INCORPORATION OF ZINC ATOMS INTO GALLOPHOSPHATE MOLECULAR SIEVE

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Abstract Zn-doped gallophosphate molecular sieve with good crystallinity was hydrothermally prepared at 170 °C, and the addition of a small amount of ZnO to the starting gel was found to promote the crystallization process and crystal growth. The characterization by chemical analysis, X-ray diffraction and molecular dynamic simulation suggested the substitution of Zn atoms for Ga atoms in the framework of Zn-doped gallophosphate molecular sieve.

INTRODUCTION

Gallophosphate molecular sieve (denoted as GaPO₄ below) with unique structure was derived from the study on isomorphous replacement of aluminophosphate molecular sieve.¹⁾ Figure 1 shows framework structure of GaPO₄. The framework structure consists of two types of double four-rings, basic structural units, which form α -cages, rpa- cages and three-dimensional channel systems, i. e. 8- and 20-membered ring channels. The 8-membered ring channels with a diameter of about 3.8 Å run through the α - and rpa-cages. The 20-membered ring channels with a diameter of about 13.2 Å are three-dimensionally surrounded by the 8-membered ring channels, and create the supercage with body diagonal of about 30 Å at intersections. As the supercage has unusual-shaped windows due to the presence of terminal hydroxyl groups, gallophosphate molecular sieve was named cloverite after the shape of the window, like four-leafed clover.

The incorporations of transition metals into the framework of zeolites and

aluminophosphate molecular sieves are of great interest in several applications such as shape-selective sorption and catalytic process. Transition metal-substituted GaPO_4 is also of interest in similar applications, because of the existence of unique three-dimensional channel systems in the structure. We have investigated the crystallization field of transition metal-doped GaPO_4 .²⁾ In this paper, we report the preparation of Zn-doped GaPO_4 (denoted as Zn- GaPO_4 below), and the characterization of the resulting compounds by chemical analysis, powder X-ray diffraction (XRD), scanning electron microscopy (SEM), thermal analysis (TG - DTA), and molecular dynamic (MD) simulation.

FIGURE 1 Framework structure of GaPO_4

EXPERIMENTAL

GaPO_4 and Zn- GaPO_4 were hydrothermally synthesized from the starting gels with compositions; $\text{Ga}_2\text{O}_3 \cdot x \text{ZnO} \cdot \text{P}_2\text{O}_5 \cdot \text{HF} \cdot 6 \text{ quinuclidine} \cdot 130 \text{ H}_2\text{O}$ ($0 \leq x \leq 0.22$), referring to previous reports.^{3, 4)} $\text{Ga}_2(\text{SO}_4)_3$ (Aldrich, special grade) and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (Kanto, special grade) were dissolved in distilled water, and H_3PO_4 (Wako, 85 %) was added to the solution with stirring. Then, HF (Wako, 47%) and quinuclidine (Aldrich, special grade) as a template were finally added to the mixture, and the mixed gel was, moreover, stirred to obtain the homogenization. The gel was loaded into a Teflon-lined autoclave, and allowed to react at 170 °C for 0.25 - 24 h. After the hydrothermal treatment, the products were filtered, washed repeatedly with deionized water, and dried at 60 °C.

The resulting materials were examined by XRD, using a Rigaku RINT2000 diffractometer with monochromated $\text{CuK}\alpha$ radiation. The morphologies of the resulting crystals were characterized by SEM, using a JEOL JSM-6300 instrument. TG-DTA was carried out with heating rate of 10 °C/min up to 1000 °C, using a Rigaku TAS-100 instrument. The chemical compositions were analyzed by

electron-probe microanalyzer (EPMA), using a JEOL JXA-733 instrument. The MD simulations were performed, using Cerius2 software (Molecular Simulations Inc.) on a SGI ONIX2 computer.

