Environ. Eng. Res. Vol. 8, No. 1, pp. 22~30, 2003
Korean Society of Environmental Engineers

SORPTION OF AQUEOUS TOXIC ANIONS ON CALCINED Mg/Al LAYERED DOUBLE HYDROXIDE: AN APPROACH TO MECHANISM

Mun Ja Kang†, Seog Woo Rhee*, and Pil Soo Hahn

Radioactive Waste Disposal Team, Korea Atomic Energy Research Institute, Daejeon 305-600, Korea

*Center for Biomedical Engineering, University of California, Irvine, CA 92697, USA

(received August 2002, accepted November 2002)

Abstract : In order to understand the sorption mechanism of TcO_4^- and CrO_4^{2-} on calcined Mg/Al layered double hydroxide (LDH), spectroscopic identifications were performed. Calcined LDH and LDH sorbed with ReO_4^- (TcO_4^- surrogate) or CrO_4^{2-} were characterized by the powder X-ray diffraction, ^{27}Al MAS NMR (Magic Angle Spinning Nuclear Magnetic Resonance), and FT-IR spectroscopies. The XRD pattern of $LDH(ReO_4)_2$ shows the broad 006 reflection of 4.78 Å. The NMR and FT-IR spectra reveal that the calcined LDH was reconstructed with intercalating ReO_4^- in the aqueous ReO_4^- solution. In the previous study the sorption of TcO_4^- and ReO_4^- onto calcined LDH was proposed to be an ion-exchange reaction: generation of LDH hydroxide, $Mg_6Al_2(OH)_{18}$, as an intermediate and then replacement of the OH^- by TcO_4^- or ReO_4^- ions. In the present study it was identified by the XRD analysis of reaction solid of ReO_4^- sorption that the LDH hydroxide is produced and exists in the reaction solid along with $LDH(ReO_4)_2$. This demonstrates that LDH hydroxide is the intermediate of the sorption process. In the case of CrO_4^{2-} sorption on the calcined LDH, the LDH hydroxide is generated together with $LDH(CrO_4)$.

Key Words : CrO_4^{2-}, layered double hydroxide, ReO_4^-, sorption, toxic anion

INTRODUCTION

Hydrotalcite is rare but naturally occurring mineral with a composition of $Mg_6Al_2(OH)_{16} \cdot CO_3 \cdot 4H_2O$.[1,2] This material has a layered structure made up of octahedral magnesium hydroxides with Al^{3+} ions replacing some Mg^{2+} sites in a random manner. The replacement of some Mg^{2+} by Al^{3+} generates positively charged layers, which are compensated by intercalated CO_3^{2-} ions and water molecules occupying the interlayer. Because the layers are stacked on top of each other, 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.[3~6] These basic materials have a relatively large surface area of 20~120 m^2g^{-1} and anion-exchange capacity of 2~5 meq g^{-1}.[7] These are also referred to as anionic clays, which become a complementary class of materials to conventional cationic clays.

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.

†Corresponding author
E-mail: munkang@kaeri.re.kr
Tel: +82-42-868-2078, Fax: +82-42-868-8850

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[8,9]. The chemical behavior of this calcined LDH is not fully understood. 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-}.[7,10,11] This property of calcined LDH may prove it to be useful for removing anionic species from industrial and nuclear wastes.[12~14]

Technetium-99 would be the most active nuclide when radioactive waste is permanently disposed of.[15] There is a strong interest in its behavior in the environment due to its long half-life. In the absence of reducing agents, technetium exists as TcO_4^-. Being this highly mobile, it hardly interact with inorganic material and migrate without retardation through geological media.[16,17] Several researchers have focused on the sorption studies of TcO_4^- on inorganic sorbents.[18,19] 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 TcO_4^- and CrO_4^{2-} on calcined Mg/Al LDH were already investigated.[20,21] The sorption of these anions on calcined LDH is found to be a ion-exchange process involving the LDH hydroxide of $Mg_6Al_2(OH)_{18}$. The ion-exchange reactions were proposed and equilibrium constants were also evaluated. The ReO_4^- ion was used as a TcO_4^- surrogate. The chemistry of technetium is most similar to that of rhenium, due to their similar size and chemical property.[22] The TcO_4^- and ReO_4^- show practically the same sorption behavior on the calcined LDH.[20]

This work discusses the sorption of aqueous TcO_4^- and CrO_4^{2-} ions onto calcined Mg/Al LDH. The formation of LDH intercalated with ReO_4^- is characterized by XRD, FT-IR and ^{27}Al MAS NMR (Magic Angel Spinning Nuclear Magnetic Resonance) spectroscopies. Emphasis of the present work can be placed upon the understanding of mechanism and the spectroscopic identification for the anion sorption on the calcined LDH.

