CHARACTERIZATION OF THE SURFACES OF PHOSPHATES BY XPS

AKIO TADA, MOTOI TAKAHASHI, AND NORIYASU OKAZAKI

Department of Applied and Environmental Chemistry, Kitami Institute of Technology,
Kitami, Hokkaido, 090-8507 Japan

Abstract Surface characterization of AlPO_4 and BPO_4 was carried out by XPS. The followings were verified. The surface acid-base property of amorphous AlPO_4 was similar to that of $\text{Al}_2(\text{SO}_4)_3$ but it was different from that of Al_2O_3 . The amount of basic sites of amorphous AlPO_4 was less than that of Al_2O_3 , and the phosphorus and oxygen of amorphous AlPO_4 surface partly desorbed when it was heat-treated in a vacuo. In addition, it was clarified that unreacted H_3BO_3 or its condensation compound, and P_2O_5 -like phosphorus compounds remained on the surface of BPO_4 as minor components.

INTRODUCTION

In the case of surface functional solid materials such as adsorbent, catalyst, etc., it is necessary to evaluate the composition and chemical state of the surface compounds. Though X-ray photoelectron spectroscopy (XPS) is an effective tool for the above evaluation, there are a few studies on the surface characterization of phosphates by XPS¹. Here, AlPO_4 and BPO_4 were employed as phosphate samples and the composition and chemical state of the surface compounds were studied, because AlPO_4 is used widely as a solid acid catalyst², a catalyst support³, etc., and BPO_4 is investigated as a promising solid acid catalyst for olefin oligomerization⁴, olefin skeletal isomerisation⁵, etc⁶.

EXPERIMENTAL

Samples

AlPO_4

Cristobalite type AlPO_4 ⁷ was prepared by dehydrating $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ (APO-1)⁷ in an organic solvent followed by drying the precipitate and calcining the dried product. Amorphous AlPO_4 ⁸ was prepared as follows. An aqueous solution containing an equimolar mixture of aluminum nitrate and phosphoric acid was neutralized with aqueous ammonia,

and then the precipitate was dried and calcined.

BPO₄

A BPO₄ sample was prepared from a equimolar mixture of boric acid and phosphoric acid by the method described elsewhere⁹. Prior to use, it was calcined at 500 °C for 2 h in air.

XPS measurement

XPS analysis was performed with a Rigaku Denki XPS-7000 spectrometer, using a MgK α or AlK α X-ray source operated at 10 kV and 30 mA¹. Binding energy values (BE) were corrected by using the value of 285.0 eV for the C1s level of the contaminated carbon. The reproducibilities of the BE values thus obtained were within ± 0.2 eV.

RESULTS AND DISCUSSION

AlPO₄

AlPO₄, Al₂(SO₄)₃, Al₂O₃

Table 1 shows the results of XPS measurements of three solid acids, AlPO₄, Al₂(SO₄)₃, and Al₂O₃. The BE of Al of AlPO₄ was nearly equal to that of Al₂(SO₄)₃ but was higher than that of Al₂O₃. This suggests that the Al of AlPO₄ is more abunding in positive charge than that of Al₂O₃. And, the BE of O of AlPO₄ is approximate to that of Al₂(SO₄)₃ but is higher than that of Al₂O₃, suggesting that the electron density of O of AlPO₄ is lower than that of Al₂O₃. Such BE data predict that Al of Al-O-P linkage of AlPO₄ will exhibit Lewis acidity by having electron withdrawing power. As the result, the electron density of O of the Al-O-P linkage will decrease, and the surface basicity of AlPO₄ will be weakened by the effect. These predictions agreed with the experimental results (not shown). In addition, the surface acid-base property of AlPO₄ is approximate to that of Al₂(SO₄)₃, and it differs in the point with its small base amount from Al₂O₃. These predictions do not contradict known facts that Al₂O₃ has basic sites, but neither Al₂(SO₄)₃ or AlPO₄ has basic sites.

TABLE 1 The results of XPS measurements of AlPO₄, Al₂(SO₄)₃, and Al₂O₃

Sample	B.E. / eV	
	Al2p	O1s
AlPO ₄	75.4 - 75.8	532.6 - 533.1
Al ₂ (SO ₄) ₃		
300 °C (in air)	75.9	532.8
800 °C (in air)	75.5	533.0
Al ₂ O ₃	74.6	531.4

Cristobalite type AlPO₄ and amorphous AlPO₄

Table 2 shows the results of examining the effects of crystallinity of AlPO₄ on the XPS BE values and surface elemental composition of Al, O, and P of AlPO₄. The BE values of the Al, O, and P of cristobalite type AlPO₄ are not almost different from those of amorphous AlPO₄. It is noticed that the composition of P and O of amorphous AlPO₄ were lower than those of cristobalite type AlPO₄ when heated in vacuo at 400, 750, or 1000 °C. This seems to be due to the elimination of P and O as a phosphorus oxide from the amorphous AlPO₄ because of its thermal instability during high-temperature evacuation processing. Amorphous AlPO₄ evacuated at high temperatures is a good catalyst for olefin geometrical isomerisation, while cristobalite type AlPO₄ has no activity for the reaction even if it was evacuated at high temperatures. Such a difference could be explained by the easiness of P and O (as P₂O₅) elimination from the amorphous AlPO₄.

