Journal of Korean Association of Crystal Growth
Vol. 8, No. 4 (1998) 651-654

Synthesis and characterization of layered basic zinc p-toluenesulfonates

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층상구조의 염기성 zinc p-toluenesulfonate의 합성 및 성질에 관한 연구

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Abstract The layered basic zinc p-toluenesulfonates has been directly synthesized by the surface modification. The chemical formula of layered basic zinc p-toluenesulfonate is determined by CHNS and TG-DTA. From the X-ray diffraction data and the guest size, the orientation of the p-toluenesulfonate onto the zinc hydroxide layer is determined. The molecular plane of the p-toluenesulfonate lies perpendicular to the zinc hydroxide layers.

요 약 층상구조의 염기성 zinc p-toluenesulfonates를 표면변형법으로 직접 합성하였다. CHNS와 TG-DTA를 통해서 화합물의 화학적 조성을 결정하였다. X-선 회절 데이타와 분자의 크기로부터 수산화 아연층에 결합된 p-toluenesulfonate의 공간배열을 확인한 결과 p-toluenesulfonate의 분자 평면은 수산화아연층에 수직되게 결합하고 있음을 확인하였다.

1. Introduction

Layered inorganic solids have been of interest in a variety of areas due to their adsorptive and catalytic properties [1, 4]. These materials are essentially two dimensional in character in the sense that the bonding forces within the layers are much stronger than those between layers. These materials exhibit the ability to exchange or intercalate organic molecules [5, 7]. This fact allows neutral molecules or charged species to be intercalated into the interlayer space and thus permits the manipulation of these intercalates in such a fashion as to create new structures. Therefore, the layered inorganic-organic hybrid materials can be synthesized by intercalating organic molecules into the interlayers of layered inorganic materials [8, 10]. Among the various classes of layered inorganic solids, layered double hydroxides (LDHs) are suited for intercalating organic anions. LDHs consist of layers of M^{2+} and M^{3+} coordinated octahedrally by six oxygen atoms, as hydroxides. The substitution of M^{3+} into the position of the M^{2+} in the layers creates the positively charged layers. Exchangeable anions located in the interlayer spaces compensate for the positive charged layers. Many studies on the preparations and applications of LDHs have been extensively performed [11, 16]. They are used as adsorbents, catalysts, catalyst precursors, anionic exchangers and antacid drugs [17, 20].

There are many reports on the intercalation of organic anions into the LDH with the main synthetic route via anionic exchange. However, it is very difficult to graft organic functional groups onto closely packed atom layer surface such like LDHs. Among a number of layered compounds, only zirconium phosphate can be easily grafted by the tips of phosphate group reacting with functional organic groups [21, 23]. Grafting of organic anions onto the LDH or metal hydroxide layer has scarcely been studied. Chiba *et al.* recently reported the new surface modified inorganic layered compounds in which metal hydroxide and LDH were reacted with an organic oxychloride [24, 25]. In the present work we report on the synthesis of a layered basic zinc p-toluenesulfonate by grafting organic p-toluenesulfonate group onto the zinc hydroxide surface. The product differs from the anion exchanged LDH because this does not need to include any anionic compounds between the layers. The method of layered basic zinc p-toluenesulfonate in this study will be simple synthesizing method of layered solids with alternating inorganic and organic layers.

2. Experimental

The layered zinc p-toluenesulfonate was synthesized by the reaction of amorphous 0.033 M $Zn(OH)_2$ with 0.087 M p-toluenesulfonic acid in water, whose pH is adjusted with 1.0 M NaOH solution. The precipitate was aged at 60℃ for 4 days, filtered, washed with decarbonated water and air dried at 80℃ for 24 hours. Chemical analysis for the organic content of product was determined using a Vario EL CHNS analyzer. X-ray diffraction pattern was obtained with a Rigaku diffractometer using Cu-Kα radiation. The thermal behavior of the layered basic zinc p-toluenesulfonate was obtained with TA instruments SDT-2960 TG-DTA apparatus at heating rate of 5℃/min under a flow of argon.