MATERIALS AND METHODS

Mg/Al LDH(CO_3) (x = 0.25) was synthesized by slowly adding 2 M NaOH (Aldrich Co. 97%) and 0.2 M Na_2CO_3 (Junsei Co. 99%) to an aqueous solution containing 0.75 M $MgCl_2 \cdot 6H_2O$ (Junsei Co. 98%) and 0.25 M $AlCl_3 \cdot 6H_2O$ (Junsei Co. 98%). The reaction solution was stirred constantly at pH 10 and 40℃. The mole ratio of aluminium to total metal, x = Al/(Mg+Al), was adjusted to 0.25. White precipitate of LDH was separated from the mother-liquor by centrifugation (4,000 rpm, 10 min; DuPont Co., Sorvall RC 28S). The precipitate was washed repeatedly with doubly deionized water until chloride ions were not detected in the supernatant. Synthesized LDH was dried in a convection oven (Precision Scientific Inc., 18EG) at 80℃ for 100 hr, finely ground into a powder (particle size $\leq$ 0.25 mm) and kept in a desiccator. The chemical composition of the synthesized LDH was analyzed.[23] The chemical formula is $Mg_{0.75}Al_{0.25}(OH)_{2.02} \cdot (CO_3)_{0.13} \cdot 0.73 H_2O$. The x value of the synthesized LDH is 0.25 and very close to that in the aqueous reaction mixture. 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 hr in air.

LDH perrhenate (LDH$(ReO_4)_2$(s)) was synthesized by slow addition of 10 mL of 0.1 M $HReO_4$ to an aqueous solution containing 0.2 g of calcined LDH. The total volume of solution was 50 mL. In an inert glove box, stirring was continued for 100 hr and the white precipitate was then separated by decantation. The precipitate was dried at 60℃ under an argon atmosphere. The mixtures of LDH perrhenate and LDH hydroxide were synthesized in the same

manner. The LDHs containing various amounts of ReO_4^- were synthesized by adjusting the ReO_4^- concentration of the reaction suspension. The LDHs intercalated by 75, 50, and 25% AEC (anion exchange capacity) of ReO_4^- were obtained by adding 7.5, 5.0, and 2.5 mL of 0.1 M $HReO_4$ to the suspended LDH, respectively. LDH hydroxide ($LDH(OH)_2(s)$) was prepared by placing the calcined LDH into decarbonated water without other anions. LDH chromate ($LDH(CrO_4)(s)$) was synthesized by the addition of 10 mL of 0.1 M H_2CrO_4 to the 40 ml aqueous solution of the calcined LDH. The LDHs containing various amounts CrO_4^{2-} were synthesized by controlling the volume of CrO_4^{2-} solution. In the case of 75, 50, and 25% AEC CrO_4^{2-}, 7.5, 5.0, and 2.5 mL of 0.1 M H_2CrO_4 were added, respectively. The procedure of synthesizing LDH chromate in the glove box filled with nitrogen gas is the same as that of LDH perrhenate.

Elemental analyses for C and H were performed using EA 1110 analyzer and Mg and Al elements were analyzed by ICP-AES (Jovin Yvon, JP50P) after dissolving the synthesized LDH in 1.0 M HNO_3 solution. Crystal structures of the synthesized LDH, calcined LDH, LDH perrhenate, and LDH chromate were investigated by powder X-ray diffraction (XRD) analysis (Rigaku, PW 2243/20) using Cu $K\alpha_1$ (λ = 0.15406 nm) in the 2θ range 3~68°. IR spectra of the solid phase were obtained with an FT-IR spectrometer (Bomem, MB 100) : KBr pellets containing 2 mg of sample in 200 mg KBr. ^{27}Al MAS NMR spectra were obtained using Brucker AM 300 operating at 78.2 MHz : 30° pulse of 5 μsec, data aquisition time of 35 msec, a delay of 2 sec and rotor speed set at 3.5 kHz. A spectrum with a good signal-to-noise ratio was obtained after 200 transients. The chemical shift is given relative to the reference 1.0 M $Al(H_2O)_6^{3+}$.