TABLE 2 The effect of crystallinity of AlPO₄ on XPS BE values and surface elemental composition of AlPO₄

Crystallinity of AlPO ₄	Evac temp. / °C	B.E. / eV			Surface elemental composition		
		Al2p	P2p	O1s	Al	P	O
Cristobalite	400	75.4	134.9	532.7	1	1.17	5.29
	750	75.6	135.0	532.8	1	1.18	5.30
Amorphous	400	75.4	134.9	532.7	1	1.10	5.08
	750	75.6	135.0	532.8	1	1.09	5.11

BPO₄

As shown in Fig. 1, P2p peak (135.0-135.4 eV) of the BPO₄ sample was located in high energy side than that of AlPO₄ (134.9 eV). XRD analysis indicates that BPO₄ sample is mainly composed of crystalline BPO₄. There is, however, no literature data of BE of the P2p peak of BPO₄. If the BPO₄ sample is isomorphic with AlPO₄, if it consists only of pure crystalline BPO₄, and if the electronegativity of B is higher than Al, it can be understood that P2p peak (135.0-135.4 eV) of the BPO₄ sample is located in higher energy side than AlPO₄ P2p peak (134.9 eV). But it is difficult to

FIGURE 1 XPS P2p spectra of BPO₄ and AlPO₄.

consider that the electronegativity of B is higher than that of Al, because B is a metalloid. Therefore, the fact that P2*p* peak (135.0-135.4 eV) of the BPO₄ sample is located in higher energy side than P2*p* peak (134.9 eV) of AlPO₄ suggests that some materials except for crystalline BPO₄ exist on the surface of the BPO₄ sample. Therefore, the deconvolution of BPO₄ P2*p* peak was carried out by assuming that it agrees with AlPO₄ P2*p* peak (Fig. 1). As the result, the other peak appeared in the higher energy side than that of BPO₄ P2*p* peak. This new peak (BE = 136.0 eV) seems to be assigned to a phosphorus compound like P₂O₅ judging from the literature¹⁰.

As seen in Fig. 2, O1*s* peak (BE = 533.0-533.3 eV) of the BPO₄ sample was located to the higher energy side than AlPO₄ O1*s* peak (BE = 532.7-533.1 eV). The result of the deconvolution of BPO₄ O1*s* peak by assuming that it agrees with AlPO₄ O1*s* peak suggested that there is the other peak in the higher energy side than that of BPO₄ O1*s* peak (Fig. 2). It agreed with that of H₃BO₃ or B₂O₃ O1*s* peak. This fact indicates the existence of H₃BO₃ or B₂O₃ on the surface.

In the XPS wide scan spectrum of BPO₄ (Fig. 3), there were three peaks, O1*s* peak, P2*p* peak, and the third peak in which B1*s* peak overlapped with P2*s* peak. Previously, we supposed that the peak having lower binding energy of the two peaks obtained by carrying out the deconvolution of the B1*s* peak would be due to B of BPO₄ without examining the BPO₄ XPS wide scan spectrum¹. As mentioned above, however, it has been proved that B1*s* peak overlapped with P2*s* peak. Therefore it is necessary to discuss the assignment of the peak in the

FIGURE 2 XPS O1*s* spectra of H₃BO₃, BPO₄, and AlPO₄.

FIGURE 3 XPS wide scan spectrum of BPO₄.

lower energy side in detail. It was anticipated that the B1s peak of BPO₄ would be located in higher energy side than the B1s peak of H₃BO₃ or B₂O₃, because the binding energy of Al of AlPO₄ was higher than that of Al₂O₃. But the peak was not found in the vicinity (Fig. 4). This fact indicates that BPO₄ B1s peak agrees with B1s peak of H₃BO₃ or B₂O₃. Then, by assuming that B1s peak of BPO₄ agrees with that of H₃BO₃ or B₂O₃, the deconvolution of BPO₄ B1s peak was carried out. As the result, the other peak appeared in the low energy side and it agreed with AlPO₄ P2s peak (Fig. 5). Therefore it was attributed to BPO₄ P2s peak. Reversely, when the existence of AlPO₄ P2s peak (or BPO₄ P2s) is assumed, the peak which agreed with B1s peak (or BPO₄ B1s) of H₃BO₃ or B₂O₃ appears in the higher energy side as the result of carrying out the deconvolution of BPO₄ B1s peak. This means that BPO₄ B1s peak agrees with B1s peak of H₃BO₃ or B₂O₃.

The above results indicate that the peak in lower energy side of the B1s peak (2 peaks) of the BPO₄ sample can be attributable to B1s peak but to P2s peak of BPO₄ and that the phosphorus compound like P₂O₅ and unreacted H₃BO₃ or its condensation compound exist on BPO₄ surface.

CONCLUSION

1) The surface acid-base property of AlPO₄ is approximate to that of Al₂(SO₄)₃, and it is different in the point with smaller base amount from that of Al₂O₃.

2) When amorphous AlPO₄ is heat-treated in vacuo, the phosphorus and oxygen of its

FIGURE 4 XPS B1s spectra of B₂O₃, H₃BO₃, and BPO₄.

FIGURE 5 XPS P2s spectra of AlPO₄ and B1s spectra of BPO₄.

surface desorbs.

3) Unreacted H_3BO_3 or its condensation compound and phosphorus compound like P_2O_5 exist on BPO_4 surface.

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