Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Journal of the European Ceramic Society 26 (2006) 459–462
ECERS
www.elsevier.com/locate/jeurceramsoc

Hydrothermal synthesis of $AlPO_4$-5 type zeolitic materials by using aluminum dross as a raw material

Norihiro Murayama, Nobuaki Okajima, Shoichi Yamaoka, Hideki Yamamoto, Junji Shibata *

Department of Chemical Engineering, Faculty of Engineering, Kansai University, Suita, Osaka 564-8680, Japan

Available online 8 August 2005

Abstract

The hydrothermal synthesis of $AlPO_4$-5, which is one of the large pore size aluminum phosphate condensates like zeolitic materials, was carried out by using aluminum dross as a raw material. Triethylamine (TEA) was used as a structure directing agent (SDA) for $AlPO_4$-5 synthesis. Various physical properties such as crystal structure, surface texture and specific surface area were investigated for the obtained reaction product.

$AlPO_4$-5 can be synthesized from aluminum dross under hydrothermal conditions at 453–473 K for 3 h. $AlPO_4$ salt as a by-product, which is a non-porous material, is formed at the same time. The crystal of the obtained $AlPO_4$-5 is hexagonal as observed by SEM photographs. It is desirable to heat-treat the reaction product at the temperature around 823 K to remove TEA. The crystal structure of $AlPO_4$-5 changes to non-porous aluminum phosphate in case of a heat treatment exceeding 973 K. The specific surface areas of the reaction product before and after heat treatment at 823 K are 18 and 360 m^2/g, respectively.

Keywords: Aluminum dross; Powders–chemical preparation; Thermal properties

1. Introduction

Aluminum and its alloys are widely used as versatile materials. Recycling of aluminum products is being promoted from the viewpoint of resources preservation and the low energy cost to purify aluminum. Aluminum dross is one of the industrial wastes which are generated in an aluminum recycle process. In the melting process of aluminum scraps, aluminum oxide and aluminum nitride are formed on the surface of melted aluminum by the reaction with oxygen and nitrogen in air. The discharged amount of aluminum dross is about 350,000 tonnes per year in Japan. A part of aluminum dross is used as deoxidizer for steel making, but the rest is treated by landfill. It is difficult to assure the disposal site in Japan, and then the development of new recycling technologies is necessary for aluminum dross.

$AlPO_4$-n, which is one of the aluminum phosphate condensates, was synthesized by Wilson and co-workers, in 1982.[1,2] The $AlPO_4$-n is a porous material having uniform and large pore due to its framework structure,[3] and it is attempted to utilize the material as a molecular sieve, a catalyst and so on by many researchers.[4–10] Various $AlPO_4$-n type materials are synthesized using SDA such as tri-ethylamine and tri-propylamine under hydrothermal conditions. $AlPO_4$-5 has unique framework topology compared with zeolitic materials of aluminosilicate.[3] Especially, $AlPO_4$-5 has a large pore size due to 12-membered rings and strong thermal stability.

Pseudo-boehmite, aluminum hydroxide and aluminum isopropoxide are used as an aluminum source to synthesize the $AlPO_4$-5. In this study, we tried to synthesize the $AlPO_4$-5 by hydrothermal reaction from reagents and aluminum dross. Time course of synthesis behavior of the $AlPO_4$-5 was observed in various conditions. Physical properties such as crystal structure, surface texture, specific surface area and so on were investigated for the reaction products.

* Corresponding author. Tel.: +81 6 6368 0856; fax: +81 6 6388 8869.
E-mail address: shibata@kansai-u.ac.jp (J. Shibata).

0955-2219/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2005.06.022

2. Experimental

Dried powder of aluminum hydroxide or aluminum dross was used as aluminum source of the $AlPO_4$-5 synthesis. These materials were slowly added to phosphoric acid solution. The mixture was kept for 1.5 h in the agitation condition, and then tri-ethylamine (TEA) was added into the mixture. The general composition is as follows; Al_2O_3:P_2O_5:TEA:H_2O = 1:1:1:40 (molar ratio). This mixture was stirred for 1.5 h to make a aluminophosphate gel, which is the starting material of $AlPO_4$-5. This gel was transferred to an autoclave, and it was heated at 453–473 K. After hydrothermal reaction, the reaction products was heated for 3 h at various temperatures to remove TEA.