RESULTS AND DISCUSSION

Characterization of synthesized Mg/Al LDH, (CO_3) (x = 0.25), calcined LDH and reconstructed LDH with ReO_4^- was performed to understand the sorption behavior of the calcined LDH in aqueous TcO_4^- solution. The principal results of their spectroscopic analysis are as follows.

X-ray studies performed with natural LDH show that the *a* parameter of the hexagonal cell unit corresponds to the distance between two metal cations in adjacent octahedra, while the *c* parameter corresponds to three times the distance between adjacent hydroxyl layers.[1,2] The carbonate and water molecules are arranged in the interlayer so that the plane containing the oxygen atoms is parallel to the brucite-like layers. The interlayer spacing can vary, depending on the size and geometry of the intercalated anion. The results of powder X-ray diffraction of Mg/Al LDH with carbonate anion synthesized in the laboratory are shown in Table 1 and Figure 1(a). The unit cell parameters of the synthesized LDH, *a*, and *c* are 3.06 and 23.40 Å, respectively. The synthesized LDH has an interlayer spacing of 3.00 Å, which is occupied by carbonate anion. These are in good agreement with other synthetic LDHs (JCPDS card No. 22-700, 1986) and hydrotalcites (JCPDS card No. 14-191, 1986).

The XRD patterns of calcined LDH and reconstructed LDH with ReO_4^- are also shown in Figure 1. The reconstructed LDH with ReO_4^- is called LDH perrhenate and can be described as $LDH(ReO_4)_2$. In the XRD pattern of the calcined LDH (Figure 1(b)), the 003 and 006 reflections at

Table 1. Powder X-ray diffraction data for synthesized LDH, LDH perrhenate, LDH chromate, and LDH hydroxide

hkl	$d_{obs.}$ (Å)			
	$LDH(CO_3)$	$LDH(ReO_4)_2$	$LDH(CrO_4)$	$LDH(OH)_2$
003	7.82		8.98	7.82
006	3.89	4.78	4.50	3.91
009	2.60		2.58	2.59
012				
015	2.34			2.31
018	1.89			1.97
0012				
110	1.53	1.53	1.53	1.53
113	1.50		1.51	1.51

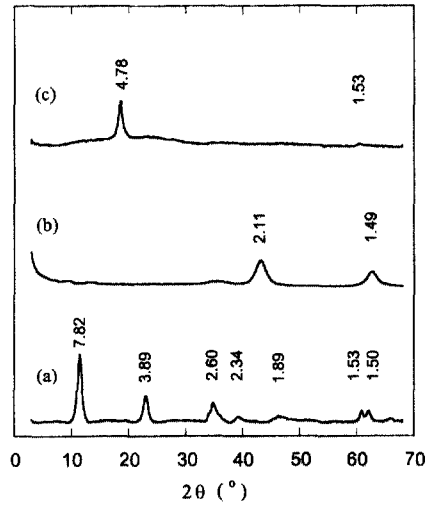

Figure 1. Powder X-ray diffraction patterns of (a) synthesized Mg/Al LDH(CO_3) (x = 0.25); (b) calcined LDH by heating synthesized LDH at 560℃; (c) reconstructed LDH(ReO_4)$_2$ formed from calcined LDH with aqueous ReO_4^- solution.

7.82 and 3.89 Å, respectively, are disappeared. This is caused by the destruction of the layered structure after heating the LDH at 560℃. Two reflections at 2.11 and 1.49 Å corresponding to the pattern of MgO are occurred.[10] Small intensity of the reflections indicates that Al is substituted into MgO and the mixed oxide with the composition of $Mg_6Al_2[\ ]O_9$ is formed at 500 ℃. The XRD pattern of the resulting solid phase of LDH perrhenate is shown in Figure 1c. This again shows 006 reflection (4.78 Å) that is shifted, comparing to the 006 reflection of synthesized LDH (Figure 1(a)). This is caused by larger size of ReO_4^- ions in the interlayer. But a 003 reflection is not observed in this XRD pattern. This may not be detected because of water sorbed on the surface of the solid phase. The observed XRD data of LDH perrhenate are summarized in Table 1.

