

Preparation and Characterization of Layered Double Hydroxide

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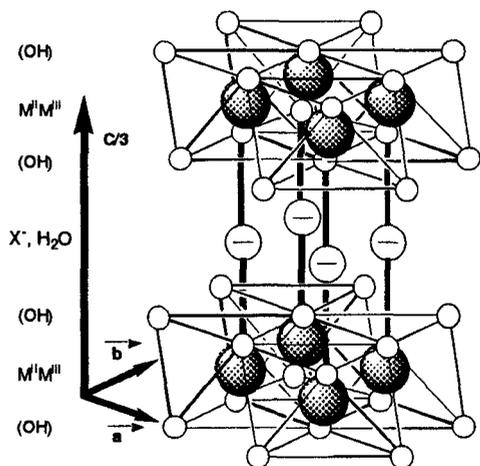
The adsorption properties of Zn-Al layered double hydroxides (LDHs) of gas molecules such as N_2 and CO_2 have been studied. The Zn-Al LDH(CO_3^{2-}) adsorbed CO_2 selectively. And the amount of CO_2 adsorbed into the Zn-Al LDH(CO_3^{2-}) increased with an increase in the Al content. The effect of surface area due to difference of cation radii of Zn^{2+} and Al^{3+} was considered. Also, Zn-Al LDH(OH) adsorbed CO_2 effectively. The Zn-Al LDH(OH) adsorbed CO_2 at high CO_2/N_2 selectivity, and it reached ca.11. It was revealed that the CO_2/N_2 selectivity of the Zn-Al LDH(OH) was higher than the conventional adsorbents such as activate carbon, silica-gel, molecular Sieve3A, and molecular Sieve5A.

Key words: adsorption properties, layered double hydroxides, surface area, adsorbents

1. INTRODUCTION

Layered double hydroxides (LDHs) were known as inorganic layered compounds in the class of clay minerals. An increasing interest exists in LDHs, which has many potential applications such as catalyst, adsorbent, optical, or electronical materials. LDHs can be represented by the formulas $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[A^{m-x/m} \cdot nH_2O]^{x-}$, where $M(II)$ =divalent cation (Ca^{2+} , Mg^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Mn^{2+}), $M(III)$ =trivalent cation (Al^{3+} , Cr^{3+} , Fe^{3+} , Co^{3+} , Mn^{3+}), and A =interlayer anion (Cl^- , NO_3^- , ClO_4^- , CO_3^{2-} , SO_4^{2-}), respectively. Their structures consist of brucite-type layers, $Mg(OH)_2$, in which trivalent metals are partially substituted for divalent metals resulting in a net positive charge, which is balanced by anion located in the interlayer spaces.

Until now, the researches on LDHs were performed largely about intercalation or ion exchange-reaction into layered structure. In this study, the gas adsorption properties of LDH of gas molecules such as N_2 , CO_2 were studied.



Scheme 1. Schematic representation of layered double hydroxide (LDH)

2. EXPERIMENTAL

2.1. Preparation of Zn-Al LDH(CO_3^{2-})

Zn-Al LDH(CO_3^{2-}), $[Zn_{1-x}Al_x(OH)_2]^{x+}[(CO_3)_{x/2}]^{x-}$ (molar ratio; $x=0.24, 0.27, 0.30, 0.33, 0.36, 0.39, 0.42$), were prepared by adding the mixture of $Zn(NO_3)_2$ ($(1-x)/2$ mol/L) and $Al(NO_3)_3$ ($x/2$ mol/L) to a Na_2CO_3 solution, whose pH was kept to ca.10 with a NaOH solution, at 333K for 2h. The precipitate was separated centrifugally, washed and dried for 48hr at 353K.

2.2 Preparation of Zn-Al LDH oxide

Zn-Al LDH oxide, $[Zn_{1-x}Al_xO_{1+x/2}]$, was prepared by calcination of the Zn-Al LDH(CO_3^{2-}) (molar ratio; $x=0.24, 0.27, 0.30, 0.33, 0.36, 0.39, 0.42$) at 773K for 3h.