For the aluminum dross and the reaction products synthesized at 473 K for 3 h, the crystal structure was identified by X-ray diffraction equipment (JDX-3530, Nihon Denshi Co. Ltd.). The XRD patterns were recorded with Cu Kα radiation (40 kV, 20 mA), 0.040° step size and 0.5 s step time. These measurements were carried out under the same experimental condition for all samples. The surface texture was investigated using a scanning electron microscope (JSM-5410, Nihon Denshi Co. Ltd.). The thermogravimetric change was measured at heating rate of 5 K/min by a thermogravimetric analyzer (TGA-50, Shimadzu Co. Ltd.). Nitrogen adsorption and desorption properties were measured by an automatic gas adsorption equipment (AS1MP-LP2, Quanta-chrome Instruments).

3. Results and discussion

The chemical composition of the aluminum dross is shown in Table 1. These values show weight percent of metal components in the solution leached by aqua-regia. The contents of Al and Mg in the aluminum dross are 89.1 and 3.8%, respectively. Si, Fe, Zn, etc. exist as impurity components in the aluminum dross. The X-ray diffraction pattern of the aluminum dross is shown in Fig. 1. In the aluminum dross, Al, AlN, Al_2O_3, SiO_2, Fe_2O_3 and so on are confirmed as a crystalline material.

The X-ray diffraction pattern of the reaction products from reagent and aluminum dross is shown in Fig. 2. The $AlPO_4$-5 can be obtained from aluminum hydroxide under the reaction condition of 453 K and 24 h, although a small amount of aluminum hydroxide is visibly present. On the other hand, the $AlPO_4$-5 is produced from aluminum dross under the condition of 473 K and 3 h, as shown in Fig. 2(b). Quartz and aluminum oxide, which are originally contained in aluminum

Table 1
Chemical composition of aluminum dross (wt%)

Al	Mg	Si	Pb	Zn	Ca	Na	K	Fe	Ti	Mn
89.1	3.8	0.2	0.2	0.7	1.3	0.7	0.8	2.5	0.004	0.6

Solid–liquid ratio: 5 g/200 cm^3-aqua regia, residue: 45%.

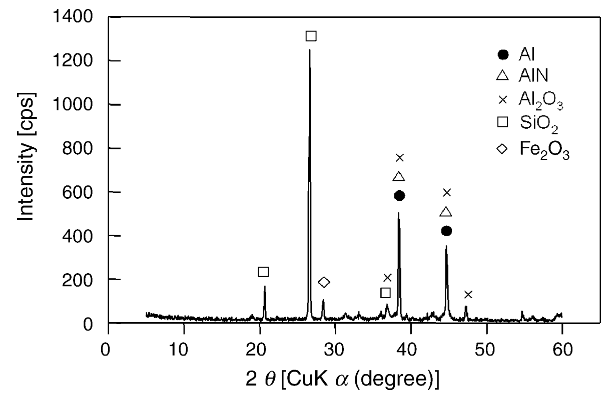


Fig. 1. X-ray diffraction pattern of aluminum dross used in this study.

dross, and $AlPO_4$ (berlinite) as a by-product are observed as well as other crystalline materials. Crystal system of berlinite has the same structure of quartz. The peak of metallic aluminum does not appear in the XRD pattern of reaction product, and this result indicates that metallic aluminum component in aluminum dross is completely used to synthesize $AlPO_4$-5.

TEA plays a role of a nucleus to form the $AlPO_4$-5 structure, that is, the aluminophosphate condensates with 12-membered rings are formed around TEA molecules in the form of an organic base under the hydrothermal condition applied. Fig. 3 shows the time course of XRD intensities of the reaction product at 473 K and pH of mother liquor. The XRD intensity of $AlPO_4$-5 shows maximum values at a reaction time of 3 h, and then the peak intensity of $AlPO_4$-5 decreases. On the other hand, the pH is increasing with an increase in reaction time, but does not change anymore after 3 h. The XRD intensities of quartz and berlinite increase with

