Mg/Al계 소성LDH에 대한 요오드와 크롬 음이온의 수착 거동

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Sorption Behavior of I^- and CrO_4^{2-} on Calcined Mg/Al LDH

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Introduction

Hydrotalcite is rare but naturally occurring mineral with a composition of $Mg_6Al_2(OH)_{16}CO_3$ $4H_2O$. This material has a layered structure made up of magnesium aluminium hydroxide. Carbonate anions and water molecules are intercalated between the layers. It is also referred to as a layered double hydroxide (LDH: Mg/Al LDH(CO_3)). The general formula of LDHs is $[(M^{2+})_{1-x}(M^{3+})_x(OH)_2]^{x+}[(A^{n-})_{x/n}\ mH_2O]^{x-}$; M^{2+}= Mg, Ni, Zn; M^{3+}= Al, Cr, Fe; A^{n-} is an exchangeable anion. A wide range of derivatives containing various combinations of M^{2+}, M^{3+} and A^{n-} ions can be readily synthesized under laboratory conditions [1,2]. These basic materials have a relatively large surface area of 20 - 120 m^2g^{-1} and anion-exchange capacity of 2 - 5 $meqg^{-1}$. The Mg/Al LDH(CO_3) is stable up to 400 ℃ and transformed to a mixed metal oxide with a composition of $Mg_{1-x}Al_xO_{1+x/2}$ upon heating. When the LDH(CO_3) is calcined in the range of 450 to 600 ℃, the layered structure is destroyed with the loss of CO_2 and water molecules. An important property of the calcined LDH is the reconstruction of layered structure (Memory effect). When the calcined LDH is in aqueous electrolyte solutions or deionized water, the layered structure is reconstructed with anionic species such as Cl^-, OH^-, PO_4^{3-} and CrO_4^{2-} [3,4]. This property of calcined LDH may prove it to be useful for removing anionic species from industrial and nuclear wastes [5-7].

Iodine-129 would be the most active nuclide when radioactive waste is permanently disposed of. There is a strong interest in its behavior in the environment due to its long half-life. Being this highly mobile, it hardly interact with inorganic material and migrate without retardation through geological media. Chromium is used commercially in the steel industry and dyeing process. Cr(VI) is major toxic element of industrial waste and exists as CrO_4^{2-} in the aqueous solution. The calcined LDH is a potential sorbent for these anions. The sorption behaviors of I^- and CrO_4^{2-} on calcined Mg/Al LDH were investigated. The sorption mechanism was proposed and equilibrium constants were also evaluated.

Experimental

Mg/Al LDH(CO_3) (x=0.25) was synthesized by the precipitation method. Details of the synthesis and analysis of Mg/Al LDH(CO3) were described in the previous study [8]. The calcined LDH, with a composition of $Mg_6Al_2O_9$ (Mw=343.79), was obtained by heating the synthesized LDH (Mg/Al LDH(CO_3), x = 0.25) at 560 ℃ for 3 h in air.

The I^- sorption experiments were carried out in a 500 ml flask thermostated at 25 ℃. The reaction solutions were kept free from CO_2 by continuously bubbling argon gas through the solution (about 5 ml min^{-1}). Argon gas passed strongly through the flask during the sampling and pH measurement. The CrO_4^{2-} sorption experiments were performed in the inert-gas glove box to simulate CO_2-free condition. The glove box was filled with N_2 gas with 99.999%

purity. An appropriate quantity of the calcined LDH was added to the prepared I^- solution. The solid-liquid suspension was formed and stirred continuously with a magnetic stirrer for 140-200 h. An aliquot (3 ml) was sampled at time intervals with a syringe and filtered with a 0.45 m microfilter of cellulose acetate membrane. Iodide solutions was prepared from NaI and 57% HI solution. Iodine-125 in the form of NaI was used as a tracer. Chromate solution was prepared from $Na_2CrO_44H_2O$. The I^- concentration of the sample solutions was determined by a low-energy NaI detector and a spectroscopy amplifier , measuring a ɣ-energy of 35.5 keV. The I^- concentration of the initial solutions before adding the radioactive tracer was also confirmed by HPLC. The CrO_4^{2-} concentration of sample solution was measured by UV/VIS spectrophotometer.