2.3 Preparation of inorganic anion intercalated LDH, Zn-Al LDH(A^n)

Zn-Al LDH(A^n), $[Zn_{1-x}Al_x(OH)_2]^{x+}[(A^n)_{x/n}]^{x-}$, were prepared by two methods. The molar ratio of the Zn-Al LDH(A^n) were $x=0.30$.

(i) Zn-Al LDH($A^n=SO_4^{2-}, Cl^-, ClO_4^-, Br^-$, or NO_3^-)

The mixture of $Zn(NO_3)_2$ ($(1-x)/2$ mol/L) and $Al(NO_3)_3$ ($x/2$ mol/L) was added to a solution including inorganic anion such as SO_4^{2-} , Cl^- , ClO_4^- , Br^- , NO_3^- . pH of the solution was kept to ca.10 with a NaOH solution at 333K for 2h. The precipitate was separated centrifugally, washed and dried for 48hr at 353K.

(ii) Zn-Al LDH($A^n=OH^-$)

Zn-Al LDH oxide was stirred in deionized water at 333K for 5h. The precipitate was separated centrifugally, washed and dried for 48hr at 353K.

2.4 Gas adsorption procedure

Sample(2g) was treated in 10ml vessel with vacuum for 30min at room temperature. The mixture gas ; N_2+CO_2 (molar ratio =1:1) was injected into the vessel. After 0, 15, 30, 45, 60min, the gas in the vessel was analyzed by gas chromatography. The typical gas adsorption

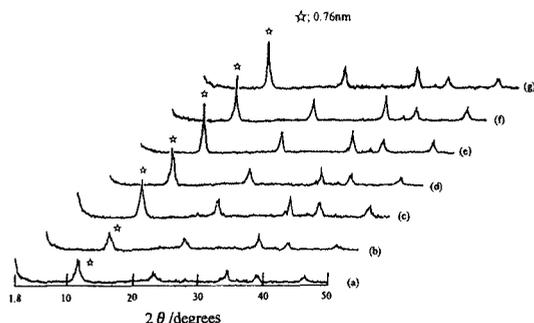


Figure 1. XRD patterns of Zn-Al LDH(CO₃²⁻) whose molar ratios, $x = \text{Al}^{3+}/(\text{Zn}^{2+} + \text{Al}^{3+})$, were (a)0.24, (b)0.27, (c)0.30, (d)0.33, (e)0.36, (f)0.39, and (g)0.42

properties of LDHs were obtained after the adsorption procedure for 60min.

2.5 Characterization

Powder X-ray diffraction (XRD) spectra were recorded on a Rigaku powder diffractometer unit, using CuK α (filtered) radiation ($\lambda = 0.154\text{nm}$) at 40kV and 20mA between 1.8 and 50°. FT-IR spectra (KBr disc method) were recorded on a Horiba FT-200. Thermal analysis (TG/DTA) of samples (5-10mg) were performed on a Seiko SSC 5000 thermal analysis system (heating rate: 10°C/min, in flowing N₂). Gas analysis were performed on Shimadzu gas chromatography GC-8A.

3. RESULTS AND DISCUSSION

3.1. Gas adsorption properties of Zn-Al LDH(CO₃²⁻)

Figure 1 shows XRD patterns of Zn-Al LDH(CO₃²⁻), [Zn_{1-x}Al_x(OH)₂]^{x+}[(CO₃)_{x/2}]^{x-} (molar ratio; $x = 0.24, 0.27, 0.30, 0.33, 0.36, 0.39, 0.42$). Presence of typical peaks of the LDH indicated that the Zn-Al LDH(CO₃²⁻) were prepared whose molar ratios, $x = \text{Al}^{3+}/(\text{Zn}^{2+} + \text{Al}^{3+})$, were from 0.24 to 0.42. Then gas adsorption properties of the Zn-Al LDH(CO₃²⁻) were investigated.