IR spectrum of the synthesized LDH containing three carbonate-related singlet frequencies (ν_3: 1,384 cm^{-1}, ν_2: 852 cm^{-1}, ν_4: 660 cm^{-1}) is shown in Figure 2. Intercalated CO_3^{2-} has a D_{3h} symmetry and lies flat between two layers.[24] Intercalated carbonate (as CO_2) and

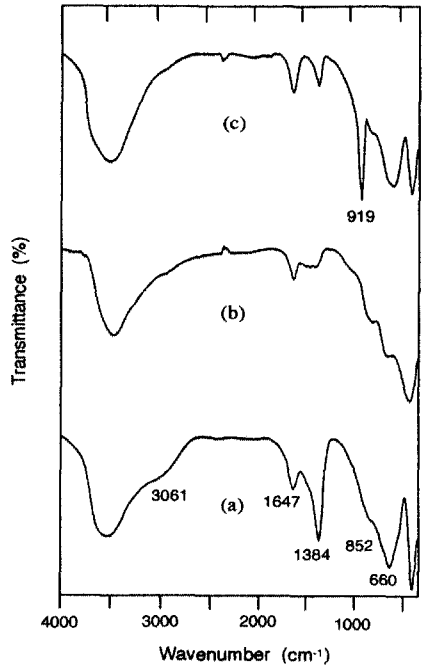

Figure 2. FT-IR spectra of (a) synthesized LDH; (b) calcined LDH; (c) reconstructed LDH(ReO_4)$_2$.

water are lost by heating, resulting in the disappearance of three CO_3^{2-} related and a considerable reduction of water related frequencies (e.g. 3,061 and 1,647 cm^{-1}) in the IR spectrum of the calcined LDH.[23] The IR spectrum of LDH(ReO_4)$_2$ again shows water related frequencies and one additional single new ReO_4^- related frequency at 919 cm^{-1}.

The structural changes of LDH by heating can also be seen from the ^{27}Al MAS NMR spectral data of the three solid phases (Figure 3). The ^{27}Al MAS NMR spectrum of the synthesized LDH (Figure 3(a)) shows a single sharp resonance at δ = 8.6 (no corrections made for second-order quadrupole), indicating that Al ions are predominately in the octahedral sites. By contrast, the spectrum of the calcined LDH has two resonances at δ = 16.2 and δ = 82.9, showing that some Al ions occupy tetrahedral sites, which are formed when hydroxides are lost as water during heating.[23] This result is in good agreement with the thermal decomposition studies of hydrotalcite made earlier using ^{27}Al

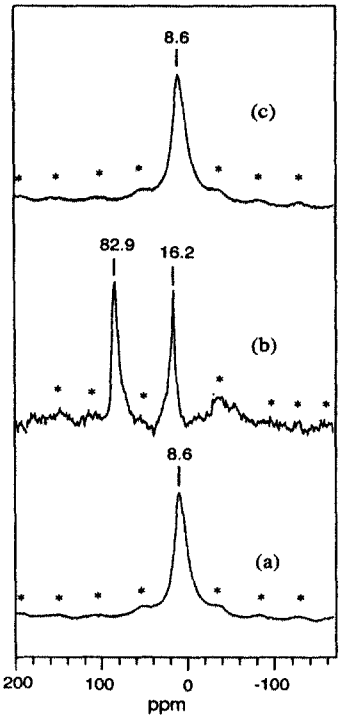

Figure 3. ^{27}Al MAS NMR spectra of (a) synthesized LDH; (b) calcined LDH; (c) reconstructed $LDH(ReO_4)_2$; *, spinning side bandsp

and ^{25}Mg MAS NMR.[25] The ^{27}Al MAS NMR spectrum of $LDH(ReO_4)_2$ has a single resonance at $\delta = 8.6$ (Figure 3(c)), demonstrating that all Al ions are occupying octahedral sites once again. Conclusively, the results of XRD, FT-IR, and ^{27}Al MAS NMR spectroscopies demonstrate that the calcined LDH is reconstructed with intercalating ReO_4^- in the aqueous ReO_4^- solution.

The sorption behaviors of TcO_4^- and CrO_4^{2-} on calcined LDH were investigated in the previous works.[20,21] Sorption studies were carried out by batch experiments at a constant temperature and inert atmosphere. The pH dependence observed demonstrates that the sorption reaction follows an ion-exchange mechanism involving a solid phase. When the calcined LDH is suspended in decarbonated water without other anions, it becomes hydrated and a LDH hydroxide, described as $Mg_6Al_2(OH)_{18}$ in the literature,[11] is formed. In the case of TcO_4^- sorption, it is assumed that one OH^- ion of the LDH hydroxide is replaced by one TcO_4^- ion. And more than one TcO_4^- is then sorbed per LDH unit at a higher TcO_4^- concentration. Therefore, the following ion-exchange equilibria are considered.

