

Preparation of new organic-inorganic nanocomposites by the reaction of Zn(OH)₂ and organic compounds

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Organic-inorganic nanocomposite was obtained by the reaction of Zn(OH)₂ with benzoic acid. The interlayer spacing of the composite was 1.49nm. The composite was fibrous compound which was confirmed by SEM images. To concentrate α -pinene in organic solution, obtained nanocomposites were used as organic solvent adsorbents. By adding 0.1g of the nanocomposite to α -pinene toluene, pentane or heptane solution, concentration of α -pinene increased from 0.266 to 0.338g/ml in the case of toluene solution, 0.384 to 0.528 g/ml in the case of pentane solution and 0.301 to 0.347g/ml in the case of heptane solution. It indicated the occurrence of selective adsorption of solution of compared to α -pinene.

Key words: organic-inorganic nanocomposite, fibrous compound, organic solvent adsorbent, α -pinene

1. INTRODUCTION

We have already reported that the reaction of Zn(OH)₂ with organic carboxylic acid gave organic-inorganic nanocomposites by self-assembly reaction.^{1) 2)} The reaction product was fibrous layered compound, when organic compounds were bulky. In this study we prepared surface modified inorganic layer compounds by the reaction of Zn(OH)₂ with benzoic acid. α -pinene was extracted by hexane in industry. Hexane was removed by evaporation. If selective adsorption of organic solvent was possible, it does not need heating process to remove hexane by evaporation. In this study to concentrate α -pinene in organic solution, organic-inorganic nanocomposites obtained in this study were used as organic solvent adsorbents.

2. EXPERIMENTAL

2.1. Preparation of Zn(OH)₂

Zn(OH)₂ was prepared by the following method. A solution containing Zn(NO₃)₂ · 6H₂O in deaerated water was added over 0.5 h to stirred

deaerated water containing NaOH at 277K. The reactant was filtered and washed. The resulting white solid was dried at 333K.

2.2. Preparation of fibrous compound

Zn(OH)₂ and benzoic acid were reacted at 333K for 5h in acetonitrile (ACN). After the reaction, the product was filtered and washed with ACN to remove unreacted acid. After then the product was dried under reduced pressure.

2.3. Characterization

X-Ray powder diffraction (XRD) data were collected on a Rigaku powder diffractometer, using CuK α radiation at 40kV and 20mA between 1.8 and 50°. FT-IR spectra were recorded on samples pressed into KBr disks using a Horiba FT-200. Thermal analyses (TG/DTA) of samples were performed on a Seiko SSC5000 thermal analysis system (heating rate: 10K/min, in the flow of N₂). The morphology and microstructure of the samples were examined using a scanning electron microscope (SEM).

2.4. Adsorption of organic solvent by nanocomposite

Fibrous nanocomposite was suspended in α -pinene organic solution, and filtrate was analyzed by GC-14.

3. RESULTS AND DISCUSSION

3.1 Preparation of organic-inorganic nanocomposite

The XRD patterns of $Zn(OH)_2$ and reaction product of $Zn(OH)_2$ with benzoic acid are shown in Fig1 (b). New peaks in XRD appeared by the reaction with benzoic acid. The d value of the reaction product of $Zn(OH)_2$ with benzoic acid was 1.49nm suggesting that the product was not zinc benzoate and benzoic acid. The IR spectra of $Zn(OH)_2$ and the reaction product of $Zn(OH)_2$ with benzoic acid were shown in Fig2. OH absorption at near 3500cm^{-1} for $Zn(OH)_2$ fairly decreased by the reaction with benzoic acid and new absorption peaks at near 1550cm^{-1} and 1390cm^{-1} appeared. The peaks at 1550cm^{-1} and 1400cm^{-1} were assigned

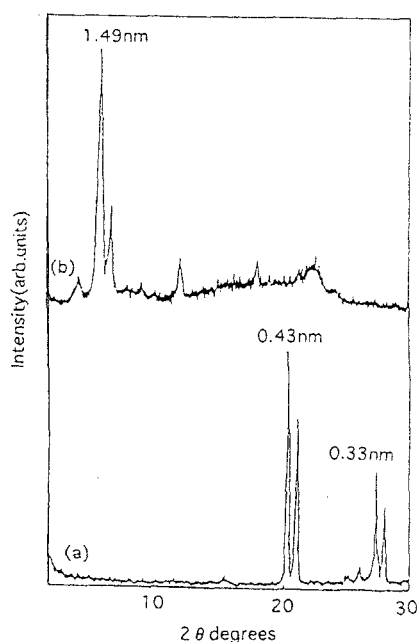


Figure 1 XRD patterns of (a) $Zn(OH)_2$ and (b) the reaction product of $Zn(OH)_2$ with benzoic acid