Figure 2 shows the amount of CO₂ adsorbed into the Zn-Al LDH(CO₃²⁻). Interlayer space of Zn-Al LDH(CO₃²⁻) is polar. Also, CO₂ was polar molecules compared with N₂, so it was considered that CO₂ was adsorbed more into the Zn-Al LDH(CO₃²⁻) than N₂. The amount of CO₂ adsorbed into the Zn-Al LDH(CO₃²⁻) increases with an increase in the Al content. At first, the effect of surface area on the phenomena was examined. In the LDHs, large surface area was expected with an increase in the Al content, since the cation radii of Zn²⁺ (0.074nm) and Al³⁺ (0.0535nm) were different. So it was considered that the increase of the amount of CO₂ adsorbed into the Zn-Al LDH(CO₃²⁻) was due to the difference of surface area.

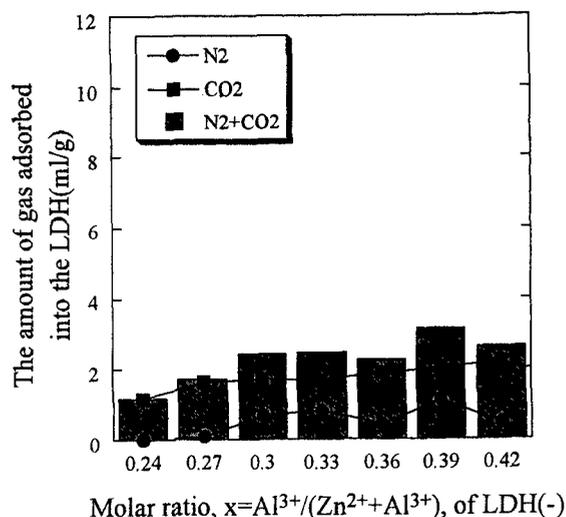


Figure 2. Gas adsorption properties on Zn-Al LDH(CO₃²⁻) whose molar ratios, $x = \text{Al}^{3+}/(\text{Zn}^{2+} + \text{Al}^{3+})$, were from 0.24 to 0.42 after the adsorption procedure for 60min

At second, the effect of metals of layers such as Zn or Al was examined. SEM image showed that the crystal morphology of hydroxide and oxide of Zn or Al were similar. Figure 3 showed the gas adsorption properties of hydroxide and oxide of Zn or Al. The hydroxide and oxide of Zn adsorbed CO₂ more than those of Al. It was considered that the electronegativity of Zn was large compared with Al. In the case of Zn-Al LDH(CO₃²⁻), the amount of CO₂ adsorbed into the Zn-Al LDH(CO₃²⁻) increased with an increase in the Al content. So it was considered that the effect of metals was small, or the effect of surface area was large.

At third, the effect of water content (total of surface water and interlayer water) of the Zn-Al

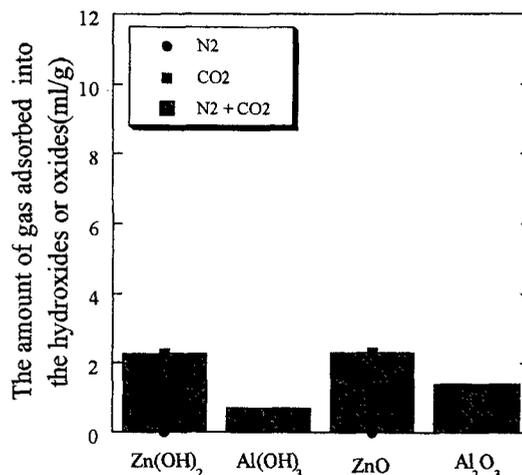


Figure 3. Gas adsorption properties of Zn(OH)₂, Al(OH)₃, ZnO, and Al₂O₃ after the adsorption procedure for 60min

