THERMAL AND OPTICAL PROPERTIES OF MOLECULAR SIEVE $\text{AlPO}_4\text{-5}$ LOADED WITH NITROANILINE ISOMERS

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Abstract Nitroaniline isomers (o-, m-, and p-NA) were loaded in the one-dimensional channels of $\text{AlPO}_4\text{-5}$ by vapor-phase diffusion process, and the resulting materials (o-NA/ $\text{AlPO}_4\text{-5}$, m-NA/ $\text{AlPO}_4\text{-5}$, and p-NA/ $\text{AlPO}_4\text{-5}$) were characterized. The maximum loadings for o-, m-, and p-NA were estimated to be about 1.8, 1.3, and 1.5 molecules per unit cell, respectively. The resulting materials exhibited nonlinear optical properties, and the order of the properties was found to be m-NA/ $\text{AlPO}_4\text{-5}$ < o-NA/ $\text{AlPO}_4\text{-5}$ << p-NA/ $\text{AlPO}_4\text{-5}$ at maximum loadings.

INTRODUCTION

$\text{AlPO}_4\text{-5}$, which is one of aluminophosphate molecular sieve, has one-dimensional 12-membered ring channels with the free diameter value of 7.3 Å in the structure as shown in Figure 1.¹⁾ The one-dimensional channels are available for synthesizing composites of guest molecules, such as pyrrole²⁾ and p-nitroaniline (p-NA)³⁻¹¹⁾, and $\text{AlPO}_4\text{-5}$. The nonlinear optical property, i. e., second harmonic generation (SHG), was found to occur to the inclusion of polar molecules like p-NA within $\text{AlPO}_4\text{-5}$.³⁻⁵⁾ After that, the geometrical

arrangement of p-NA in the channel has attracted attention and vigorously been investigated by spectroscopic techniques and so on;⁶⁻¹¹⁾ nevertheless, it has not been clarified. Moreover, the effects of the encapsulation of nitroaniline isomers on the SHG have been neglected. It was expected to be helpful for the investigation of geometrical arrangement to examine the relation between the magnitude of polarity and SHG intensity.

In this paper, we report the encapsulation of nitroaniline isomers (o-, m-, and p-NA) into the one-dimensional channels of $\text{AlPO}_4\text{-5}$ and the characterization

of resulting materials by XRD, TG-DTA, and FTIR, together with measurement of SHG.

Chemical formula; $(\text{Al}_{12}\text{P}_{12}\text{O}_{48}) \cdot \text{R} \cdot q\text{H}_2\text{O}$
 Space group; P6cc
 Cell parameters; $a=13.7$, $c=8.4 \text{ \AA}$
 Pore size; 12-ring $7.3 \times 7.3 \text{ \AA}$

FIGURE 1 Framework structure of $\text{AlPO}_4\text{-5}$

EXPERIMENTAL

$\text{AlPO}_4\text{-5}$ was prepared referring to the report by Wilson et al.¹²⁾ Boemite (Shokubai Kasei) and phosphoric acid (85 % Wako) as starting materials and tri-n-propylamine (Pr_3N , Tokyo Kasei) as a template were used in the present work. Boemite was dispersed in deionized water, and phosphoric acid then was added with stirring. After the dropwise addition of Pr_3N , the mixture was stirred further for 1 h to ensure a homogenous reaction gel. The mixed gel with composition of $\text{Al}_2\text{O}_3 : \text{P}_2\text{O}_5 : \text{Pr}_3\text{N} : 150\text{H}_2\text{O}$ was put into a teflon-lined autoclave, and heated at 170°C for 48h. The resulting products were washed repeatedly with deionized water, and dried at 60°C .

$\text{AlPO}_4\text{-5}$ was calcined at 750°C for 2 h to eliminate template prior to the encapsulation of guest molecules. $\text{AlPO}_4\text{-5}$ and nitroaniline were weighted into respective glass ampoules, which were connected to a vacuum line. After zeolitic water was removed at 200°C under 0.02 Pa for 5 h, nitroaniline guests were loaded by vapor-phase diffusion process for 12 h. $\text{AlPO}_4\text{-5}$ was allowed to contact with o-NA at about 110°C , m-NA at

about 125°C, and p-NA at about 150°C, respectively, considering respective melting point under atmospheric pressure. The loading was controlled by the amount of nitroaniline sealed in a glass ampoule.

XRD patterns were taken with a Rigaku RAD-IIC diffractometer using monochromated $\text{CuK}\alpha$ radiation. TG-DTA was made up to 1000°C with a Rigaku TAS-100 instrument. FTIR spectra by KBr methods were recorded with a JASCO FT/IR 350 spectrometer. SHG intensities relative an urea reference were measured by the powder technique, using a Q-switched Nd: YAG laser ($\lambda = 1064 \text{ nm}$).

RESULTS AND DISCUSSION

XRD revealed that $\text{NA}/\text{AlPO}_4\text{-5}$, whose color was yellow, maintained the $\text{AlPO}_4\text{-5}$ structure, and there were no peaks caused by nitroaniline. FTIR spectra before and after encapsulation of nitroaniline are shown in Figure 2. Each spectrum after the encapsulation showed characteristic absorption peaks of respective guest molecule in the range from 1800 to 400 cm^{-1} . In addition, the absorption bands based on hydrogen bonds between molecules were observed at about 3400 cm^{-1} , and the intensities decreased with decreasing amount of loading. The results of XRD and FTIR suggested that o-, m-, and p-NA were incorporated in the one-dimensional channels of $\text{AlPO}_4\text{-5}$.