$$LDH(OH)_2(s) + TcO_4^- \overset{K_1}{\rightleftharpoons} LDH(OH)(TcO_4)(s) + OH^-$$

$$LDH(OH)(TcO_4)(s) + TcO_4^- \overset{K_2}{\rightleftharpoons} LDH(TcO_4)_2(s) + OH^-$$

$Mg_6Al_2(OH)_{18}(s)$ and $Mg_6Al_2(OH)_{16}(TcO_4)_2(s)$ can be described as $LDH(OH)_2(s)$ and $LDH(TcO_4)_2(s)$, respectively. The equilibrium constants of the ion-exchange reaction, K_1 and K_2 are given by

$$K_1 = \frac{[LDH(OH)(TcO_4)(s)]_{eq}[OH^-]_{eq}}{[LDH(s)]_{eq}[TcO_4]_{eq}} \quad (i)$$

$$K_1K_2 = \frac{[LDH(TcO_4)_2(s)]_{eq}[OH^-]_{eq}^2}{[LDH(s)]_{eq}[TcO_4^-]_{eq}^2} = K_{Tc}. \quad (ii)$$

The $[LDH(s)]_{eq}$ is equal to the $[LDH(OH)_2\ (s)]_{eq}$ because the hydration of calcined LDH occurs fast and completely. In the case of CrO_4^{2-} sorption, CrO_4^{2-} ion is sorbed instead of two exchangeable OH^- ions of LDH hydroxide by ion-exchange process.

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

$Mg_6Al_2(OH)_{16}(CrO_4)(s)$ represents $LDH(CrO_4)$ (s). The equilibrium constant, K_{Cr} is given by

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

The equilibrium constants are evaluated by a non-linear least square fit. The resulting values of K_1 and K_{Tc} for the sorption equilibria of both ReO_4^- and TcO_4^- anions are 1.4 ± 0.1 and 0.5 ± 0.2, respectively. The dominant reaction for practical application is the first ion-exchange equilibrium. The TcO_4^- and ReO_4^- have the same

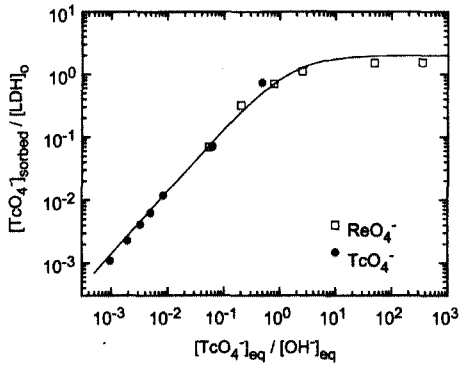

Figure 4. Experimental and calculated values of the ratio $[TcO_4^-]_{sorbed}/[LDH]_0$ as a function of $[TcO_4^-]_{eq}/[OH^-]_{eq}$ in the TcO_4^- sorption on calcined LDH

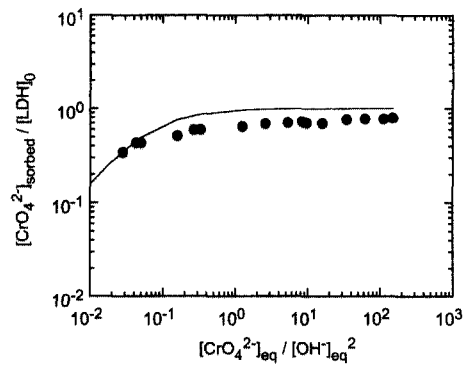

Figure 5. Experimental and calculated values of the ratio $[CrO_4^{2-}]_{sorbed}/[LDH]_0$ as a function of $[CrO_4^{2-}]_{eq}/[OH^-]_{eq}^2$ in the CrO_4^- sorption on calcined LDH.

sorption behavior on calcined LDH because of their similar size and chemical property.[22] The value of K_{Cr} for the sorption equilibrium of CrO_4^{2-} is 18.7 ± 1.0. The experimental results of the ratio $[anion]_{sorbed}/[LDH]_0$ are expressed as a function of the ratio $[anion]_{eq}/[OH^-]_{eq}$ and compared to the calculated values. The results of the TcO_4^- and ReO_4^- sorption on calcined LDH are shown in Figure 4.[20] The results of the CrO_4^{2-} sorption are also shown in Figure 5.[21] The calculated curves agree very well with the experimental data. Conclusively, it is found that the proposed ion-exchange equilibria are proper to explain the sorption reaction of TcO_4^- and CrO_4^{2-} onto the calcined LDH.

