Adsorption Property of Water Vapor on AlPO₄-5 Synthesized from Aluminum Dross

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The aluminophosphate type zeolitic material, AlPO₄-5 was synthesized by hydrothermal method using aluminum dross as a raw material, and its water vapor adsorption property was studied. Porous AlPO₄-5 and nonporous AlPO₄ were formed, and the selectivity of their formation was determined by varying the reactant ratios. Both AlPO₄-5 and tridymite type AlPO₄ (nonporous phosphate) were obtained from aluminum dross when the reaction products were synthesized with the following composition, Al₂O₃ : P₂O₅ : triethylamine (TEA) : H₂O = 1 : 1 : 1 : 4₀. While AlPO₄-5 was preferentially synthesized as a main product when the compositions were Al₂O₃ : P₂O₅ : TEA : H₂O = 2 : 1 : 1 : 4₀ and 1 : 1 : 2 : 4₀. The variation in the reactant ratio dictated the specific surface area of the resulting reaction products. The formation of AlPO₄-5 with a composition of 1 : 1 : 2 : 4₀ generated surface area of 353 m²/g. The reaction products synthesized at 2 : 1 : 1 : 4₀ and 1 : 1 : 1 : 4₀ generated surface areas of 187 and 75 m²/g, respectively. All the aluminophosphate products exhibited the type IV or V isotherm by IUPAC classification for water vapor adsorption due to the AlPO₄-5 pore with strong affinity. This study demonstrated the efficacy of AlPO₄-5 obtained from aluminum dross as desiccant, that is, the aluminum dross-derived AlPO₄-5 demonstrated high adsorption capacity and adsorption properties suitable as an adsorbent or a desiccant. [doi:10.2320/matertrans.M-M2013831]

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1. Introduction

Aluminum dross is a hazardous by-product that is generated in primary aluminum smelters and recycling processes. About 5 million tons of aluminum dross is generated annually all over the world.¹ Generally, the main components of dross are metallic aluminum, aluminum oxide, its chloride or nitride.²⁻³ Aluminum dross is mainly recycled as a deoxidizer in steel-manufacturing processes in Japan, but its demand is limited. Finally, large amount of aluminum dross that cannot be recycled for various reasons including economic issues, discard of quality and quantity with the requirements for existing recycling methods, and the presence of harmful impurities, are disposed of in landfills. This practice is of significant concern. The metallic aluminum (Al) and/or aluminum nitride (AIN) components of dross are considered to be hazardous, when disposed of in landfills because of their potential to initiate spontaneous combustion and to generate harmful gas including H₂ and NH₃. These reasons have motivated the push for developments of more effective disposal and recycling technologies for aluminum dross.¹⁻⁴

Wilson first reported the synthesis of a series of porous aluminophosphate type zeolitic materials (AlPO₄-n, n: number). These functional zeolitic materials have an uniform pore distribution based on the crystal framework structure.⁵ Further studies have revealed the application of AlPO₄-n as molecular sieve, catalyst support and adsorbent.⁶⁻⁸ In spite of the unique properties of AlPO₄-n, its commercial use has been limited, mainly due to its production cost. The use of mineral processing residues in the synthesis of AlPO₄-n may provide a lower cost option for manufacturing this kind of zeolitic materials. We have reported, for the first time, the use of recycled aluminum dross in the synthesis of AlPO₄-5 by a hydrothermal method.² We have further revealed the effect of structure-directing agent on the formation behavior of AlPO₄-n from the aluminum dross.¹⁰

Aluminophosphate type zeolitic materials including AlPO₄-5 synthesized using reagent as raw materials have been shown to have application as an adsorbent for water vapor for heat pump or desiccant, and have adsorption properties comparable to silica gel and aluminosilicate type zeolite.¹¹⁻¹² The synthesis of AlPO₄-5 from aluminum dross rather than pure reagents for this application may contribute to the effective use of aluminum dross and the potential to lower the cost of production of AlPO₄-5. To date, it appears that no research has been conducted in synthesizing AlPO₄-5 from aluminum dross for water vapor adsorption. This concept is an effective and unique method for recycling aluminum dross and a novel engineering research.