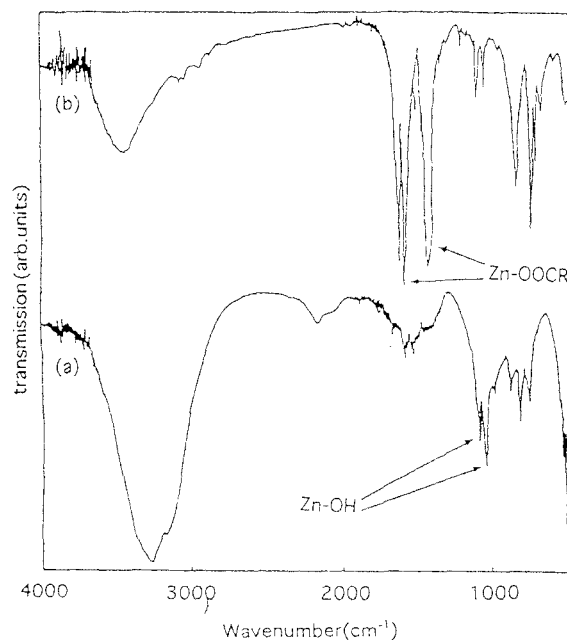


Figure 2 IR spectra of (a) $Zn(OH)_2$ and (b) the reaction product of $Zn(OH)_2$ with benzoic acid

to the symmetric stretching vibration of carboxylate. These two peaks indicate the formation of COO-Zn bond. The IR absorption peaks of benzoic acid were not observed. These results indicate that $Zn(OH)_2$ reacted with benzoic acid giving organic-inorganic nanocomposite in which benzoic acid reacted with Zn-OH giving RCOO-Zn bond. The thermal behavior of $Zn(OH)_2$, benzoic acid and obtained organic-inorganic nanocomposite were measured by TG/DTA. 13% weight of $Zn(OH)_2$ decreased up to 393K , suggesting the evolution of absorbed water. TG analysis of benzoic acid alone shows that weight loss occurred at between 365 and 450K . In contrast, weight loss of the reaction product of $Zn(OH)_2$ with benzoic acid was observed at between $580 \sim 750\text{K}$, and was more thermally stable than that of benzoic acid. CHN elemental analyses gave empirical formula represented as $Zn(OH)_{0.95}(-\text{OOC-C}_6\text{H}_5)_{1.05}$ indicating that about

50% of OH groups reacted with benzoic acid. SEM images indicating the microstructures of Zn(OH)₂ and obtained organic-inorganic nanocomposite. Although Zn(OH)₂ was plate-like structure, obtained organic-inorganic nanocomposite was fiber-shape structure.

3.2. Adsorption of organic solvent

We confirmed that obtained fiber-shaped compounds adsorbed organic solvent. Fiber-shape nanocomposite into tea-pack like bag was suspended in organic solvent. After 30 minutes, bag was weighted as shown in Fig3. It indicated obtained fiber-shape composite retained hexane, and adsorbed hexane. By adding 0.1g nanocomposite to α -pinene toluene, pentane or heptane solution, concentration of α -pinene increased from 0.266 to 0.338g/ml in the case of toluene solution, 0.384 to 0.528g/ml in the case of pentane solution and 0.301 to 0.347g/ml in the case of heptane as shown in Fig4. Immediately α -pinene and organic solvent were adsorbed with fiber-shaped compound as shown Fig5. It indicated the occurrence of selectional adsorption of organic solution of solvent compared to α -pinene.