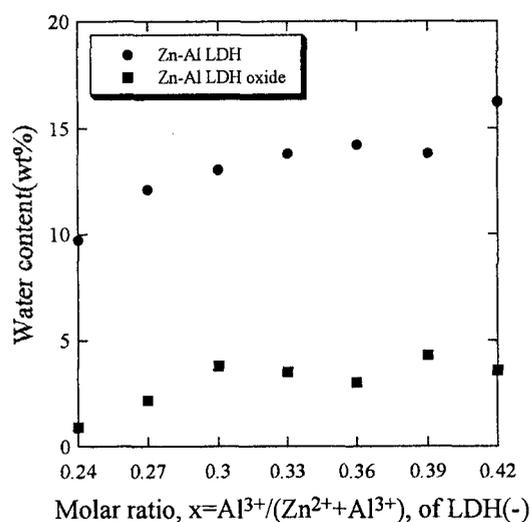


Figure 4. Water content of Zn-Al LDH(CO_3^{2-}), and Zn-Al LDH oxide whose molar ratios, $x = \text{Al}^{3+}/(\text{Zn}^{2+} + \text{Al}^{3+})$, were from 0.24 to 0.42

LDH(CO_3^{2-}) was examined. On thermal analysis of the Zn-Al LDH(CO_3^{2-}), the water content (ca. 10~15wt% of Zn-Al LDH(CO_3^{2-})) was increased with an increase in the Al content (Figure 4). It was due to increase of the interlayer water with an increase in interlayer anion. Because CO_2 has large solubility on water, it was considered that the amount of CO_2 adsorbed into Zn-Al LDH(CO_3^{2-}) increased with an increase in water content of the LDH. To examine the effect of interlayer water, the gas adsorption properties of calcined Zn-Al LDH(CO_3^{2-}) at 443K was investigated. The interlayer water desorbed from interlayer space of the LDH by thermal treatment at 443K was observed from thermal analysis. By the calcination of the Zn-Al LDH(CO_3^{2-}) at 443K for 1h, the typical XRD peaks of Zn-Al LDH(CO_3^{2-}) after calcination were disappeared. So Zn-Al LDH(CO_3^{2-}) was calcined at 423K for 1h. Thermal analysis of the calcined Zn-Al LDH(CO_3^{2-}) showed the desorption of interlayer water from interlayer space of LDHs. XRD patterns of the calcined Zn-Al LDH(CO_3^{2-}) showed typical patterns of LDHs. SEM image of calcined Zn-Al LDH(CO_3^{2-}) showed that the crystal morphology was the same as that of Zn-Al LDH(CO_3^{2-}). The amount of CO_2 adsorbed into the calcined Zn-Al LDH(CO_3^{2-}) at 423K for 1h increased compared with that of original Zn-Al LDH(CO_3^{2-}). So it was revealed that interlayer water decreased the adsorption sites of CO_2 into the Zn-Al LDH(CO_3^{2-}). Also, due to increase water content with an increase in the Al content, the decrease of the adsorption sites of CO_2 into Zn-Al LDH(CO_3^{2-}) was considered. But the amount of CO_2 adsorbed into the Zn-Al LDH(CO_3^{2-}) increased, so the effect of surface area was large.

At fourth, the effect of interlayer anion was con-

sidered. Due to increase of the interlayer anion with an increase in the Al content, the decrease of the adsorption sites of CO_2 in Zn-Al LDH(CO_3^{2-}) was considered. In the case of Zn-Al LDH(CO_3^{2-}), the amount of CO_2 adsorbed into the Zn-Al LDH(CO_3^{2-}) increased with an increase in the Al content. So it was considered that the effect of interlayer anion was small, or the effect of surface area was large.

3.2. Gas adsorption properties of Zn-Al LDH oxide

Figure 5 shows XRD patterns of the Zn-Al LDH oxide, $[\text{Zn}_{1-x}\text{Al}_x\text{O}_{1+x/2}]$ (molar ratio; $x = 0.24, 0.27, 0.30, 0.33, 0.36, 0.39, 0.42$). Peaks of Zn-Al LDH(CO_3^{2-}) disappeared in XRD pattern indicating that amorphous materials were obtained. On thermal analysis of Zn-Al LDH oxide, weight loss of surface water (ca. 1~5wt% of Zn-Al LDH oxide) was observed, but interlayer water and interlayer anion (CO_3^{2-}) were not observed. It was due to desorption of interlayer water and interlayer anion (CO_3^{2-}) by the calcination of the Zn-Al LDH(CO_3^{2-}) at 773K for 3h. Figure 6 shows that the amount of CO_2 adsorbed into the Zn-Al LDH oxide