In this study, AlPO₄-5 was hydrothermally synthesized using the aluminum dross discharged from an aluminum recycling process. The crystal structure and morphology of the resulting products were characterized with X-ray diffraction and scanning electron microscopy, respectively. The water vapor adsorption property of the reaction products was studied.

2. Experimental

Aluminum dross used in this study was derived from an aluminum recycling company in Japan and from various wastes such as car engine and sash. The aluminum dross also differs from those used in our previous studies.²,¹⁰ As mentioned below, this by-product demonstrated highly acid-soluble Al content as nature of aluminum dross. The chemical composition of the aluminum dross leachate dissolved with aqua regia is shown in Table 1. The mass percent for each metal component was calculated by defining the total metal content in the leachate as 100%. The Al

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content of the leachates was 89.6 mass%. Other metals detected included Cu, Ca, Mg and Fe. The percentage of aluminum dross leached was shown to be 73.1% by mass.

AlPO₄-5 was synthesized using the aluminum dross, 85 mass% H₃PO₄, triethylamine (TEA) and distilled water as a raw material. TEA was used as a structure-directing agent for the AlPO₄-5 synthesis. The syntheses of AlPO₄-5 were carried out by varying the reactant composition using Al₂O₃ : P₂O₅ : TEA : H₂O = x : 1 : y : 40 (molar ratio; x = 1 or 2, y = 1 or 2). The Al content in the aluminum dross sample used in this study was supposed to be about 65 mass%. This means that 8.3 or 16.6 g of the aluminum dross was used in the case of x = 1 or 2, respectively. To prepare AlPO₄-5 as a reference sample, Al(OH)₃ of 15.6 g at x = 1 was also used as an Al source instead of aluminum dross. The aluminum dross or Al(OH)₃ was added slowly to a mixture of 85 mass% H₃PO₄ of 23.1 g and water of 68.5 g, and then this was kept for 1.5 h with agitation using a magnetic stirrer. TEA of 10.1 or 20.2 g at y = 1 or 2 was added to the mixture. The mixture was stirred for 1.5 h again, to prepare the gel-like precursor of AlPO₄-n.

The mixture was heated up to 453 K in an autoclave without agitation, and kept at 453 K. Reaction time (keeping time) at 453 K was set at 6 h for aluminum dross and 12 h for Al(OH)₃, respectively. The solid reaction product and mother liquor were separated by a vacuum filtration. The wet cake product was washed with distilled water, and then dried at 383 K for 12 h. The TEA in the reaction product was removed by the calcination conducted at 823 K for 3 h in air with a tube type electric furnace (Isuzu Seisakusyo Co. Ltd., EPKRO-13K). The resulting product after the heat treatment was used as the adsorbent for water vapor adsorption tests. The flow diagram of AlPO₄-5 synthesis is summarized in Fig. 1.

The crystal structure and surface texture of the aluminum dross and reaction products were analyzed by an X-ray diffraction equipment (Rigaku Co. Ltd., RINT-TTRIII) and a scanning electron microscope (Hitachi High-Technologies Co. Ltd., HITACHI S-4800), respectively. Water vapor adsorption was measured at 298 K using an automatic gas adsorption equipment (BEL Japan Inc., BELSOP-18PLUS). Specific surface area of the reaction product was determined using the BET equation to nitrogen gas adsorption (Quantachrome Instruments Co. Ltd., AS1MP-LP2).