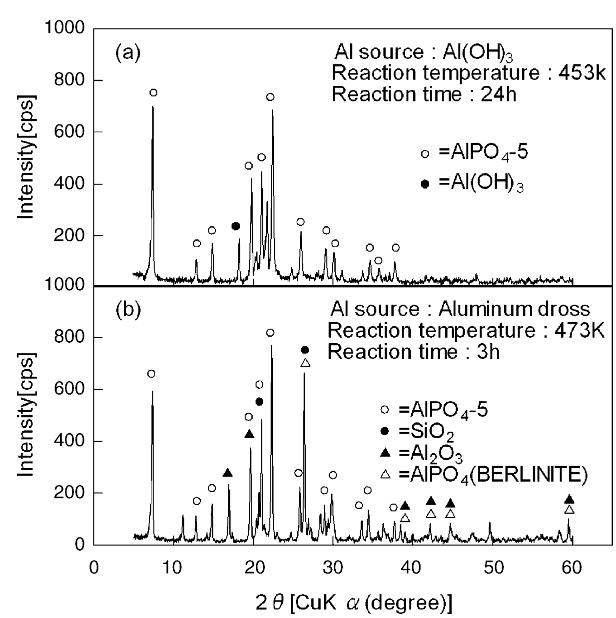


Fig. 2. X-ray diffraction pattern of reaction products from reagent and aluminum dross.

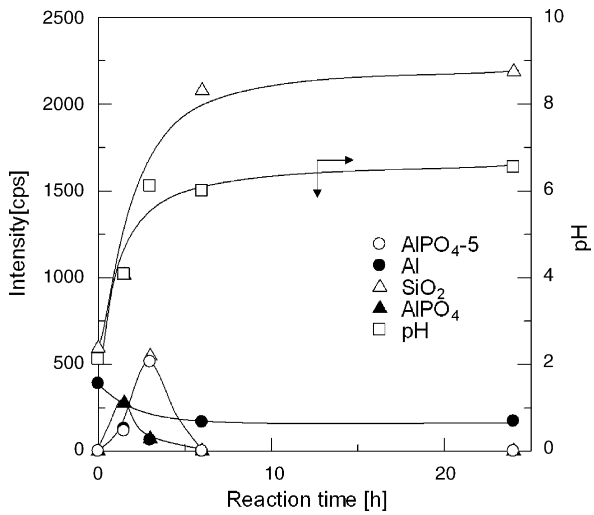


Fig. 3. Change in XRD intensities of reaction product and pH of mother liquor as a function of reaction time.

reaction time. The $AlPO_4$-5 crystal is unstable at 473 K, and the crystal transition to berlinite occurs in short reaction time. Although the result of hydrothermal synthesis at 453 K is not shown as a figure, the XRD intensity of $AlPO_4$-5 increases with reaction time to approach a constant value, but the values are smaller than that at 473 K. The $AlPO_4$-5 crystal is comparatively stable at 453 K compared with that at 473 K, though the produced amount of $AlPO_4$-5 is very small.

Photo 1 shows the SEM observation of aluminum dross and the reaction product obtained from aluminum dross. Large and angular particles partially exist, and the particle size widely distributes. The angular particles are mainly SiO_2 from the result of fluorescent X-ray analysis. On the other hand, about 30 μm of the $AlPO_4$-5 hexagonal crystal is recognized. Many small particles having hexagonal and cubic structures aggregate to form particles of about 10 μm. The cubic structure of particles is caused by berlinite and quartz.

Fig. 4 shows the TGA for the reaction product from aluminum dross. The heating rate is set to be 5 K/min. The prominent weight loss is confirmed from 273 to 823 K, and the

