2CO_3 11.7 wt%-carbon, (II) after evacuation at 650 ℃ for 2 h, (III) after contact with O_2 of 0.4 torr at room temperature for 30 min, (IV) after evacuation at 450 ℃, and (V) after evacuation at 650 ℃.

As being expected, potassium peak grew up markedly by the contact with O_2 even at room temperature and almost recovered by evacuation at 650 ℃. These changes of X-ray photoelectron spectra may be described, in conclusion, as

$$K_2O + C = 2K + CO$$

$$2K + CO_2 = K_2O + CO$$

Evacuation at temperatures higher than 650 ℃ is required to form potassium oxide in the case of CO_2, while room temperature is enough to form potassium oxide by the use of O_2. Promoting effect of potassium salts for the oxidation of carbon is, thus, responsible to the reaction of carbon with K_2O.

References and note

1) P.L. Walker, Chemistry and Physics of Carbon, 4, 287 (1968).
2) H.S. Taylor and H.A. Neville, J. Am. Chem. Soc., 43, 2055 (1921).
3) H. Harker, Proc. 4 th. Conf. Carbon, Pergamon Press, London (1960).
4) F.G. Long and K.W. Sykes, J. Chim. Phys., 47, 361 (1950).
5) D.A. Fox and A.H. White, Ind. Eng. Chem., 23, 259 (1931).
6) D.W. Mckee and D. Chatterji, Carbon, 13, 381 (1975).
7) S. Yokoyama, K. Miyahara, K. Tanaka, I. Takakuwa and J. Tashiro, Fuel, 58, 510 (1979).

8) Contrary to the general tendency that the binding energy of metal oxides is higher than that of metal, the reverse was found in this case, though the interpretation remains unknown.
9) This finding was obtained by using potassium carbonate labelled with carbon-13, and will be reported elsewhere.

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