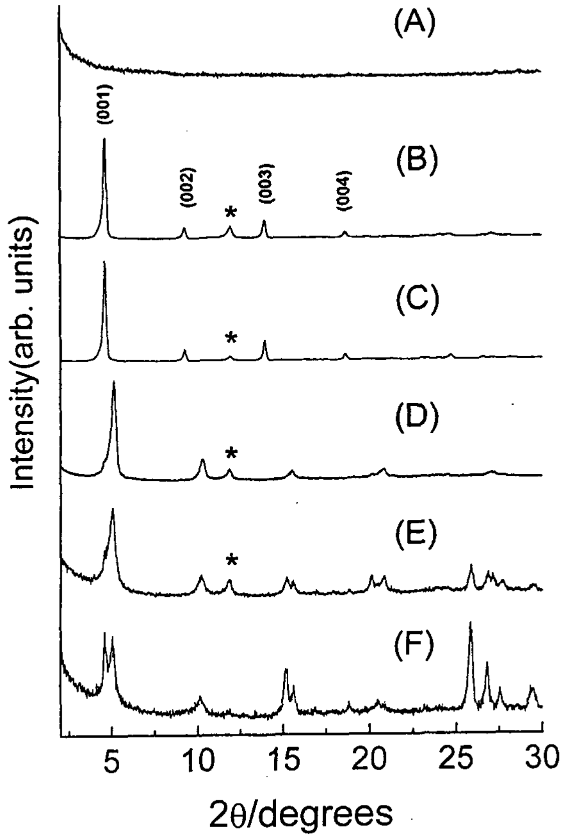

Fig. 1. X-ray diffraction spectra of (A) $Zn(OH)_2$ and $Zn(OH)_{2-X}(O_3SC_6H_4CH_3)_X \cdot mH_2O$ at (B) pH=6.5, (C) pH=7.0, (D) pH=8.0, (E) pH=9.2, and (F) pH=10.0.

3. Results and Discussion

The layered basic zinc p-toluenesulfonate, $Zn(OH)_{2-X}(O_3SC_6H_4CH_3)_X \cdot mH_2O$, was directly synthesized by the reaction of the mixture of $Zn(OH)_2$ and p-toluenesulfonic acid in water, whose pH was adjusted with NaOH solution. Figure 1 shows the X-ray diffraction patterns of amorphous $Zn(OH)_2$ and layered $Zn(OH)_{2-X}(O_3SC_6H_4CH_3)_X \cdot mH_2O$ at various pH values. Figure 1(A) displays the X-ray diffraction patterns of amorphous $Zn(OH)_2$. No clear peaks were observed in the XRD of $Zn(OH)_2$. Figure 1(B) shows the X-ray diffraction pattern of $Zn(OH)_{2-X}(O_3SC_6H_4CH_3)_X \cdot mH_2O$ at pH = 6.5. It shows the characteristic X-ray diffraction pattern of the layered crystalline compound. The basal spacing of the layered basic zinc p-toluenesulfonate corresponds to the distance between adjacent zinc hydroxide layers. The basal spacing was calculated to be 19.3 Å from averaging of the positions (001), (002) and (003) peaks. Figure 1(C), 1(D), 1(E), and 1(F) show the X-ray diffraction spectra of the layered basic zinc p-toluenesulfonate at the pH values of 7.0, 8.0, 9.2, and 10.0, respectively. In the lower pH regions up to pH = 7.0, layered crystalline compounds were synthesized with the basal spacing of 19.3 Å. The asterisked peak at $2\theta = 11.9$ is the unidentified diffraction peak of the layered basic zinc p-toluenesulfonate. As increasing the pH, less crystalline compounds were obtained with the dual basal spacings of 19.3 Å and 17.2 Å. The structure for the basal spacing of 17.2 Å is thought to be another form of the basic zinc p-toluenesulfonate, which is still under investigation. Therefore, the best layered crystalline basic zinc p-toluenesulfonate was obtained at pH = 7.0.

The content of organic p-toluenesulfonate in the $Zn(OH)_{2-X}(O_3SC_6H_4CH_3)_X \cdot mH_2O$ was estimated by CHNS elemental analysis. From chemical analysis, the content of organic p-toluenesulfonate, x, of $Zn(OH)_{2-X}(O_3SC_6H_4CH_3)_X \cdot mH_2O$ at pH values of 6.5, 7.0, 8.0, 9.2, and 10.0 are 0.20, 0.27, 0.19, 0.14, and 0.09, respectively. The x values decreased with

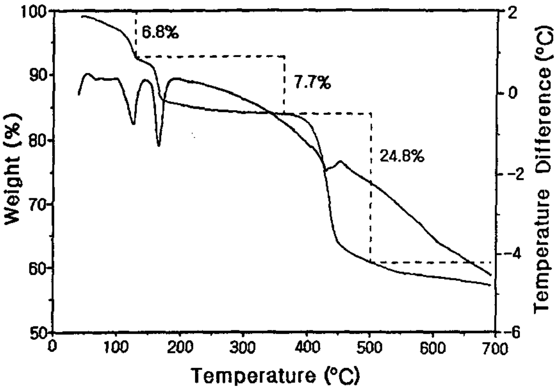

Fig. 2. TG and DTA of $Zn(OH)_{1.73}(O_3SC_6H_4CH_3)_{0.27} \cdot 0.72H_2O$.

increasing pH value, except for the product prepared at pH = 6.5. Because of steric repulsion, only 13 % of the hydroxy groups are substituted with organic p-toluenesulfonate at pH = 7.0.