The LDH hydroxide, described as $LDH(OH)_2$, is assumed to be the intermediate compound of sorption reaction in this study. This intermediate compound was characterize in the sorption experiments of ReO_4^- onto calcined LDH. Powder X-ray diffraction patterns of the mixture of $LDH(ReO_4)_2$ and $LDH(OH)_2$ are shown in Figure 6. The XRD pattern of $LDH(OH)_2$ synthesized in this study is in good agreement with that of the literature.[11] The observed XRD data are listed in Table 1. The unit cell parameters of the synthetic $LDH(OH)_2$, *a* and *c*, are 3.06 and 23.40 Å, respectively. The interlayer spacing with hydroxide ion is 3.00 Å. Figure 6(a) shows 003 (7.82 Å) and 006 (3.91 Å) reflections with sharp peaks. When the

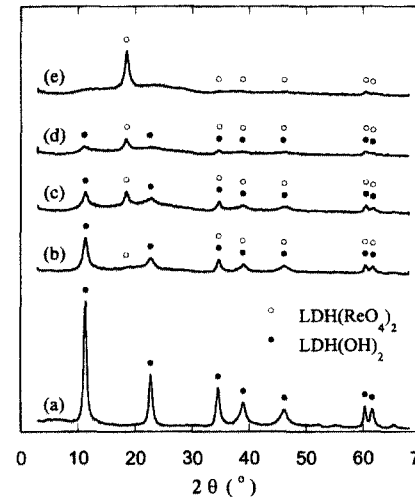

Figure 6. Powder X-ray diffraction patterns of (a) $LDH(OH)_2$ (decarbonated water); (b) mixture of $LDH(ReO_4)_2$ and $LDH(OH)_2$ (25% AEC ReO_4^-); (c) mixture of LDH $(ReO_4)_2$ and $LDH(OH)_2$ (50% AEC ReO_4^-); (d) mixture of LDH $(ReO_4)_2$ and $LDH(OH)_2$ (75% AEC ReO_4^-); (e) $LDH(ReO_4)_2$ (100% AEC ReO_4^-).

ReO_4^- anion is added to the solution containing LDH hydroxide, reflections of $LDH(ReO_4)_2$ appear.

This is shown in Figure 6b. When a ReO_4^- solution of 50% AEC reacts with calcined LDH, the reflections of $LDH(OH)_2$ and $LDH(ReO_4)_2$ exist together in the XRD pattern of reaction solid. The 006 reflections of $LDH(OH)_2$ (3.91 Å) and $LDH(ReO_4)_2$ (4.78 Å) are found to

have similar quantities as shown in Figure 6(c). The reflections of LDH(ReO_4)$_2$ grow by increasing the contents of ReO_4^-. In the case of ReO_4^- solution of 100% AEC, the pattern of LDH (ReO_4)$_2$ is confirmed. From the results of XRD analysis, it is verified that the LDH(ReO_4)$_2$ and LDH(OH)$_2$ are produced together in the solid of sorption reaction. In the absence of other anions, the LDH hydroxide exists only in the reaction solid, and the LDH perrhenate is produced when the ReO_4^- is added. This means that the LDH hydroxide is an intermediate in the process of sorption.

To get more information about the mechanism of anion sorption on calcined LDH, the experiments for reconstruction of the calcined LDH with CrO_4^{2-} was also carried out. The results of XRD, ^{27}Al MAS NMR, FT-IR, and UV/VIS spectroscopies were already reported[21] and the reconstruction of LDH containing intercalated CrO_4^{2-} was confirmed. The observed XRD data of LDH chromate are also shown in Table 1. The 003 and 006 reflections correspond to 8.98 and 4.50 Å, respectively. The XRD patterns of the mixtures of LDH hydroxide and LDH chromate are shown in Figure 7. As shown in Figure 7(e), the 003 and 006 reflections of LDH (CrO_4) are somewhat broad. These are shifted to left because of the large size of CrO_4^{2-} ion. The a and c parameters of LDH(CrO_4) are 3.06 Å and 26.97 Å, respectively. The interlayer spacing with chromate is 4.19 Å. The LDH hydroxide shows the characteristic sharp 003 and 006 reflections in Figure 7(a). These reflections indicate that it is also a typical layered material. When the CrO_4^{2-} was added to the solution containing LDH(OH)$_2$, the reflections of LDH(CrO_4) also appears and the intensities of the reflections increase with increasing CrO_4^{2-} contents. These results are very similar to those of ReO_4^- sorption.