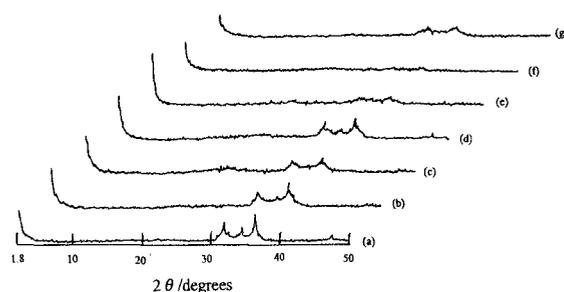


Figure 5. XRD patterns of Zn-Al LDH oxide whose molar ratios, $x = \text{Al}^{3+}/(\text{Zn}^{2+} + \text{Al}^{3+})$, were (a) 0.24, (b) 0.27, (c) 0.30, (d) 0.33, (e) 0.36, (f) 0.39, and (g) 0.42

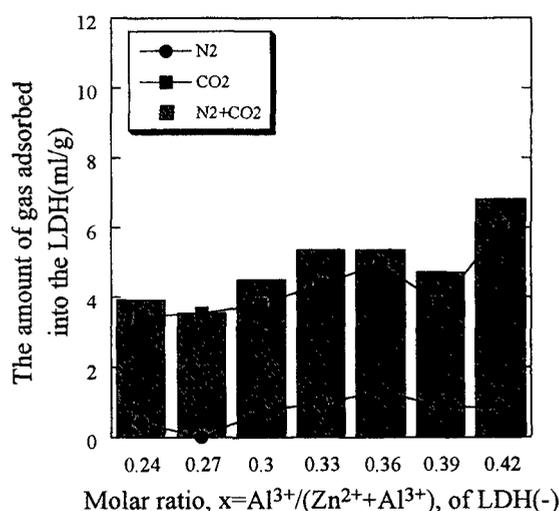


Figure 6. Gas adsorption properties of Zn-Al LDH oxide whose molar ratios, $x = \text{Al}^{3+}/(\text{Zn}^{2+} + \text{Al}^{3+})$, were from 0.24 to 0.42 after the adsorption procedure for 60min

ide. The amount of CO_2 adsorbed into the Zn-Al LDH oxide increases with an increase in the Al content. Similarly to the gas adsorption properties of Zn-Al LDH(CO_3^{2-}), the effect of surface area was considered. In the Zn-Al LDH oxide, because the amount of water content was small (ca. 1~5wt% of Zn-Al LDH oxide), it was considered that the effect of water content was small. Also, the amount of CO_2 adsorbed into the Zn-Al LDH oxide was large compared with the Zn-Al LDH(CO_3^{2-}). SEM image showed that surface area of Zn-Al LDH oxide was large compared to that of Zn-Al LDH(CO_3^{2-}).

3.3. Gas adsorption properties of inorganic anion intercalated LDH, Zn-Al LDH(A^n)

LDHs has an anion in the interlayer spaces to compensate a net positive charge of layers. It was known that many kinds of anions were incorporated into the interlayer spaces. Therefore, gas adsorption properties were investigated about inorganic anion intercalated LDH, Zn-Al LDH(A^n), which incorporated a various kinds of anions such as Cl^- , NO_3^- , ClO_4^- , CO_3^{2-} , SO_4^{2-} , Br^- , and OH^- . Figure 7 shows gas adsorption properties of Zn-Al LDH(A^n) whose molar ratios, $\text{Al}^{3+}/(\text{Zn}^{2+}+\text{Al}^{3+})$, were 0.3. It was confirmed that the amount of gas adsorbed into the Zn-Al LDH(OH^-) was large compared with other Zn-Al LDH(A^n).