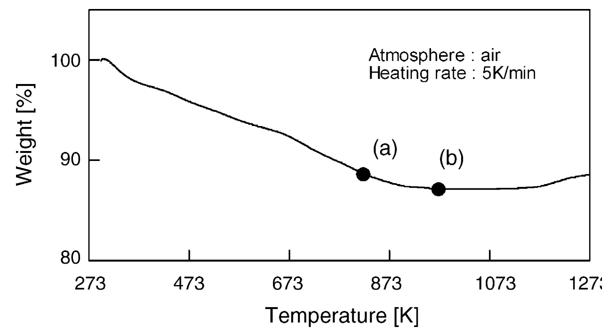
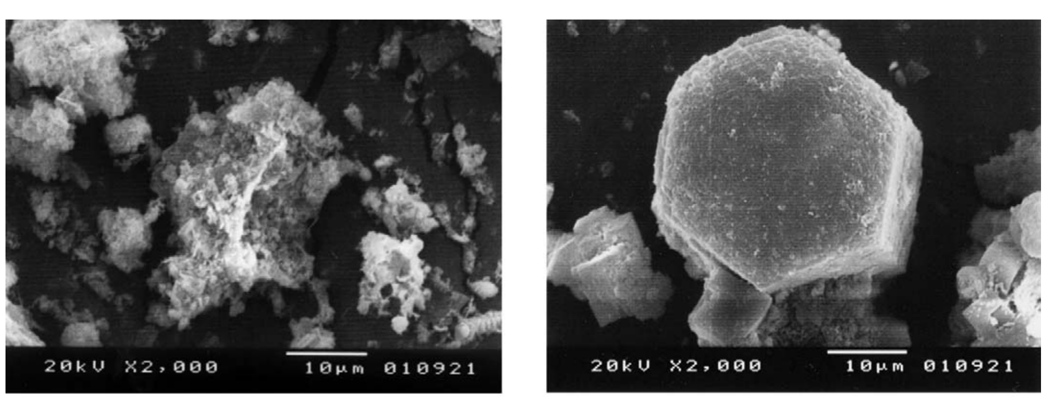


Fig. 4. TGA for the reaction product from aluminum dross.

weight of reaction product becomes constant at about 823 K. TEA in the pore of $AlPO_4$-5 is decomposed and removed by heating until 823 K. The XRD shows that the $AlPO_4$-5 crystal structure is maintained below 823 K (Fig. 4(a)), while the $AlPO_4$-5 structure is disintegrated at 973 K (Fig. 4(b)). After heating at 973 K, $AlPO_4$-5 changes into tridymite which is one of $AlPO_4$ crystals and does not have porous structure. From these results, it is desirable to remove TEA at 823 K.

Fig. 5 shows the adsorption and desorption isotherms of nitrogen at 77 K for the reaction products synthesized from aluminum dross. The amount of nitrogen adsorption is very small for the $AlPO_4$-5 product before heat treatment, and the BET specific surface area (S_{BET}) is calculated to be about 18 m^2/g. This is caused by pore filling of $AlPO_4$-5 by TEA. On the other hand, nitrogen adsorption significantly increases for the $AlPO_4$-5 after heating at 823 K, and the S_{BET} shows about 360 m^2/g. By the heat treatment at 823 K, TEA can be removed without disintegrating the crystal structure of $AlPO_4$-5, and nitrogen molecules are adsorbed in the pore of $AlPO_4$-5. The nitrogen desorption isotherm does not correspond to the adsorption isotherm at low relative pressure. Nitrogen adsorption decreases for the product heated at 973 K. This phenomenon is due to the crystal disintegration as shown in Fig. 4(b).

Fig. 6 shows the pore size distribution of the reaction product calculated by the SF model analysis of nitrogen adsorption data. The main pore size of the reaction product is about



(a) Aluminum dross (b) Reaction product

Photo 1. SEM observation of aluminum dross and reaction product.

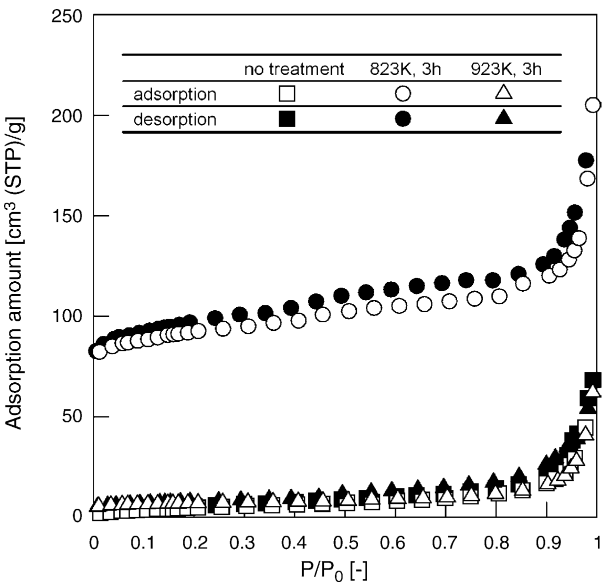


Fig. 5. Adsorption and desorption isotherms of nitrogen at 77 K for the reaction products from aluminum dross.