RESULTS AND DISCUSSION

XRD patterns of the resulting specimens are shown as a function of x , $\text{ZnO} / \text{Ga}_2\text{O}_3$ ratio, in the starting gel in Figure 2. All specimens were basically identified as a GaPO_4 -type with cubic structure. The crystallinity of Zn-GaPO_4 increased, especially the XRD intensity peak at around $2\theta = 3.5^\circ$ increased with increasing $\text{ZnO} / \text{Ga}_2\text{O}_3$ ratio up to $x = 0.14$ in the starting gel. An impurity, however, coexisted with Zn-GaPO_4 in the products obtained from the starting gels with $\text{ZnO} / \text{Ga}_2\text{O}_3$ ratio greater than $x = 0.14$, and the crystallinity of Zn-GaPO_4 decreased. These mean that the addition of a small amount of ZnO to the starting gel yields Zn-GaPO_4 with good crystallinity. After that, Zn-GaPO_4 prepared from the

FIGURE 2 XRD patterns of Zn-GaPO_4 as a function of $\text{ZnO} / \text{Ga}_2\text{O}_3$ ratio in starting gel

FIGURE 3 XRD patterns of GaPO_4 and Zn-GaPO_4 as a function of reaction time

starting gel with $\text{ZnO} / \text{Ga}_2\text{O}_3 = 0.14$ was, therefore, employed in the characterization. The unit cell dimensions estimated from the XRD patterns were $a = 51.97(3)$ and $52.12(4)$ Å for GaPO_4 and Zn-GaPO_4 , respectively. The unit cell of Zn-GaPO_4 significantly expands, compared with that of GaPO_4 . This result suggests that Zn atoms are incorporated into the framework, because the ionic radius of Zn^{2+} ion is larger than that of Ga^{3+} ion.⁵⁾

XRD patterns of GaPO_4 and Zn-GaPO_4 are shown as a function of reaction time in Figure 3. The crystallization rates were quite different from each other. Namely, a trace of GaPO_4 phase was observed in the product treated for 3 h, and then the XRD intensities of GaPO_4 phase gradually increased with elongating reaction time. On the other hand, Zn-GaPO_4 phase already appeared in the product treated for 1 h, and the XRD intensities of Zn-GaPO_4 phase drastically increased in a short reaction time. The crystallization process was found to be accelerated by the addition of ZnO to the starting gel.

SEM microphotographs of GaPO_4 and Zn-GaPO_4 after 24 h treatment are displayed in Figure 4. The crystals of both specimens were quite different in size, although they exhibited typical morphologies, i. e., truncated cubes.³⁾ Zn-GaPO_4 crystals are extremely large and exhibit a morphology of truncated cubes with edge dimension of about 20 μm , compared with GaPO_4 crystals with edge dimension less than 1 μm . This result indicates that the addition of ZnO to the starting gel is effective in promoting the crystal growth.

EPMA showed that atomic ratios estimated were 1.0Ga : 1.0P for GaPO_4 and 0.1Zn : 0.9Ga : 1.0P for Zn-GaPO_4 , respectively. Namely, it is suggested that about 10 % of Ga atoms in the framework of GaPO_4 are replaced with Zn atoms. This suggestion is consistent with the expansion of unit cell in Zn-GaPO_4 .
Quinuclidine molecules

Figure 4 SEM microphotographs of GaPO_4 and Zn-GaPO_4 after 24 h treatment

encapsulated in the unique channel systems of GaPO_4 and Zn-GaPO_4 were estimated to be 135 and 168 per unit cell from TG - DTA, respectively. GaPO_4 and Zn-GaPO_4 were collapsed by the heat treatment up to 500 °C, suggesting the presence of quinuclidine was essential to maintain the framework structure.