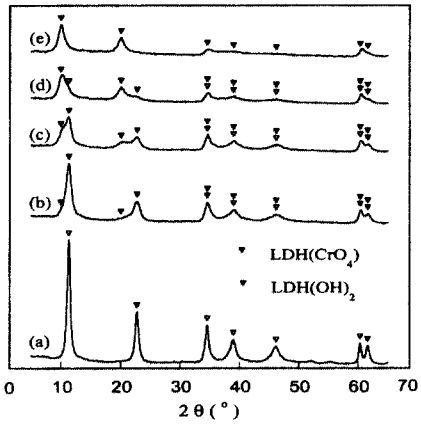

Figure 7. Powder X-ray diffraction patterns of (a) LDH(OH)$_2$ (decarbonated water); (b) mixture of LDH(CrO_4) and LDH(OH)$_2$ (25% AEC CrO_4^{2-}); (c) mixture of LDH(CrO_4) and LDH(OH)$_2$ (50% AEC CrO_4^{2-}); (d) mixture of LDH(CrO_4) and LDH(OH)$_2$(75% AEC CrO_4^{2-}); (e) LDH (CrO_4)(100% AEC CrO_4^{2-}).

CONCLUSION

The powder X-ray diffraction pattern of Mg/Al LDH reconstructed with ReO_4^- anion shows the broad 006 reflection of 4.78 Å. The ^{27}Al MAS NMR spectrum of LDH(ReO_4)$_2$ has a single resonance at δ 8.6, demonstrating that all Al ions are occupying octahedral site. These characterization results including FT-IR spectroscopy reveal that the calcined LDH is reconstructed with intercalating ReO_4^- in the aqueous ReO_4^- solution. The reconstruction of LDH containing CrO_4^{2-} was also confirmed. The XRD patterns of mixture of LDH(ReO_4)$_2$ and LDH (OH)$_2$ demonstrate that an intermediate of the sorption process is LDH hydroxide, $Mg_6Al_2(OH)_{18}$. The sorption of TcO_4^- and ReO_4^- onto calcined LDH is found to be a stepwise ion-exchange reaction involving LDH hydroxide. The first ion-exchange equilibrium, exchanging one OH^- ion in the LDH hydroxide by the TcO_4^- ion, is the formation of LDH(OH)(TcO_4) (s). In second equilibrium, LDH(TcO_4)$_2$(s) is formed successively. In the XRD analysis of reaction solid of CrO_4^{2-} sorption, the LDH(OH)$_2$ is produced together with LDH(CrO_4). The CrO_4^{2-} ion sorbed instead of two exchangeable OH^- ions of LDH hydroxide. The LDH(CrO_4)(s) is formed by ion-exchange reaction.

