CHARACTERIZATION OF THE SURFACES OF PHOSPHATES BY XPS

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Abstract Surface characterization of AlPO₄ and BPO₄ was carried out by XPS. The followings were verified. The surface acid-base property of amorphous AlPO₄ was similar to that of Al₂(SO₄)₃ but it was different from that of Al₂O₃. The amount of basic sites of amorphous AlPO₄ was less than that of Al₂O₃, and the phosphorus and oxygen of amorphous AlPO₄ surface partly desorbed when it was heat-treated in a vacuo. In addition, it was clarified that unreacted H₃BO₃ or its condensation compound, and P₂O₅-like phosphorus compounds remained on the surface of BPO₄ 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, AlPO₄ and BPO₄ were employed as phosphate samples and the composition and chemical state of the surface compounds were studied, because AlPO₄ is used widely as a solid acid catalyst², a catalyst support³, etc., and BPO₄ is investigated as a promising solid acid catalyst for olefin oligomerization⁴, olefin skeletal isomerisation⁵, etc⁶.

EXPERIMENTAL

Samples
AlPO₄
Cristobalite type AlPO₄⁷ was prepared by dehydrating AlPO₄·2H₂O (APO-1)⁷ in an organic solvent followed by drying the precipitate and calcining the dried product. Amorphous AlPO₄⁸ 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.

$BPO_4$

A $BPO_4$ sample was prepared from an equimolar mixture of boric acid and phosphoric acid by the method described elsewhere\textsuperscript{9}. 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 Mg$K\alpha$ or Al$K\alpha$ X-ray source operated at 10 kV and 30 mA\textsuperscript{1}. 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**

$AlPO_4$

$AlPO_4$, $Al_2(SO_4)_3$, $Al_2O_3$

Table 1 shows the results of XPS measurements of three solid acids, $AlPO_4$, $Al_2(SO_4)_3$, and $Al_2O_3$. The BE of Al of $AlPO_4$ was nearly equal to that of $Al_2(SO_4)_3$ but was higher than that of $Al_2O_3$. This suggests that the Al of $AlPO_4$ is more abounding in positive charge than that of $Al_2O_3$. And, the BE of O of $AlPO_4$ is approximate to that of $Al_2(SO_4)_3$ but is higher than that of $Al_2O_3$, suggesting that the electron density of O of $AlPO_4$ is lower than that of $Al_2O_3$. Such BE data predict that Al of Al-O-P linkage of $AlPO_4$ 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 $AlPO_4$ will be weakened by the effect. These predictions agreed with the experimental results (not shown). In addition, the surface acid-base property of $AlPO_4$ is approximate to that of $Al_2(SO_4)_3$, and it differs in the point with its small base amount from $Al_2O_3$. These predictions do not contradict known facts that $Al_2O_3$ has basic sites, but neither $Al_2(SO_4)_3$ or $AlPO_4$ has basic sites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>B.E. / eV</th>
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<tbody>
<tr>
<td></td>
<td>Al2p</td>
</tr>
<tr>
<td>$AlPO_4$</td>
<td>75.4 - 75.8</td>
</tr>
<tr>
<td>$Al_2(SO_4)_3$</td>
<td>75.9</td>
</tr>
<tr>
<td>$300 \text{ °C} (\text{ in air})$</td>
<td>75.5</td>
</tr>
<tr>
<td>$800 \text{ °C} (\text{ in air})$</td>
<td>74.6</td>
</tr>
<tr>
<td>$Al_2O_3$</td>
<td></td>
</tr>
</tbody>
</table>

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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>
<thead>
<tr>
<th>Crystallinity of AlPO₄</th>
<th>Evac temp. / °C</th>
<th>B.E. / eV</th>
<th>Surface elemental composition</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Al2p</td>
<td>P2p</td>
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<tr>
<td>Cristobalite</td>
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<td>75.4</td>
<td>134.9</td>
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<td></td>
<td>750</td>
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<tr>
<td></td>
<td>750</td>
<td>75.6</td>
<td>135.0</td>
</tr>
</tbody>
</table>

**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

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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 P2p peak (135.0-135.4 eV) of the BPO4 sample is located in higher energy side than P2p 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 P2p peak was carried out by assuming that it agrees with AlPO4 P2p peak (Fig. 1). As the result, the other peak appeared in the higher energy side than that of BPO4 P2p 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, O1s peak (BE = 533.0-533.3 eV) of the BPO4 sample was located to the higher energy side than AlPO4 O1s peak (BE = 532.7-533.1 eV). The result of the deconvolution of BPO4 O1s peak by assuming that it agrees with AlPO4 O1s peak suggested that there is the other peak in the higher energy side than that of BPO4 O1s peak (Fig. 2). It agreed with that of H3BO3 or B2O3 O1s 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, O1s peak, P2p peak, and the third peak in which B1s peak overlapped with P2s peak. Previously, we supposed that the peak having lower binding energy of the two peaks obtained by carrying out the deconvolution of the B1s 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 B1s peak overlapped with P2s peak. Therefore it is necessary to discuss the assignment of the peak in the

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FIGURE 2 XPS O1s 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 is 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
surface desorbs.

3) Unreacted $\text{H}_3\text{BO}_3$ or its condensation compound and phosphorus compound like $\text{P}_2\text{O}_5$ exist on $\text{BPO}_4$ surface.

REFERENCES