Results and Discussion

The experimental data of I^- sorption are summarized in Table 1. The concentration of sorbed I^- ($[I^-]_{sorbed}$) corresponds to the difference between the concentration of the initial I^- ($[I^-]_0$) and the equilibrium I^- ($[I^-]_{eq}$). The concentration $[I^-]_{sorbed}$ increased by an increment of $[I^-]_0$. pH_0 is the pH of the initial I^- solution before adding the calcined LDH. pH_{eq} is the pH of the reaction solution at equilibrium including the basicity of the calcined LDH itself.

The pH dependence observed demonstrates that the sorption reaction follows an ion-exchange mechanism involving a solid-phase [5]. When the calcined LDH is suspended in decarbonated water without other anoions, it become hydrated and a LDH hydroxide, described as $Mg_6Al_2(OH)_{18}$ in the literature [4], is formed. In the case of I^- sorption, it is assumed that one OH^- ion of the LDH hydroxide is replaced by one I^- ion. And more than one I^- is then sorbed per LDH unit at a higher I^- concentration. Ion-exchange equilibria of the sorption reaction of I^- on calcined LDH are demonstrated as follows.

$$LDH(OH)_2(s) + I^- \xrightleftharpoons{K_1} LDH(OH)(I)(s) + OH^-$$

$$LDH(OH)(I)(s) + I^- \xrightleftharpoons{K_2} LDH(I)_2(s) + OH-$$

$Mg_6Al_2(OH)_{18}(s)$ and $Mg_6Al_2(OH)_{16}(I)_2(s)$ can be described as $LDH(OH)_2(s)$ and $LDH(I)_2(s)$, respectively. The equilibrium constants of the ion-exchange reaction, K_1 and K_2, are given by

$$K_1 = \frac{[LDH(OH)(I)(s)]_{eq}[OH^-]_{eq}}{[LDH(s)]_{eq}[I^-]_{eq}} \quad (1) \qquad K_1K_2 = \frac{[LDH(I)_2(s)]_{eq}[OH^-]^2_{eq}}{[LDH(s)]_{eq}[I^-]^2_{eq}} = K_{I}. \quad (2)$$

The $[LDH(s)]_{eq}$ is equal to the $[LDH(OH)_2(s)]_{eq}$ because the hydration of calcined LDH occurs fast and completely. The concentration of sorbed I^- can be expressed by Eq. (3). All of the concentrations involved in this equation are known by experimental results, except the concentration of the dissolved LDH.

$$[I^-]_{sorbed} = \frac{[LDH]_0 - [LDH]_{dissolved}}{1 + K_1\frac{[I^-]_{eq}}{[OH^-]_{eq}} + K_2{\frac{[I^-]_{eq}}{[OH^-]_{eq}}}^2} \, K_1\frac{[I^-]_{eq}}{[OH^-]_{eq}} + 2K_2{\frac{[I^-]_{eq}}{[OH^-]_{eq}}}^2 \quad (3)$$

The solubility of the calcined LDH was investigated as a function of pH in previous study [9]. The concentration of dissolved Mg^{2+} decreased with an increasing pH. The dissolved Al^{3+} concentration was below 3×10^{-5} mol/L in the pH range of 9.8 to 13.0. Extremely low Al^{3+}

concentration being considered, the assumption $[LDH]_{sorbed} = [LDH]_0 - [LDH]_{dissolved}$ is made in the treatment of the experimental data.

The equilibrium constants were evaluated by a non-linear least squares fit using Eq. (3). By minimizing the differences between the experimental and calculated values of $\log[I^-]_{sorbed}$, the equilibrium constants were determined. The values of K_1 and K_2 are 7.4 ±1.0 and 0.2 ±0.4, respectively. The following Eq. (4) is derived from Eq. (3) with evaluated K_1 and K_2 constants. The experimental values of the ratio $[I^-]_{sorbed}/[LDH]_0$ as a function of the ratio $[I^-]_{eq}/[OH^-]_{eq}$ are compared with the values calculated using Eq. (4).

