Int. J. Miner. Process. 93 (2009) 110–114

Contents lists available at ScienceDirect

Int. J. Miner. Process.

journal homepage: www.elsevier.com/locate/ijminpro

Effect of structure-directing agent on $AlPO_4$-n synthesis from aluminum dross

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ARTICLE INFO

Article history:
Received 14 June 2008
Received in revised form 20 April 2009
Accepted 3 July 2009
Available online 13 July 2009

Keywords:
Structure-directing agent
$AlPO_4$-n
Aluminum dross
Recycle

ABSTRACT

The hydrothermal synthesis of $AlPO_4$-n which is a functional material of aluminophosphate, was conducted from two kinds of aluminum dross discharged in an aluminum regeneration factory. The effect of structure-directing agent (SDA) on the formation behavior of $AlPO_4$-n from aluminum dross, the suitable condition to obtain $AlPO_4$-n efficiently, and the pore structure and gas adsorption property were investigated in this study. $AlPO_4$-5 and $AlPO_4$-34 are mainly formed from aluminum dross as a raw material, and it is possible to make $AlPO_4$-5 successfully as a main product by adjusting the amount of triethylamine (TEA) as SDA. The gas adsorption amount with $AlPO_4$-5 is the following order; ammonia>dipropylamine>benzene, and it is found that this order mainly corresponds with the polarity of molecule among them.

1. Introduction

Large quantities of aluminum dross are generated as a waste from aluminum production or aluminum recycle processes, and a new recycle technology for aluminum dross is required. For example, in a melting process of aluminum scraps, the aluminum dross composed of aluminum oxide and aluminum nitride are formed on the surface between air and melted aluminum. The amount of dross in aluminum regeneration process is estimated to be over 350,000 t/year in Japan. The aluminum dross discharged in aluminum regeneration factories is mainly used as a deoxidizer for steel making, but the rest is often treated by landfill, because no effective technology is found for the recycle and reuse methods of aluminum dross. It is difficult to assure a disposal site in Japan, and the development of new recycling technologies is necessary for aluminum dross.

In our previous study (Murayama et al., 2006a), it has been suggested that a functional inorganic material, $AlPO_4$-5 is synthesized from aluminum dross as a raw material, as one of effective use of aluminum dross. $AlPO_4$-n (porous aluminophosphate, n:number) is well-known as a zeolitic material having uniform and large pore based on its crystal framework structure. Since a series of $AlPO_4$-n type zeolitic materials was synthesized (Wilson et al., 1982), many researchers (Choudhary et al., 1988; Dong et al., 1992; Newalkar et al., 1994; Xu et al., 1989) have studied to apply the $AlPO_4$-n to a molecular sieve, a catalyst, an adsorbent and so on.

Structure-directing agent (SDA) which mainly acts as a precursor and a nucleating material in the formation process of $AlPO_4$-n crystals, is needed to synthesize $AlPO_4$-n, and lower amine like triethylamine (TEA) is often used as a SDA. However, the formation mechanism of $AlPO_4$-n and the role of SDA are not clarified adequately. Especially, no paper is found for the mechanism of $AlPO_4$-n synthesis from aluminum dross.

In this study, the hydrothermal synthesis of $AlPO_4$-n was carried out from two kinds of aluminum dross. The effect of SDA on the $AlPO_4$-n formation from aluminum dross and the suitable condition to obtain $AlPO_4$-n efficiently were investigated. Furthermore, the pore structure and gas adsorption property were studied for the $AlPO_4$-5 obtained from aluminum dross.

2. Experimental

2.1. Hydrothermal synthesis of $AlPO_4$-n zeolitic materials

Various wastes such as aluminum dross, residual ash, dust, waste solution and so on are exhausted in the recycling process of aluminum products (Murayama et al., 2006b). The aluminum dross used in this study, which floats on the surface of molten aluminum in the furnace, is generated from various wastes of Al alloys like car bodies, engine components and aluminum sash. Two kinds of aluminum dross (D-1 and D-2) were used as an aluminum source of $AlPO_4$-n synthesis. The chemical composition of D-1 is a little different from that of D-2. The aluminum dross of D-1 and D-2 was collected from different sampling points in the same Al regeneration process, though these are generated in the same factory in Japan. The lot number of D-2 is also the same as the dross used in our previous study (Murayama et al, 2006a).