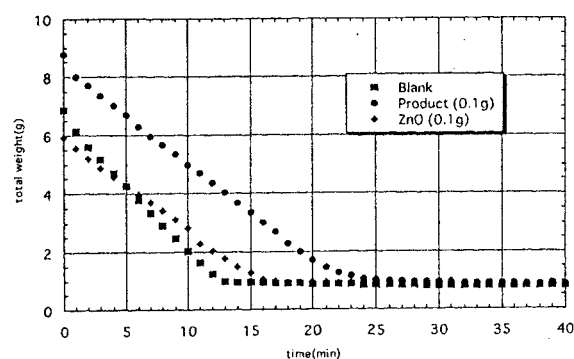


Figure3 Adsorption of hexane

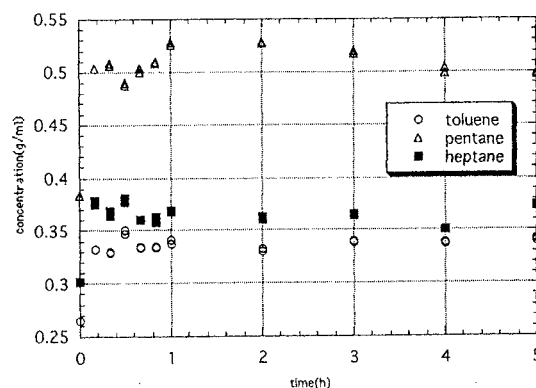


Figure4 Concentration of α -pinene \circ in toluene \triangle in pentane \blacksquare in heptane with benzoic acid derivative organic inorganic nanocomposite

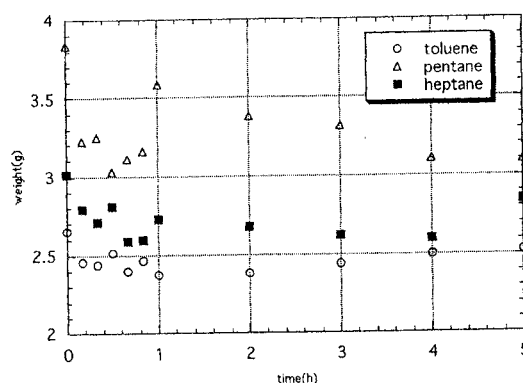


Figure5 Weight of α -pinene \circ in toluene \triangle in pentane \blacksquare in heptane in heptane with benzoic acid derivative organic inorganic nanocomposite

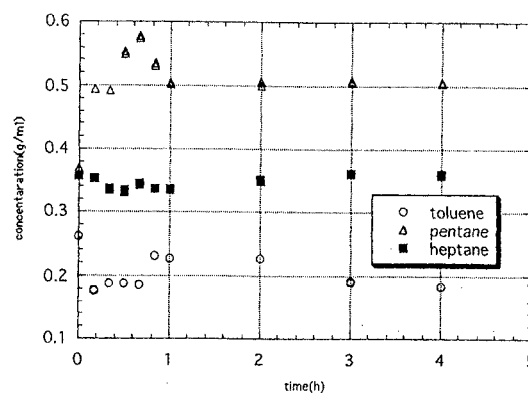


Figure6 Concentration of α -pinene \circ in toluene \triangle in pentane \blacksquare in heptane with cyclohexanecarboxylic acid derivative organic inorganic nanocomposite

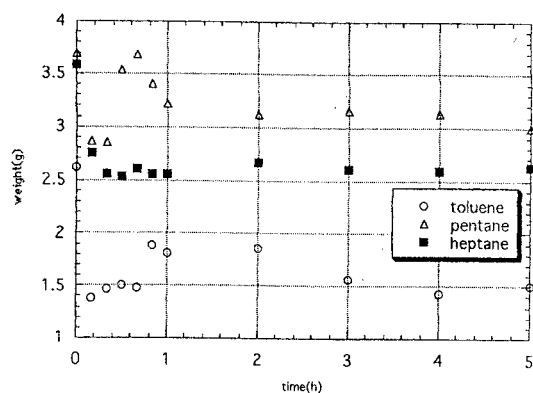


Figure 7 Weight of α -pinene \circ in toluene \triangle in pentane \blacksquare in heptane in heptane with cyclohexanecarboxylic acid derivative organic inorganic nanocomposite

But cyclohexanecarboxylic acid derivative organic-inorganic nanocomposites were used as organic solvent adsorbents. concentration of α -pinene decreased from 0.262 to 0.176g/ml in the case of toluene solution, 0.369 to 0.508 g/ml in the case of pentane solution and 0.358 to 0.331g/ml in the case of heptane as shown in Fig6. Immediately α -pinene and organic solvent were adsorbed with fiber-shaped compound. And adsorption rate was α -pinene more rapidly than organic solvent. Therefore α -pinene weight went temporarily up and down as shown Fig7. It indicated the occurrence of selectional adsorption of α -pinene solution of solvent compared to α -pinene.

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