$$\frac{[I^-]_{sorbed}}{[LDH]_0} = \frac{K_1\frac{[I^-]_{eq}}{[OH^-]_{eq}} + 2K_2\frac{[I^-]_{eq}}{[OH^-]_{eq}}^2}{1 + K_1\frac{[I^-]_{eq}}{[OH^-]_{eq}} + K_2\frac{[I^-]_{eq}}{[OH^-]_{eq}}^2} \qquad (4)$$

The experimental data agree well with the calculated curve, as shown in Fig. 1. When the value $[I^-]_{eq}/[OH^-]_{eq}$ was below 0.2, the $[I^-]_{sorbed}/[LDH]_0$ increased linearly with the value of $[I^-]_{eq}/[OH^-]_{eq}$. When the value $[I^-]_{eq}/[OH^-]_{eq}$ was 12, the experimental value of $[I^-]_{sorbed}/[LDH]_0$ was 1.2. Theoretically, the calculated curve approaches a value of 2. The first ion-exchange equilibrium is the replacement of one OH^- ion of the LDH hydroxide by an I^- ion to form LDH(OH)(I)(s). The second equilibrium reaction, the sorption of two I^- ions on a LDH unit, hardly occurs because of a very low K_2 value.

The experimental data of CrO_4^{2-} sorption are also listed in Table 2. The concentration $[CrO_4^{2-}]$sorbed was in the range of 1.0×10^{-3}-2.4×10^{-3} mol/L with an increment of $[CrO_4^{2-}]_0$. In this CrO_4^{2-} sorption, CrO_4^{2-} ion is sorbed instead of two exchangeable OH^- ions of LDH hydroxide by ion-exchange precess.

$$LDH(OH)_2(s) + CrO_4^{2-} \underset{}{\overset{K_{Cr}}{\rightleftarrows}} LDH(CrO_4)(s) + 2OH^-$$

The equilibrium constant, K_{Cr} is given by

$$K_{Cr} = \frac{[LDH(CrO_4)(s)]_{eq}[OH^-]_{eq}^2}{[LDH(s)]_{eq}[CrO_4^{2-}]_{eq}}. \qquad (5)$$

The equilbrium constant is also evaluated by a non-linear least square fit. As shown in Fig. 2, the experimental results of the ratio $[CrO_4^{2-}]_{sorbed}/[LDH]_0$ are expressed as s function of the ratio $[CrO_4^{2-}]_{eq}/[OH^-]_{eq.}$

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Table 1. Experimental results of the I^- sorption

$[I^-]_0$ (mol/L)	$[LDH]_0$ (mol/L)	$[I^-]_{eq}$ (mol/L)	$[I^-]_{sorbed}$ (mol/L)	pH_0	pH_{eq}
1.80×10^{-5}	1.18×10^{-3}	2.89×10^{-6}	1.51×10^{-5}	5.48	11.24
4.60×10^{-5}	1.22×10^{-3}	6.40×10^{-6}	3.96×10^{-5}	5.77	11.26
8.33×10^{-5}	1.19×10^{-3}	1.72×10^{-5}	6.62×10^{-5}	4.95	11.11
1.34×10^{-4}	1.19×10^{-3}	2.79×10^{-5}	1.06×10^{-4}	5.64	11.50
3.68×10^{-4}	1.20×10^{-3}	9.72×10^{-5}	2.71×10^{-4}	5.57	11.26
8.25×10^{-4}	1.20×10^{-3}	2.34×10^{-4}	5.91×10^{-4}	5.30	11.25
1.17×10^{-3}	1.20×10^{-3}	4.40×10^{-4}	7.30×10^{-4}	5.51	11.27
3.45×10^{-3}	1.19×10^{-3}	2.49×10^{-4}	9.56×10^{-4}	5.43	11.23
1.07×10^{-2}	1.22×10^{-3}	9.16×10^{-3}	1.51×10^{-3}	5.25	10.88
5.32×10^{-2}	1.19×10^{-3}	5.18×10^{-2}	1.36×10^{-3}	5.16	10.62