Dried powder of the aluminum dross (14.6 g) was added slowly to a 28.2 wt.% phosphoric acid solution of 93.7 g. This mixture was kept for 1.5 h in the agitation condition with a magnetic stirrer, and then 8.3–13.7 g of TEA which plays a role on SDA, was added to the mixture. By a series of operations mentioned above, the composition of mixture

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doi:10.1016/j.minpro.2009.07.002

is set as follows: Al_2O_3:P_2O_5:TEA:H_2O = 1:1:x:40 (TEA molar ratio x = 0.5–1.0). This mixture was stirred again for 1.5 h to make an aluminophosphate gel which is a starting material of $AlPO_4$-n. This gel-like material was transferred to an autoclave of 200 cm^3, and it was heated at 453 K without agitation for various reaction times (keeping time at 453 K). The solid cake and mother liquor were separated by a vacuum filtration. The reaction products were washed with distilled water, and then dried at 383 K for 12 h.

For the aluminum dross and various reaction products, the crystal structure was identified by an X-ray diffraction equipment (JDX-3530, Nihon Denshi Co., Ltd.). The surface texture was observed using a scanning electron microscope (JSM-5410, Nihon Denshi Co., Ltd.). Nitrogen adsorption amount was measured by an automatic gas adsorption equipment (AS1MP-LP2, Quanta-chrome Instruments).

2.2. Gas phase adsorption with $AlPO_4$-n zeolitic materials

For the $AlPO_4$-5 synthesized from D-2 (−105 μm), a heat treatment was conducted at 823 K for 3 h in air, in order to remove TEA in the reaction product (Murayama et al., 2006a) . The heating rate was set to 5 K/min. This sample after heat treatment was used as an adsorbent. As an adsorbate gas, ammonia, benzene and dipropylamine were prepared to be about 100 ppm by diluting them with nitrogen gas. These gases were generated by a bubbling operation of nitrogen gas into ammonia, benzene and dipropylamine solutions, respectively. One gram of adsorbent and the diluted gas mentioned above were introduced into 3 dm^3 of tedler-bag, and then the residual gas concentration was measured with gas detector tubes of 3L, 3La, 121SP, 121, 180 and 180L (Gas Tech Co., Ltd.).

3. Results and discussion

The XRD patterns of two kinds of aluminum dross used in this study are shown in Figs. 1 and 2. The content of metal aluminum in the D-1 is about 55%, and it is larger than that in the D-2 (about 45%). In case of D-1, the peak patterns of Al, Al_2O_3, MgO and SiO_2 (Quartz) are recognized as a crystalline material. On the other hand, the XRD diagram of D-2 in Fig. 2 indicates the existence of Al, AlN, Al_2O_3, MgO and SiO_2, and the XRD intensity derived from SiO_2 is extremely high compared with the D-1. Though SiO_2 is an impurity component for the $AlPO_4$-n synthesis, it is considered that the particles of SiO_2 in aluminum dross can be removed easily with the classification treatment with a sieve, because a large part of SiO_2 in the dross exists as large cubic particles over 100 μm. So the classification treatment with a sieve of 105 μm was conducted to the dross. The samples whose particle size are smaller than 105 μm, are expressed as D-1 (−105 μm) and D-2 (−105 μm) in the figures. In case of D-1 and D-1 (−105 μm), no difference appears in the XRD patterns before and after the classification operation, because the content of SiO_2 is originally small in the D-1. Whereas the XRD intensity of SiO_2 decreases remarkably after classification to the D-2 (−105 μm), and it is found that the removal of SiO_2 particles can be achieved with the classification operation from the D-2, which has a large amount of SiO_2 particles.

