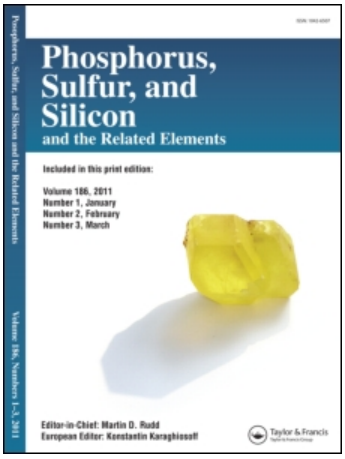

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Template-Free Synthesis of AlPO 4 -H1 by Microwave Heating

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TEMPLATE-FREE SYNTHESIS OF $AlPO_4$-H1 BY MICROWAVE HEATING

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Microwave heating enhanced the crystallization of aluminophosphate gels, and $AlPO_4$-H1 was successfully obtained without using organic template reagents in a short reaction time. The use of amorphous aluminum hydroxide as an aluminum source and the addition of hydrochloric acid were found to be essentially important to obtain $AlPO_4$-H1 as a single phase. Nitrogen and water adsorption properties were studied by measuring the adsorption isotherms.

Keywords: $AlPO_4$-H1; microwave heating; template-free synthesis

INTRODUCTION

Much attention has been paid to the use of microwave heating to hydrothermal synthesis of advanced materials.[1,2] The irradiation of microwave enhances molecular rotation and creates heat caused by the friction of the molecules. The reactant can be heated quickly and homogeneously from the inside of the system. The microwave hydrothermal reaction has been applied to the synthesis of zeolites[3] and aluminophosphate molecular sieves ($AlPO_4$s), where the effect of the use of microwave heating was found in the preparation of large $AlPO_4$-5 crystals[4] and in rapid synthesis.[1,2] Most of $AlPO_4$s are prepared using organic templates as structure-directing reagents. Template-free synthesis of $AlPO_4$-H1 was reported by Duncan et al.[5] by conventional heating. $AlPO_4$-H1 was considered to be isostructural with VPI-5,[6] which has 18-membered tetrahedral rings. In this study, template-free synthesis

of $AlPO_4$-H1 has been attempted using microwave heating, and the single phase has been efficiently obtained. The adsorption properties of $AlPO_4$-H1 are also studied.

EXPERIMENTAL

Synthesis

Amorphous aluminum hydroxide (Aldrich, 54% Al_2O_3) dispersed in deionized water, orthophosphoric acid and hydrochloric acid were mixed into a suspension in various molecular ratios. The gels without aging were heated using a microwave oven (Shikoku Instrumentation Co. Ltd.) at 125°C for 1 h. The frequency and maximum power of the microwave radiation were 2.45 GHz and 1.5 kW, respectively. The products obtained were centrifuged, washed with deionized water, and dried at room temperature.

Analyses

X-ray powder diffraction (XRD) patterns were measured using graphite monochromated CuK α radiation. Nitrogen adsorption isotherms were measured at liquid nitrogen temperature by a volumetric apparatus. $AlPO_4$-H1 was degassed at 200°C for 3 h in vacuum before the measurement. Adsorption isotherms of water vapor were measured at 25°C by a gravimetric apparatus. Chemical analysis was performed by using an inductively coupled plasma (ICP) spectrometer on the samples dissolved in a mixture of hydrochloric acid and nitric acid solutions.

RESULTS AND DISCUSSION

Synthesis of $AlPO_4$-H1

Table I summarizes the typical preparation conditions examined in this study and the products obtained. The single phase $AlPO_4$-H1 was obtained when the molar ratio of the aluminophosphate gels (Al_2O_3: P_2O_5: HCl: H_2O) was within a range of 1: 0.6–0.8: 0.8–1.2: 50. The chemical analysis revealed that the sample calcined at 800°C had a stoichiometric composition; Al_2O_3 (42.8%), P_2O_5 (56.5%) with an atomic ratio Al/P = 1.06. The selection of the aluminum source is essentially important. The use of boehmite instead of amorphous aluminum hydroxide yielded $AlPO_4$-H4. Duncan et al.[5] obtained $AlPO_4$-H1 by a similar

TABLE I Microwave Synthesis of $AlPO_4$-H1 at 125°C

	Gel compositions (mol)					
Reaction	Al_2O_3	P_2O_5	HCl	H_2O	Time (h)	Products
#1	1.0	0.8	1.2	50	1	H1
#2	1.0	0.6	1.2	50	1	H1
#3	1.0	0.8	0.8	50	1	H1
#4	1.0	0.8	0	50	1	H1, H2
#5	1.0	1.2	1.2	50	1	H4

template-free synthesis but by a conventional heating in furnace. In the conventional heating, the crystallization occurred at a higher temperature of 140°C and required a longer reaction time of 4 h. Note that the crystallization by microwave heating in this study was completed within a shorter reaction time of 1 h at 125°C. The microporous $AlPO_4$-H1 transformed into $AlPO_4$-8 with 14-membered rings on heating at 100°C in air. Under vacuum conditions, $AlPO_4$-H1 was stable at least up to 400°C.

Adsorption Properties

The nitrogen adsorption-desorption isotherm of $AlPO_4$-H1 had a Langmuir surface area of 580 m^2/g. Adsorption-desorption isotherm for water measured at 25°C is shown in Figure 1. The isotherm is very similar to that reported for VPI-5 by Kenny et al.;[7] it had a threshold vapor pressure for adsorption. The total amount of water adsorbed was 0.32 ml/g.

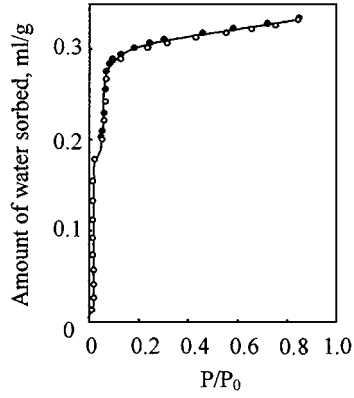

FIGURE 1 Water adsorption-desorption isotherm of $AlPO_4$-H1 measured at 25°C. ○, adsorption; ●, desorption.

CONCLUSIONS

Template-free synthesis method for $AlPO_4$-H1 has been developed using microwave heating. It crystallized at a relatively low temperature and in a short reaction time. The adsorption isotherm for water is comparable with that of VPI-5.

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