Thermal decomposition behavior of the product was determined by TG-DTA as shown in Fig. 2. The endothermic peak at 125°C corresponds to desorption of water on the surface, and another peak at 170°C can be ascribed to the desorption of interlayer water of the layered product. The last peak at 435°C may be due to the complete thermal decomposition of organic p-toluenesulfonate and the liberation of structural water from the layered hydroxides. It reveals that the layered structure collapses at this temperature. The amount of the interlayered water for the $Zn(OH)_{1.73}(O_3SC_6H_4CH_3)_{0.27} \cdot mH_2O$ was estimated by the second peak. The content of water, m, is 0.72. Therefore, the typical chemical formula of the layered basic zinc p-toluenesulfonate can be written as $Zn(OH)_{1.73}(O_3SC_6H_4CH_3)_{0.27} \cdot 0.72H_2O$.

From the X-ray diffraction study, the orientation of the grafted organic species can be roughly estimated. The size of the p-toluenesulfonate was calculated by using Alchemy program. The length of the p-toluenesulfonate is 9.6 Å, when the van der Waals radii of oxygen and hydrogen are to assumed to be 1.4 Å and 1.2 Å, respectively [26]. The basal spacing from the monolayer structure of the product is 14.4 Å when the thickness of the $Zn(OH)_2$ (4.8 Å) is simply added [27]. Since a part of the oxygen atom in p-toluenesulfonate anion was buried in the hydroxide layer, the estimated basal spacing of the product is less than 14.4 Å, whereas the measured basal spacing is 19.3 Å. The measured basal spacing is much larger than that of the monolayer type structure. However, most of intercalated compouds of LDH have the monolayered structures, the product may be the monolayered one. Moreover, the amount of substituted p-toluenesulfonate onto the layered hydroxides is too small to form the bilayerd structure. The product incorporates significant amount of interlayer water. Therefore, the basal space is occupied by p-toluenesulfonate and interlayer water. Schematic illustration of layered basic zinc p-toluenesulfonate is shown in Fig. 3.

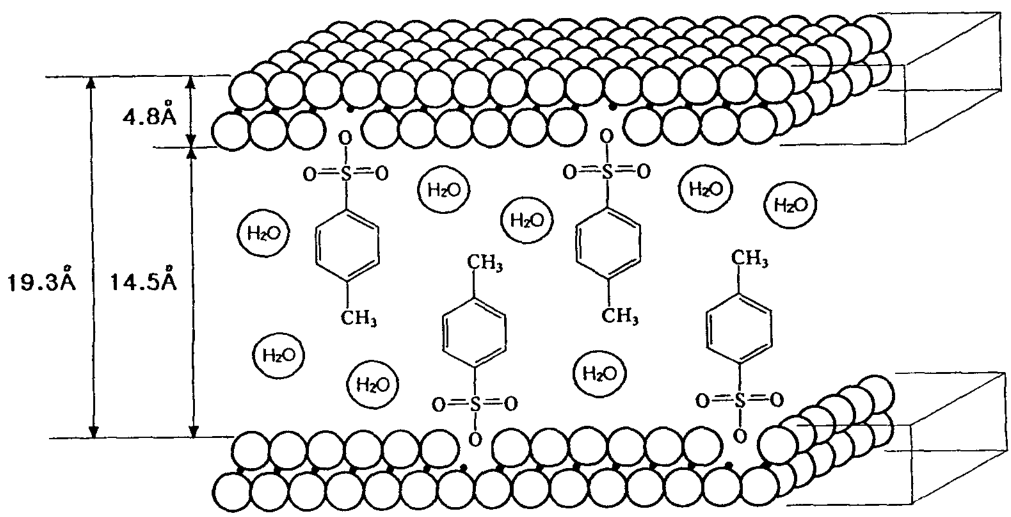

Fig. 3. Schematic illustration of the orientation of $Zn(OH)_{1.73}(O_3SC_6H_4CH_3)_{0.27} \cdot 0.72H_2O$. (○; OH layers, ●; Zn).

4. Conclusions

We synthesized the layered basic zinc p-toluenesulfonates by reaction of amorphous $Zn(OH)_2$ with p-toluenesulfonic acid with NaOH at various pH values. The typical chemical formula of layered basic zinc p-toluenesulfonate, $Zn(OH)_{1.73}(O_3SC_6H_4CH_3)_{0.27} \cdot 0.72H_2O$, was determined by CHNS and TG-DTA. From the X-ray diffraction data, the orientation of the p-toluenesulfonate onto the zinc hydroxide layer was determined. The molecular plane of the p-toluenesulfonate lies perpendicular to the zinc hydroxide layers.

Acknowledgment

This research was supported financially by the grant of Dankook University.

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