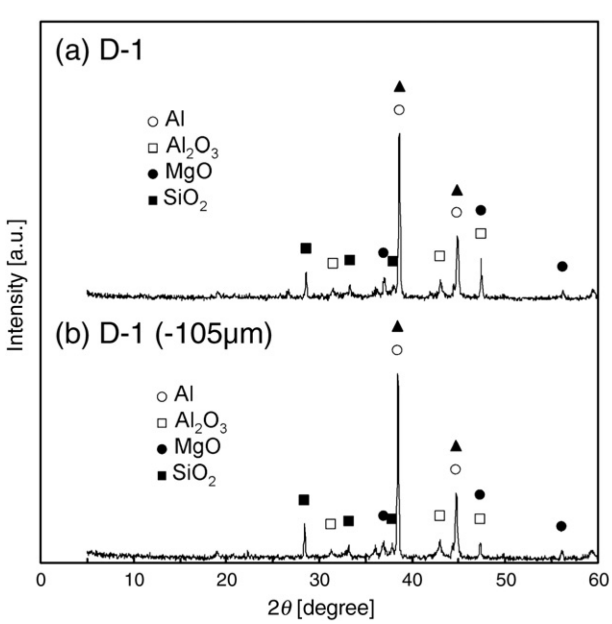

Fig. 1. XRD pattern of (a) aluminum dross D-1 and (b) D-1 (−105 μm) after classification.

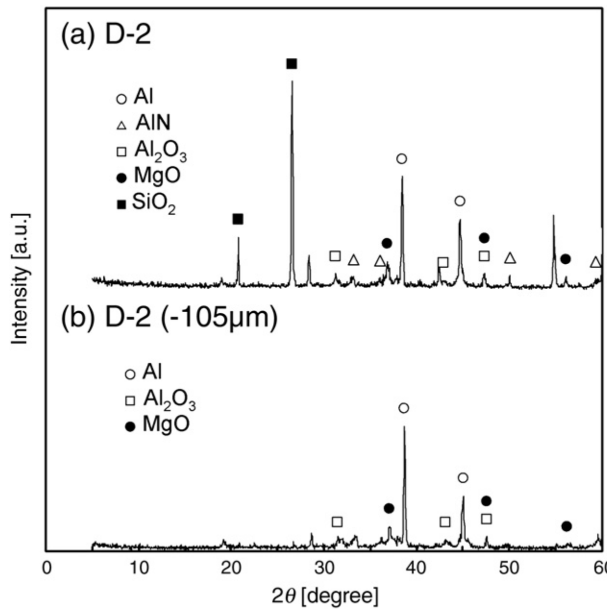

Fig. 2. XRD pattern of (a) aluminum dross D-2 and (b) D-2 (−105 μm) after classification.

The chemical composition of two kinds of aluminum dross is shown in Table 1. These values show the weight percent of acid-soluble components in the solution dissolved with aqua-regia. The weight percents of Al in the D-1 and D-2 are 77.5% and 89.1%, respectively. The aluminum dross, D-1 contains a lot of soluble components like Ti, Zn, Fe, Mn etc. shown as "Others" in Table 1. There are insoluble components such as SiO_2 in the D-1 and D-2, and the weight percents of D-1 and D-2 residues after leaching with aqua-regia are about 40% and 45%, respectively.

According to the report (Wilson et al., 1982), SDA is a very important factor to form $AlPO_4$-n type zeolitic material, and SDA mainly acts as an alkaline material, a precursor, a nucleating material and so on in the $AlPO_4$-n formation process. The hydrophobicity of SDA is also one of the important factors. The hydrothermal syntheses of $AlPO_4$-n were carried out by using the aluminum dross D-1, D-1 (−105 μm), D-2 and D-2 (−105 μm) as an aluminum source, and the role of TEA on $AlPO_4$-n synthesis from aluminum dross was investigated. For example, the XRD pattern of reaction product obtained from D-2 (−105 μm) is shown in Fig. 3 as a function of TEA additional amount. In case of TEA ratio x = 1.0 (Fig. 3(a)), the XRD patterns of both $AlPO_4$-5 with 12-membered rings

Table 1
Chemical composition of aluminum dross.

	Al	Mg	Si	Ca	K	Others
Aluminum dross (D-1)	77.5	4.8	0.4	1.3	0.1	15.9
Aluminum dross (D-2)	89.1	3.8	0.2	1.3	0.8	4.8

Solid/liquid ratio: 5 g/200 cm^3-aqua-regia.
Residue after leaching: 40% (D-1), 45% (D-2).