

Stereoselective Intercalation of Hexose for Layered Double Hydroxide by Calcination-Rehydration Reaction

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The intercalation of four kinds of hexose for Mg–Al layered double hydroxide (LDH) by the calcination–rehydration reaction using the Mg–Al oxide precursor has been investigated. In spite of non-ionized organic guest, hexose was intercalated for the LDH, and the intercalation behavior of hexose was greatly influenced by the number of axial OH group. The intercalation driving force was thought to be based on hydrogen bond between axial OH group of the intercalated hexose and hydroxide basal layer.

One of the 2-D layered compounds, LDH has an anion exchange property and is so-called an anionic clay or hydrotalcite-like compound. The general formula of LDH is represented by $[M^{2+}_{1-x}M^{3+}_x(OH)_2][A^{n-}_{x/n} \cdot yH_2O]$, where M^{2+} , and M^{3+} represents metallic cations such as Mg^{2+} , Ni^{2+} , Mn^{2+} or Zn^{2+} and Al^{3+} , Cr^{3+} , or Fe^{3+} , etc., and A^{n-} is exchangeable inorganic or organic anion. x value is a charge density of LDH basal layer and equal to the molar ratio of $M^{3+}/(M^{2+} + M^{3+})$.¹ Recently, LDH has received considerable interests due to their potential technological applications such as catalysts, electrode, optical memory, sensitizer, separator, and for synthesis of new organic–inorganic nanocomposite.^{2–6} In particular, the intercalation of biomolecule for LDH such as pentose, nucleotide, deoxyribonucleic acid, amino acid, and polypeptide has been investigated in order to prepare the biomolecule/LDH nanocomposites.^{7–14}

Sugar is widely known as a component of nucleotide, and the intercalation of non-ionized organic guest such as sugar for LDH is new approach for the synthesis of organic–inorganic nanocomposite. We have reported the intercalation of pentose, ribose and deoxyribose, for the Mg–Al LDH by the calcination–rehydration reaction.¹⁵ In this paper, we describe the stereoselective intercalation of non-ionized organic guest, hexose (fructose, glucose, mannose, and galactose), to the Mg–Al LDH by the same manner.

The Mg–Al carbonated LDH (CO_3 /LDH), $Mg_{0.75}Al_{0.25}(OH)_2(CO_3)_{0.13} \cdot 0.66H_2O$, was prepared following the standard coprecipitation described by Miyata.¹⁶ The CO_3 /LDH was calcined at 773 K for 2 h to prepare the Mg–Al oxide precursor. In the test for the intercalation of hexose, 50 cm³ of hexose aqueous solution with various concentrations was placed in a 100-cm³-Erlenmeyer flask together with 0.2 g of the Mg–Al oxide and shaken in a water-bath set at 298 K for 24–144 h under nitrogen atmosphere. Hexose concentrations before and after the intercalation were measured using a Shimadzu TOC-5000 total organic carbon analyzer.

First, the time dependence of the amount of fructose and glucose intercalated is shown in Figure 1. The amount of hexose intercalated was increased continuously until the equilibrium was reached after 48 h. The maximum amount of fructose and

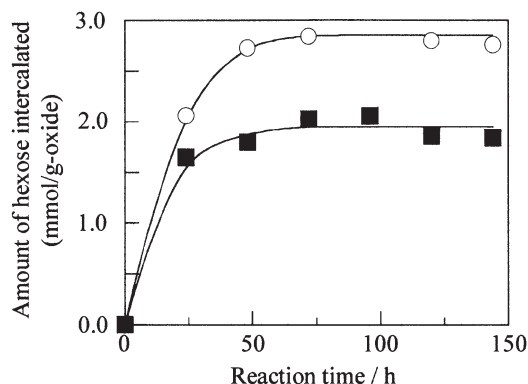


Figure 1. Time dependence of amount of fructose and glucose intercalated by Mg–Al oxide precursor in 50 mmol/dm³ solution. (○) fructose and (■) glucose.

glucose intercalated is 2.84 and 1.86 mmol/g-oxide, respectively. In general, LDH is known to intercalate easily the anions having high charge density into its interlayer space. However, the intercalation of hexose was also observed in spite of non-ionized guest. This result confirms that LDH has an ability to intercalate the non-ionized organic guest.

The amount (X/M) of hexose intercalated was determined at various initial concentrations, and the result is shown in Figure 2. The amount of hexose intercalated was increased with an increase in equilibrium concentration of hexose solution. In all the cases, the Freundlich isotherm (1) was applicable.

$$\log(X/M) = 1/n(\log C) + \log k \quad (1)$$

X (mmol) is the amount of hexose intercalated, M (g-oxide) is the amount of the Mg–Al oxide, C (mmol/dm³) is equilibrium concentration of hexose solution, k (mmol/g-oxide) and n (–) are constants. The k and n values were estimated from the intercept and slope of the isotherms, and these values are indicated in Table 1. The amount of hexose intercalated was as follows: fructose > mannose ≈ galactose > glucose. This result indicates that fructose was preferentially intercalated approximately 3 times higher than that of glucose. The relationship between the number of axial OH group of hexose is also indicated in Table 1. We described that the amount of ribose intercalated was much