REFERENCES

1. Allmann, R., "The Crystal Structure of Pyroaurite," *Acta Crystallogr.*, Sect.B, **24**, 972~977 (1968).
2. Brindley, G. W. and Kikkawa, S., "A Crystal-Chemical Study of Mg,Al and Ni,Al Hydroxy-Perchlorates and Hydroxy-Carbonates," *Am. Mineral*, **64**, 836~843 (1979).
3. Taylor, H. F. W., "Crystal Structure of Some Double Hydroxide Minerals," *Mineral. Mag.*, **39**, 377~389 (1973).
4. Miyata, S., "Physico-Chemical Properties of Synthetic Hydrotalcites in Relation to Composition," *Clays Clay Miner.*, **28**, 50~55 (1980).
5. Chibwe, M. and Jones, W., "Intercalation of Organic and Inorganic Anions into Layered Double Hydroxides," *J. Chem. Soc., Chem. Commun.*, 926~929 (1989).
6. Cavani, F., Trifiro, F., and Vaccari, A., "Hydrotalcite-Type Anionic Clays: Preparation, Properties and Applications," *Catal. Today*, **11**, 173~301 (1991).
7. Miyata, S., "Anion-Exchange Properties of Hydrotalcite-Like Compounds," *Clays Clay Miner.*, **31**, 305~311 (1983).
8. Reichle, W. T., Kang, S. Y., and Everhardt, D. S., "The Nature of the Thermal Decomposition of a Catalytically Active Anionic Clay Mineral," *J. Catal.*, **101**, 352~359 (1986).
9. Reichle, W. T., "Synthesis of Anionic Clay Minerals (Mixed Metal Hydroxides, Hydrotalcite)," *Solid States Ionics*, **22**, 135~141 (1986).
10. Sato, T., Kato, K., Endo, T., and Shimada, M., "Preparation and Chemical Properties of Magnesium Aluminum Oxide Solid Solutions," *React. Solids*, **2**, 253~260 (1986).
11. Constantino, V. R. L., and Pinnavaia, T. J., "Basic Properties of $Mg^{2+}_{1-x}Al^{3+}_{x}$ Layered Double Hydroxides Intercalated by Carbonate, Hydroxide, Chloride, and Sulfate Anions," *Inorg. Chem.*, **34**, 883~892 (1995).
12. Sato, T., Wakabayashi, T., and Shimada, M., "Adsorption of Various Anions by Magnesium Aluminum Oxide ($Mg_{0.7}Al_{0.3}O_{1.15}$)," *Ind. Eng. Chem. Prod. Res. Dev.*, **25**, 89~92 (1986).
13. Parker, L. M., Milestone, N. B., and Newman, R. H., "The use of Hydrotalcite as an Anion Absorbant," *Ind. Eng. Chem. Res.*, **34**, 1196~1202 (1995).
14. Goswamee, R. L., Sengupa, P., Bhattacharyya, K. G., and Dutta, D. K., "Adsorption of Cr(VI) in Layered Double Hydroxides," *Applied Clay Science*, **13**, 21~34 (1998).
15. Lieser, K. H., "Technetium in the Nuclear Fuel Cycle, in Medicine and in the Environment," *Radiochim. Acta*, **63**, 5~8 (1993).
16. Fried, S., Friedman, A. M., Cohen, D., Hines, J. J., and Strickert, R. G., The Migration of Long-Lived Radioactive Processing Wastes in the Selected Rocks, ANL-78~46 (1978).
17. Palmer, D. A. and Meyer, R. E., "Adsorption of Technetium on Selected Inorganic Ion-Exchange Materials and on a Range of Naturally Occurring Minerals under Oxic Conditions," *J. Inorg. Nucl. Chem.*, **43**, 2979~2984 (1981).
18. Dyer, A. and Jamil, M. A., Inorganic Anion Exchangers for the Treatment of Radioactive Wastes, Report DOW/RW/88- 100 (1988).
19. Zhuang, H. E., Zheng, J. S., Xia, D. Y., and Zhu, Z. G., "Retardation of Technetium and Iodine by Antimony- and Mercury-Containing Minerals," *Radiochim. Acta*, **68**, 245~249 (1995).
20. Kang, M. J., Rhee, S. W., Moon, H., Neck, V., and Fanghänel, Th., "Sorption of MO_4^- (M = Tc, Re) on Mg/Al Layered Double Hydroxide by Anion Exchange," *Radiochim. Acta*, **75**, 169~173 (1996).
21. Rhee, S. W., Kang, M. J., Kim, H., and Moon, H., "Removal of Aqueous Chromate Ion Involving Rehydration Reaction of Calcined Layered Double Hydroxide (Mg-Al $-CO_3$)," *Environ. Technol.*, **18**, 231~236 (1997).
22. Cotton, F. A. and Wilkinson, G., Advanced

Inorganic Chemistry, John Wiley & Sons, Inc., Sigapore (1988).
23. Rhee, S. W., Kang, M. J., and Moon, H., "Characterization of Layered Double Hydroxides (Mg-Al-CO_3 systems) and Rehydration Reaction of Their Calcined Products in Aqueous Chromate Solution," *J. Kor. Chem. Soc.*, **39**(8), 627~634 (1995).
24. Brown, G. and Gastuche, M. C., "Mixed Magnesium-Aluminum Hydroxides: II. Structure and Structural Chemistry of Synthetic Hydroxycarbonates and Related Minerals and Compounds," *Clay Miner.*, **7**, 193~201 (1967).
25. MacKenzie, K. J. D., Meinhold, R. H., Sherriff, B. L., and Xu, Z., "^{27}Al and ^{25}Mg Solid-State Magic-Angle Spinning Nuclear Magnetic Resonance Study of Hydrotalcite and its Thermal Decomposition Sequence," *J. Mater. Chem.*, **3**, 1263~1269 (1993).