Table 2. Experimental results of the CrO_4^{2-} sorption

$[CrO_4^{2-}]_0$ (mol/L)	$[LDH]_0$ (mol/L)	$[CrO_4^{2-}]_{eq}$ (mol/L)	$[CrO_4^{2-}]_{sorbed}$ (mol/L)	pH_0	pH_{eq}
1.02×10^{-3}	2.97×10^{-3}	2.92×10^{-6}	1.02×10^{-3}	11.92	12.01
1.28×10^{-3}	2.95×10^{-3}	4.38×10^{-6}	1.28×10^{-3}	11.89	12.00
1.28×10^{-3}	2.96×10^{-3}	5.12×10^{-6}	1.27×10^{-3}	11.89	12.00
1.53×10^{-3}	2.96×10^{-3}	1.68×10^{-5}	1.51×10^{-3}	11.86	12.01
1.79×10^{-3}	2.96×10^{-3}	3.28×10^{-5}	1.76×10^{-3}	11.83	12.00
2.04×10^{-3}	2.96×10^{-3}	1.33×10^{-4}	1.91×10^{-3}	11.79	12.01
2.30×10^{-3}	2.98×10^{-3}	2.42×10^{-4}	2.06×10^{-3}	11.75	11.98
2.55×10^{-3}	2.96×10^{-3}	4.50×10^{-4}	2.10×10^{-3}	11.71	11.96
2.81×10^{-3}	2.98×10^{-3}	6.51×10^{-4}	2.16×10^{-3}	11.67	11.94
3.06×10^{-3}	2.95×10^{-3}	1.01×10^{-3}	2.05×10^{-3}	11.41	11.83
3.83×10^{-3}	2.97×10^{-3}	1.56×10^{-3}	2.27×10^{-3}	11.19	11.76
4.85×10^{-3}	2.96×10^{-3}	2.56×10^{-3}	2.29×10^{-3}	10.71	11.68
5.11×10^{-3}	2.98×10^{-3}	2.75×10^{-3}	2.36×10^{-3}	8.80	11.63

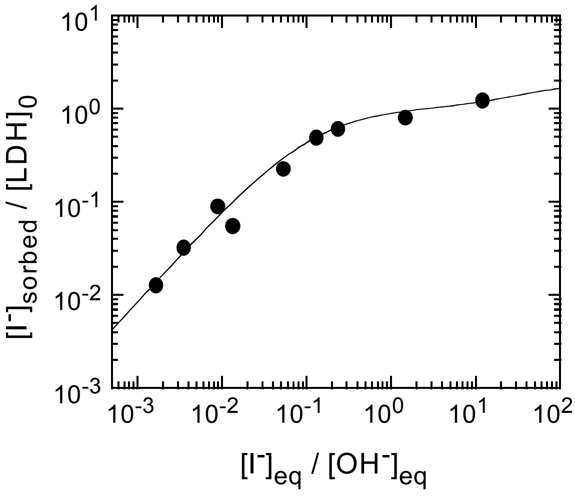

Fig.1 Experimental values and calculated curve of the ratio $[I^-]_{sorbed}/[LDH]_0$ as a function of $[I^-]_{eq}/[OH^-]_{eq}$ in I^- sorption.

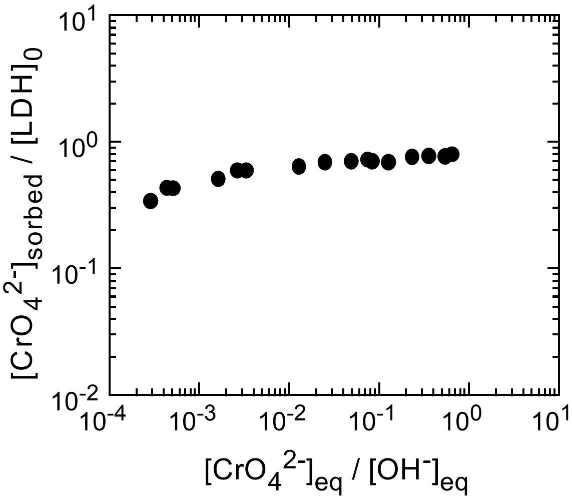

Fig.2 Experimental values of the ratio $[I^-]_{sorbed}/[LDH]_0$ as a function of $[I^-]_{eq}/[OH^-]_{eq}$ in CrO_4^{2-} sorption.