Next, the MD simulations were performed in order to investigate the locations of Zn atoms, because it is difficult to experimentally clarify the locations of Zn atoms by X-ray Rietveld method. The chemical compositions per unit cell used in the MD simulation were assumed to be $\text{Ga}_{768}\text{P}_{768}\text{O}_{2976}(\text{OH})_{192}\text{F}_{135}\text{Q}_{135}$ (Q: quinuclidine) for GaPO_4 and $\text{Zn}_{77}\text{Ga}_{691}\text{P}_{768}\text{O}_{2976}(\text{OH})_{192}\text{F}_{91}\text{Q}_{168}$ for Zn-GaPO_4 , respectively, considering the results of chemical analyses and the electrical neutrality of unit cell. The framework structure used in the MD simulations was constructed, referring to the previous report.¹⁾ First, the five models (Zn-GaPO_4 1 ~ 5), where Zn atoms individually occupied five crystallographic framework sites for Ga atoms ($\text{Ga1} \sim \text{Ga5}$), as shown in Figure 5, were examined for Zn-GaPO_4 structure. Ga atoms were replaced with Zn atoms, using a disorder module of Cerius2 software, and quinuclidine molecules were loaded into the models by Monte Carlo adsorption simulations at synthetic conditions. After the energies of initial models were minimized on the MD simulations, the configurations of templates were examined by fixing the framework atoms. The simulations of 50,000 steps at interval of 1 ns were carried out at 300 K, using Universal Force Field (UFF) and NTP ensemble.

The resulting total energies and unit cell dimensions of the models on the MD simulations are listed in Table 1. The total energy of Zn-GaPO_4 was anticipated to be much lower than that of

FIGURE 5 Crystallographic framework sites of GaPO_4

TABLE 1 Unit cell dimensions and total energies of structural models by MD simulations at 300 K

Models	a (Å)	Total energy (kJ mol ⁻¹)
GaPO_4	52.71	3.77×10^5
Zn-GaPO_4 1	52.77	3.52×10^5
Zn-GaPO_4 2	52.77	3.56×10^5
Zn-GaPO_4 3	52.79	3.50×10^5
Zn-GaPO_4 4	52.87	3.81×10^5
Zn-GaPO_4 5	52.76	3.71×10^5
Zn-GaPO_4 6	52.84	3.48×10^5
Zn-GaPO_4 7	52.83	3.58×10^5

GaPO₄, since the doping Zn atoms promote the crystallization process. Although the total energy of Zn-GaPO₄3 model was lowest, the unit cell dimension hardly expanded. Accordingly, new models were made by locating Zn atoms evenly at Ga1 and 3 sites for Zn-GaPO₄6, and by locating Zn atoms evenly at Ga1, 2 and 3 sites for Zn-GaPO₄7, respectively, considering the total energies of Zn-GaPO₄1 ~ 3 models were lower than that of GaPO₄ model. The MD simulation of Zn-GaPO₄6 model resulted in a larger unit cell expansion and a lower total energy than that of Zn-GaPO₄3 model, whereas the MD simulation of Zn-GaPO₄7 model resulted in a larger unit cell expansion and a higher total energy than that of Zn-GaPO₄3 model, as listed in Table 1. Consequently, Zn-GaPO₄6 model, which indicates that Zn atoms occupy the sites on α -cage and rpa-cage close to α -cage, was selected as the most suitable model for Zn-GaPO₄ structure. The MD simulation of Zn-GaPO₄6 model also revealed the configurations of quinuclidine molecules in the structure. Namely, quinuclidine molecules were located at every corners of the supercage, in the 8-membered ring channels, and furthermore around the terminal OH⁻ groups in the 20-membered ring channels.

In conclusion, the addition of ZnO to the starting gel up to ZnO / Ga₂O₃ = 0.14 was found to promote the crystallization process and bring much larger Zn-GaPO₄ crystals than GaPO₄. The MD simulation of Zn-GaPO₄6 model supported the experimental results, i. e. the crystallization process and unit cell expansion, indicating that Zn atoms were incorporated into the framework of gallophosphate molecular sieve.

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