Table 1. Freundlich's constants k and n and number of axial OH group in hexose molecule

Hexose	k (mmol/g-oxide)	n (–)	Number of axial OH group	
			α type	β type
Fructose	3.41	0.89	3	3
Galactose	2.73	0.36	2	1
Mannose	3.01	0.50	2	1
Glucose	1.12	0.23	1	0

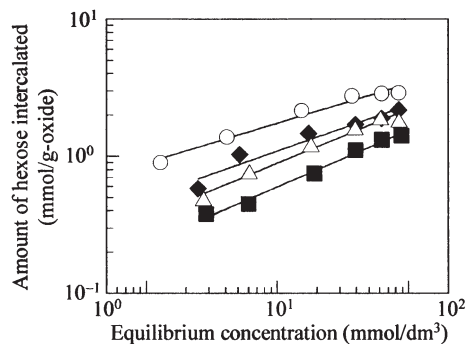


Figure 2. Intercalation isotherms of (○) fructose, (◆) mannose, (△) galactose, and (■) glucose for Mg–Al oxide precursor.

larger than that of deoxyribose. Deoxyribose lacks only C-2 position OH of ribose. This result confirms that the amount of pentose intercalated was influenced by the number of OH group in sugar molecule. The amount of hexose intercalated was increased with an increase in the number of axial OH group, suggesting that the configuration of OH group of hexose is very important for the intercalation of hexose. The equilibrium pH value of hexose solution was found to be between 8 and 10, indicating that the hexose/LDH contains a higher amount of OH^- to compensate the layer positive charge. During the intercalation reaction, the isomerization of hexose is expected with rising pH. Therefore, the supernatant solution was analyzed by using HPLC (RI). The result of HPLC indicates that the isomerization of hexose was hardly occurred.

The XRD patterns of the pristine CO_3/LDH , Mg–Al oxide and resulting solid products are shown in Figure 3. The main diffraction peaks ($d_{003} = 0.78$ and $d_{006} = 0.39$ nm) are observed with the LDH structure (Figure 3a), which values are correspond to the hydrotalcite-like compounds. The LDH structure was destroyed with heating at 773 K for 2 h, which can be seen by the disappearance of d_{003} and d_{006} diffraction peaks (Figure 3b). The broad diffraction peaks are observed with the LDH structure (Figures 3c,d), meaning that the LDH structure is regenerated with rehydration and intercalation reaction. The expanded basal

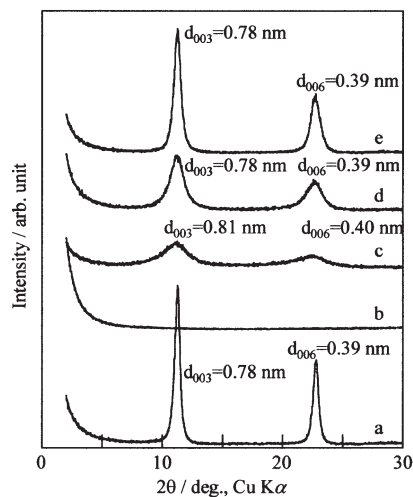


Figure 3. XRD patterns of (a) pristine CO_3/LDH , (b) Mg–Al oxide precursor, (c) fructose/LDH, (d) glucose/LDH, and (e) CO_3/LDH (reconstructed by 50 mmol/dm³ Na_2CO_3 solution).

spacing ($d_{003} = 0.81$ and 0.78 nm) are observed in the fructose/LDH and glucose/LDH. However, the broadness of these peaks suggests that the hexose/LDH does not constitute an organized stacking arrangement, which was attributed to disordered layers of OH^- within the hexose/LDH. As the thickness of LDH basal layer is 0.48 nm, the interlayer space is calculated as 0.33 and 0.30 nm, respectively. In the case of fructose/LDH, this value support that molecular plane of hexose is horizontally oriented to the hydroxide basal layers as shown in Figure 4. The glucose/LDH contained small amount of glucose in the interlayer space. Therefore, the interlayer distance of the glucose/LDH is the same as that of the OH or CO_3/LDH . The FT-IR spectra of the hexose/LDH (data not shown) indicate the weak adsorption peaks of the intercalated hexose at 2930 and 1040 cm^{-1} , characteristic of C–H and C–O stretching in hexose.

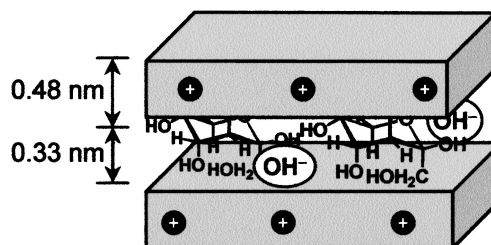


Figure 4. Schematic model of fructose/LDH.

The hexose/LDH can be prepared by the calcination–rehydration reaction. The intercalation driving force of non-ionized hexose is assumed to be the cointercalation of the coexisted anion OH^- with water molecule and the formation of hydrogen bond between hydroxy group of the intercalated hexose and the LDH hydroxide basal layer. We can propose a new method for the intercalation of non-ionized organic guests for LDH. Sugar/LDH nanocomposites would be received considerable attention in the future as environmental and economical materials.

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