3. Results and Discussion

3.1 Hydrothermal synthesis of AlPO₄-5

The XRD pattern of the aluminum dross is illustrated in Fig. 2. The aluminum dross contains Al, AlN, Al₂O₃, Fe₂O₃ and SiO₂ as crystalline materials. The Al and AlN in aluminum dross, which are also hazardous components in landfill, may be mainly transformed into the Al parts of the AlPO₄-5 crystal structure by a hydrothermal treatment. A reference sample of AlPO₄-5 was generated using reagents. Figs. 3 and 4 show the XRD pattern and SEM photograph of reaction product synthesized from Al(OH)₃. The peak pattern derived from the AlPO₄-5, appears clearly under the reaction condition of Al₂O₃ : P₂O₅ : TEA : H₂O = 1 : 1 : 1 : 40, 453 K and 12 h. AlPO₄-5 has large pores of

<table>
<thead>
<tr>
<th>Metal</th>
<th>Al</th>
<th>Cu</th>
<th>Ca</th>
<th>Mg</th>
<th>Fe</th>
<th>Zn</th>
<th>Si</th>
<th>Ti</th>
<th>Mn</th>
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<tbody>
<tr>
<td>mass%</td>
<td>89.6</td>
<td>3.5</td>
<td>2.1</td>
<td>2.1</td>
<td>1.5</td>
<td>0.5</td>
<td>0.3</td>
<td>0.2</td>
<td>0.2</td>
</tr>
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</table>

Leaching ratio: 73.1 mass% (Residue: 26.9 mass%), Solid-liquid ratio: 2.5 g/100 cm³, Leaching time: 5 h

![Flow diagram of AlPO₄-5 synthesis by hydrothermal reaction.](image)

![X-ray diffraction pattern of aluminum dross.](image)

![X-ray diffraction pattern of reaction product synthesized from Al(OH)₃.](image)
formed using reagent grade Al(OH)₃. It is considered that this 0.73 nm due to 12-membered rings. Figure 4 shows that the hexagonal crystals with submicron to 10 µm due to the AlPO₄-5 structure were formed by coagulation of the fine particles.

The hydrothermal syntheses of AlPO₄-5 were conducted using the aluminum dross as a raw material. The XRD patterns of the reaction products synthesized at 453 K for 6 h are illustrated in Fig. 5. The peak patterns of AlPO₄-5 and tridymite type AlPO₄ (nonporous phosphate) are identified at (a) Al₂O₃ : P₂O₅ : TEA : H₂O = 1 : 1 : 1 : 40. It appears that the formation of tridymite type AlPO₄ is predominant compared with that of AlPO₄-5. The product obtained at (b) Al₂O₃ : P₂O₅ : TEA : H₂O = 2 : 1 : 1 : 40 is found to have strong diffraction peaks of AlPO₄-5, though some unknown peak also appears. The result in Fig. 5(c) shows that AlPO₄-5 was also formed as a main component of the crystalline material. The chemical composition of the precursor to obtain AlPO₄-5 from aluminum dross successfully differs from that formed using reagent grade Al(OH)₃. It is considered that this phenomenon is mainly caused by the structure or configuration of Al component in the aluminum dross. The quantity of Al in the aluminum dross available for AlPO₄-5 through the hydrothermal treatment may be limited, and an increase in the amount of dross (x = 2) or TEA amount (y = 2) is thought to be needed for the effective generation of AlPO₄-5.

Figure 6 shows the SEM photograph of the aluminum dross-derived AlPO₄-5. The hexagonal crystals of AlPO₄-5 and the rhombohedral crystals which may appear to be tridymite type AlPO₄ are both observed with the reagent compositional ratio of (a) Al₂O₃ : P₂O₅ : TEA : H₂O = 1 : 1 : 1 : 40. The aspect ratio of tridymite type AlPO₄ particles is a little different from the previous results. It is considered that this is attributed to the differences in synthesis condition and variation in the chemical composition of aluminum dross. In the case of compositional ratio of (b) Al₂O₃ : P₂O₅ : TEA : H₂O = 2 : 1 : 1 : 40, about 10 µm of AlPO₄-5 hexagonal crystals were confirmed by SEM analysis. Similar hexagonal crystals were also found in Fig. 6(c), but the particle sizes are obviously smaller than those observed in Figs. 6(a) and 6(b). Generally, TEA plays a role in directing the structure and in promoting the nucleating for the AlPO₄-5 formation.

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Generally, TEA plays a role in directing the structure and in promoting the nucleating for the AlPO₄-5 formation.