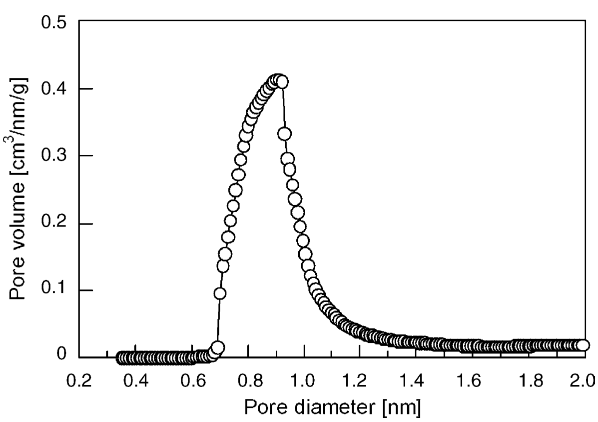


Fig. 6. Pore size distribution of reaction products synthesized from aluminum dross by SF model.

0.7–1.2 nm and the pore size curve shows a sharp peak at about 0.9 nm. The pore size of $AlPO_4$-5 observed in this study is a little bit larger than that of the known pore size of $AlPO_4$-5, 0.73 nm.

4. Conclusions

As one of effective usages of aluminum dross, $AlPO_4$-5 of porous material was synthesized from aluminum dross as raw materials. Various physical properties such as surface texture, crystal structure and specific surface area were investigated for the obtained products.

The $AlPO_4$-5 can be obtained from aluminum dross by the hydrothermal reaction at 453–473 K for 3 h. At the same time, berlinite, which is not a porous material, is formed as a by-product. TEA can be removed by heating at 823 K. The S_{BET} of TEA-removed product is about 360 m^2/g. In the heat treatment of 973 K, the crystal structure is disintegrated.

Acknowledgement

This work was supported by MEXT, Grant-in-Aid (Exploratory Research, 15656232) and the Kansai University Grant-in-Aid for promotion of Advanced Research in Graduate Course, 2003.

References

1. Wilson, S. T., Lok, B. M., Messina, C. A., Cannan, T. R. and Flanigen, E. M., Aluminophosphate molecular sieves – a new class of microporous crystalline inorganic solids. *J. Am. Chem. Soc.*, 1982, **104**, 1146–1147.
2. Wilson, S. T., Lok, B. M. and Flanigen, E. M., Crystalline Metallophosphate Compositions. U.S. Patent 4310440, 1982.
3. Baerlocher, Ch., *Atlas of Zeolite Framework Types*. Elsevier, Amsterdam, 2001, pp. 34–35.
4. Newalkar, B. L., Jasra, R. V., Kamath, V. and Bhat, T. S. G., A rapid synthesis of the moleclar sieve alpo$_4$-5 with aluminium triisopropoxide. *J. Chem. Soc. Chem. Commun.*, 1994, 1041–1042.
5. Szostak, R., *Handbook of Molecular Sieves*. Van Nostrand Reinhold, New York, 1992.
6. Xu, Y., Maddox, P. J. and John, J. M., Preparation and characterization of molecular sieves based on aluminium phosphate. *Polyhedron*, 1989, **8**(6), 819–826.
7. Yosio, O., Structure and character of alumino-phosphate type molecular sieve. *Petrotech*, 1993, **3**, 225–229.
8. Concepción, P., López Nieto, J. M., Mifsud, A. and Pérez-Pariente, J., Preparation and characterization of Mg-containing AFI and chabazite-type materials, *Zeolites*, 1996, **16**, 56–64.
9. Choudhary, V. R., Akolekar, D. B., Singh, A. P. and Sansare, S. D., Influence of thermal, hydrothermal, and acid–base treatments on structural stability and surface and catalytic properties of $AlPO_4$-5. *J. Catal.*, 1988, **111**, 254–263.
10. Dong, J., Li, J., Liu, G., Wu, F., Chang, J. and Xu, W., Synthesis of the molecular sieve $AlPO_4$-5 with an unequal molecular ratio of Al_2O_3 to P_2O_5. *J. Chem. Soc. Chem. Commun.*, 1992, 277–278.