3.4. Comparison of gas adsorption properties of the Zn-Al LDH(OH^-) and conventional adsorbents.

Gas adsorption properties of the Zn-Al LDH(OH^-) was compared with those of the conventional adsorbents (Activated carbon, Silica-gel, Molecular Sieve 3A, Molecular Sieve 5A). Figure 8 shows gas adsorption properties of the Zn-Al LDH(OH^-) and the conventional adsorbents. The Zn-Al LDH(OH^-)

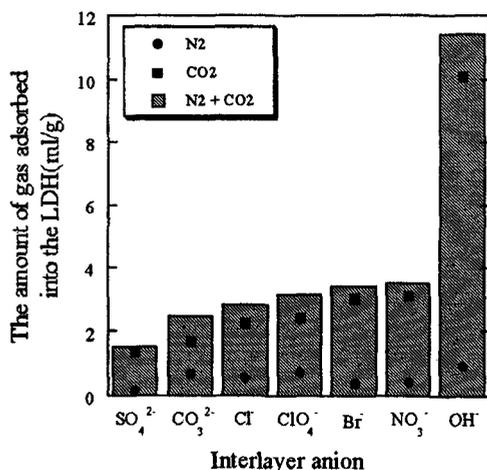


Figure 7. Gas adsorption properties of Zn-Al LDH($\text{A}^n = \text{SO}_4^{2-}$, Cl^- , ClO_4^- , Br^- , NO_3^- , and OH^-) whose molar ratios were $x=0.30$ after the adsorption procedure for 60min

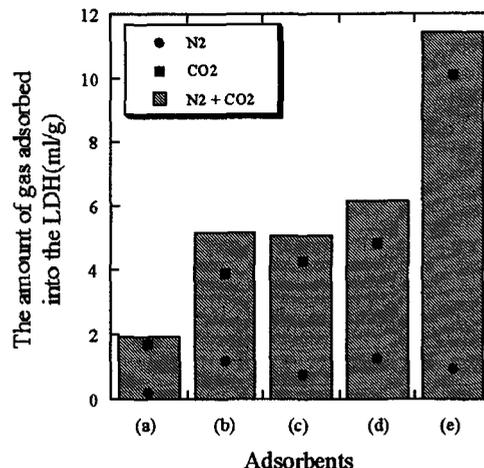


Figure 8. Gas adsorption properties of Zn-Al LDH(OH^-) whose molar ratio were $x=0.30$ and conventional adsorbents after the adsorption procedure for 60min; (a) Molecular Sieve 3A, (b) Activate Carbon, (c) Silica-Gel, (d) Molecular Sieve 5A, and (e) Zn-Al LDH(OH^-)

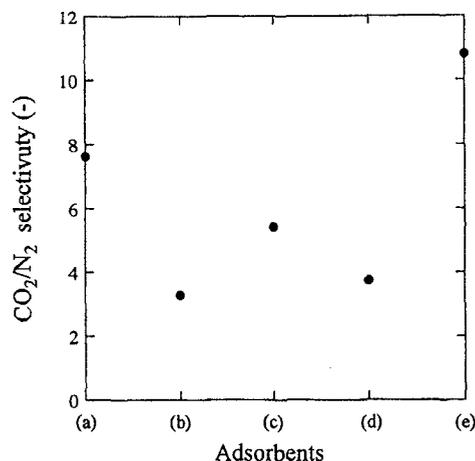


Figure 9. N_2/CO_2 selectivity on Zn-Al LDH(OH^-) whose molar ratio were $x=0.30$ and conventional adsorbents after the adsorption procedure for 60min; (a) Molecular Sieve 3A, (b) Activate Carbon, (c) Silica-Gel, (d) Molecular Sieve 5A, and (e) Zn-Al LDH(OH^-)

adsorbed CO_2 gas more than the conventional adsorbents. Additionally, Figure 9 shows CO_2/N_2 selectivity of adsorbed gas molecules on the Zn-Al LDH(OH^-) and the conventional adsorbents. The Zn-Al LDH(OH^-) adsorbed CO_2 at high CO_2/N_2 selectivity, and it reaches ca. 11. It was revealed that the CO_2/N_2 selectivity of the Zn-Al LDH(OH^-) was higher than the conventional adsorbents.

4. REFERENCE

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