3.2 Adsorption of water vapor with reaction product

Figure 7 shows the water vapor adsorption isotherm at 298 K of the aluminophosphate type zeolitic materials synthesized from Al(OH)₃. Adsorption amount is increasing slightly with an increase in relative pressure until about 0.25. Rapid increase in adsorption occurs at P/P₀ = 0.25 followed by a slight increase to P/P₀ = 0.3 and above. The adsorption amount at P/P₀ = 1 is estimated to be about 0.19 g H₂O/g-adsorbent. The shape of adsorption isotherm may be classified as the type V isotherm by IUPAC, and this result is approximately similar to the other reports. It is considered that H₂O molecules are adsorbed in the pore of AlPO₄-5 and the water vapor adsorption increases sharply at the P/P₀ = 0.25 because of the strong interaction between H₂O molecules in the AlPO₄-5 pore due to the hydrogen bond.

Adsorption isotherms of water vapor in the aluminum dross-derived AlPO₄-5 are shown in Figs. 8, 9 and 10. Although the amount of water vapor adsorbed is remarkably different among these isotherms, the shapes all correspond to the type IV or V isotherm. The adsorption isotherm shape in Fig. 9, in particular, is qualitatively similar to Fig. 7.
(AlPO₄-5 synthesis from Al(OH)₃). Figure 10 shows that the amount of water adsorbed is also higher at the low $P/P_0$ region below 0.1, compared with Fig. 7. Small quantities of metal compounds including Cu, Ca, Mg, Fe in aluminum dross are thought to affect the adsorption property of water vapor in the low $P/P_0$ region. The water vapor adsorbed has the following order; product synthesized at Al₂O₃: P₂O₅: TEA: H₂O = 1:1:1:40 > product at 2:1:1:40 > product at 1:1:2:40. These results suggest that water vapor adsorption is promoted by the formation of AlPO₄-5 crystals.

Table 2 shows the specific surface area of various reaction products. The large specific surface area of reaction products suggests the presence of the pores by AlPO₄-5 formation. The product obtained from Al(OH)₃ has the largest specific surface area (404 m²/g) by a BET method. On the other hand, the products from aluminum dross have specific surface area in the order of product generated using the following compositions: Al₂O₃: P₂O₅: TEA: H₂O = 1:1:2:40 > product at 1:1:1:40 > product at 2:1:1:40. (353

**Fig. 6** SEM photograph of reaction products synthesized from aluminum dross at Al₂O₃: P₂O₅: TEA: H₂O = (a) 1:1:1:40, (b) 2:1:1:40 and (c) 1:1:2:40.

**Fig. 7** Adsorption isotherm of water vapor with reaction product synthesized from Al(OH)₃.

**Fig. 8** Adsorption isotherm of water vapor with reaction product synthesized from aluminum dross.

**Fig. 9** Adsorption isotherm of water vapor with reaction product synthesized from aluminum dross.
capacity for the aluminum dross-derived AlPO4-5, as shown in Fig. 10.

The adsorption amount of water vapor for desiccant system. The resulting adsorption amount at 12% was 0.055 kgH2O/kg-adsorbent and is considered to be high capacity for the aluminum dross-derived AlPO4-5, as shown in Fig. 11.

The ΔQ for other reaction products were calculated using the same method, and the resulting adsorption amount at 12% RH is summarized in Table 2. The reaction product obtained from Al(OH)3 showed the highest ΔQ value (0.114 kgH2O/kg-adsorbent). While the ΔQ of the products synthesized from aluminum dross has the following order; product at 1 : 1 : 1 : 40 (187 m²/g) > product at 1 : 1 : 1 : 40 (75 m²/g). This order is also consistent with the water vapor adsorption.