TG-DTA curves of $\text{NA}/\text{AlPO}_4\text{-5}$ are shown in Figure 3. Endothermic peaks at about 100°C were attributed to the elimination of adsorbed water molecules. The weight losses in the range 150 to 700°C were assigned to the combustion of occluded nitroaniline, showing the exothermic peaks at around 300 and 520°C. TG-DTA revealed that the thermal stability of nitroaniline fixed tightly in the channel was very high. Endothermic peaks were observed in the range from 200 to 300°C on the DTA curves of specimens with loadings greater than about 15, 10,

FIGURE 2 FTIR spectra of $\text{AlPO}_4\text{-5}$ before and after encapsulation of nitroaniline.

and 12 mass% for o-, m-, and p-NA, respectively. These peaks were considered to be due to the desorption of excess nitroaniline on the surface of $\text{AlPO}_4\text{-5}$ crystals. The maximum amounts of o-, m-, and p-NA encapsulated in the one-dimensional channels were, therefore, estimated to be about 15, 10, and 12.0 mass%, namely 1.8, 1.3, and 1.5 molecules per unit cell, respectively. The amount of p-NA fixed in the channel was consistent with the previous results.³⁻⁵⁾ Provided that nitroaniline molecules were aligned along the channel, the numbers of o-, m-, and p-NA encapsulated were calculated to be 1.5, 1.4, and 1.1 molecules per unit cell. Consequently, nitroaniline molecules were supposed to be stuffed on the tilt.

The measured SHG intensities of $\text{NA}/\text{AlPO}_4\text{-5}$ as a function of loading in $\text{AlPO}_4\text{-5}$ are shown in Figure 4. The SHG signals of o- and m- $\text{NA}/\text{AlPO}_4\text{-5}$ were observed, suggesting that these materials also had nonlinear optical properties similar to p- $\text{NA}/\text{AlPO}_4\text{-5}$, though the SHG intensities were weak. The SHG threshold of p- $\text{NA}/\text{AlPO}_4\text{-5}$ was estimated to be about 4 mass% loading, and the SHG intensity drastically increased to the saturation at about 8 mass% loading. The SHG intensity of o- $\text{NA}/\text{AlPO}_4\text{-5}$ gradually increased with increasing

FIGURE 3 TG-DTA curves of $\text{NA}/\text{AlPO}_4\text{-5}$

FIGURE 4 SHG intensities of $\text{NA}/\text{AlPO}_4\text{-5}$ as a function of loading in $\text{AlPO}_4\text{-5}$

amount of loading, and was saturated at about 8 mass% loading. The SHG intensity of p-NA/ $\text{AlPO}_4\text{-5}$ was much stronger than that of o-NA/ $\text{AlPO}_4\text{-5}$. The SHG intensity of m-NA/ $\text{AlPO}_4\text{-5}$ was weak, and the dependence of the SHG on loading was hardly observed. From the results, the order of SHG intensities was found to be m-NA/ $\text{AlPO}_4\text{-5}$ < o-NA/ $\text{AlPO}_4\text{-5}$ << p-NA/ $\text{AlPO}_4\text{-5}$ at maximum loadings. Although it is known that the SHG intensity is proportional to square of hyperpolarizability on a molecule,¹³⁾ the order of the measured SHG intensities was incompatible with that of hyperpolarizabilities on nitroaniline molecules, o-NA < m-NA < p-NA. The SHG intensity was, therefore, guessed to be considerably governed by the geometrical arrangement of nitroaniline molecules in the channel.

The geometrical arrangements of o-, m-, and p-NA in the one-dimensional channels were constructed by a computer simulation based on the molecular dynamic method in order to speculate the occurrence of SHG. The simulation was performed on the simulation system of HyperChem Ver. 4.0 (Hypercube Inc., Canada). The molecular dynamic simulation was based on the MM2 + force field. The force field parameter of Si atom was used instead of that of P atom, because that of P atom for inorganic compounds was not supported in the software. All the atoms of $\text{AlPO}_4\text{-5}$ host were fixed in the process, while those of nitroaniline molecules were moved freely without restriction. The step interval for the simulation was set to be 1 fs. The resulting geometrical arrangements by the simulation are shown in Figure 5. The results revealed that some of nitroaniline molecules were oriented in the one-dimensional channels, and the overall hyperpolarizabilities were directed in the one way. It was probably necessary to create the suitable force field parameter of P atom and to simulate larger structural models in order to obtain the geometrical arrangements further corresponding to the experimental results.

In conclusion, $\text{AlPO}_4\text{-5}$ loaded with nitroaniline isomers exhibited nonlinear optical properties, and nitroaniline molecules were considered to be self-assembled with a certain

FIGURE 5 Geometrical arrangements of nitroaniline molecules in the channel by simulation. Arrow represents direction of hyperpolarizability.

of the orientation in the one-dimensional channels.

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