According to the paper about the fundamental evaluation as adsorbent for desiccant from the viewpoint of adsorption equilibrium, it may be suitable to investigate the water vapor adsorption between 12% and 32% relative humidity (RH). So similar evaluation as an adsorbent for desiccant using waste heat of lower temperature was carried out to the adsorption isotherm obtained. Typical example of simple evaluation is illustrated in Fig. 11. At first the adsorption quantities were determined at 12% and 32% RH, respectively. Then the difference in adsorption (ΔQ) was calculated, which may be also the effective adsorption–desorption amount in a desiccant system. Lager ΔQ value resulting in rapid increase in adsorption in the region of 12% to 32% is desirable for the practical use of adsorbent. For example, ΔQ is estimated to be 0.055 kgH2O/kg-adsorbent and is considered to be high capacity for the aluminum dross-derived AlPO4-5, as shown in Fig. 11.

Table 2 Specific surface area and adsorption amount of water vapor from RH12% to RH32% on various reaction products.

<table>
<thead>
<tr>
<th>Al source</th>
<th>Al2O3 : P2O5 : TEA : H2O</th>
<th>Specific surface area (BET method) [m²/g]</th>
<th>Adsorption amount of water vapor, ΔQ [kgH2O/kg-ads.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(OH)3</td>
<td>1 : 1 : 1 : 40</td>
<td>404</td>
<td>0.114</td>
</tr>
<tr>
<td></td>
<td>1 : 1 : 1 : 40</td>
<td>75</td>
<td>0.017</td>
</tr>
<tr>
<td>Aluminum dross</td>
<td>2 : 1 : 1 : 40</td>
<td>187</td>
<td>0.055</td>
</tr>
<tr>
<td></td>
<td>1 : 1 : 2 : 40</td>
<td>353</td>
<td>0.069</td>
</tr>
</tbody>
</table>

m²/g) > product at 2 : 1 : 1 : 40 (187 m²/g) > product at 1 : 1 : 1 : 40 (75 m²/g). This order is also consistent with the water vapor adsorption.

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The ΔQ for other reaction products were calculated using the same method, and the resulting adsorption amount at 12% to 32% RH is summarized in Table 2. The reaction product obtained from Al(OH)3 showed the highest ΔQ value (0.114 kgH2O/kg-adsorbent). While the ΔQ of the products synthesized from aluminum dross has the following order; product at 1 : 1 : 2 : 40 (0.069 kgH2O/kg-adsorbent) > product at 2 : 1 : 1 : 40 (0.055 kgH2O/kg-adsorbent) > product at 1 : 1 : 1 : 40 (0.017 kgH2O/kg-adsorbent). This order is essentially based on the shape of adsorption isotherm of the AlPO4-5 formed.

Because AlPO4-5 can be obtained as main component from aluminum dross by adjusting the chemical composition of the precursor successfully, likewise the water vapor adsorption property of the adsorbent may be controlled in the same way, to obtain more suitable adsorption isotherm for desiccant system. These results reveal that the aluminum dross-derived AlPO4-5 with high capacity and suitable property of water vapor as an adsorbent for desiccant can be synthesized hydrothermally from aluminum dross, though it is a little inferior to the AlPO4-5 derived from Al(OH)3 reagent.

4. Conclusion

As one of effective uses of aluminum dross, the hydrothermal syntheses of AlPO4-5 for adsorbent of water vapor were carried out by using aluminum dross as a raw material. For various reaction products obtained, the adsorption property of water vapor and simple evaluation as an adsorbent for desiccant were investigated in this study.

Both AlPO4-5 and tridymite type AlPO4 are formed hydrothermally from the aluminum dross at Al2O3 : P2O5 : TEA : H2O = 1 : 1 : 1 : 40 by XRD analysis and SEM observation. It is found that AlPO4-5 was the main component at the compositional ratio of 2 : 1 : 1 : 40 and 1 : 1 : 2 : 40. The shapes of adsorption isotherms of the products synthesized from aluminum dross are similar to the type IV or V isotherm by IUPAC classification. The products from aluminum doss have specific surface area in the order of product at compositional ratio of 1 : 1 : 2 : 40 (353 m²/g) > product at 2 : 1 : 1 : 40 (187 m²/g) > product at 1 : 1 : 1 : 40 (75 m²/g). This study showed the aluminum dross-derived AlPO4-5 has high capacity and suitable property as an adsorbent for desiccant.
Acknowledgments

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