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Oxidation of Cr(III) to Cr(VI) Species During the Thermal Decomposition Process of Zn/Cr-layered Double Hydroxide Carbonate

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The intermediates obtained from thermal decomposition of Zn/Cr-layered double hydroxide carbonates (Zn/Cr-LDH; $Zn_{0.66}Cr_{0.34}(OH)_2(CO_3)_{0.17}0.57H_2O$) were studied by XRD, TPD, FT-IR, ESCA and chemical analyses. It was found that Cr(III) ions embedded originally in the hydroxide layers were oxidized to Cr(VI) species in the temperature range between 473 and 773 K where the layer structure was lost, and reduced again to Cr(III) in the spinel phase over 773 K.

Mixed metal layered double hydroxides, $Zn_2Cr(OH)_6X{\cdot}nH_2O$ (Zn/Cr-LDH; X=anions), have been studied for their various potential uses such as anion exchange materials,[1] anion conductors,[2] and anion sorbents.[3] Although Lal et al. have studied the thermal decomposition of the LDHs by TG-DTA and XRD measurements,[4] the intermediate solids appearing in the various steps of thermal decomposition have not been examined in details, especially on valence change of Cr ions occurring in them. Since the detail of the thermal decomposition process including valence change of Cr ions is considered to be essential when LDHs are practically used, e.g. as an electrical conductor or a catalyst, we wish to report the oxidation of Cr(III) to Cr(VI) species in the intermediate solids thermally decomposed at various temperatures.

The carbonate type LDH was prepared by coprecipitation method. Mixed aqueous solution of $ZnCl_2$ and $CrCl_3$, having total cation concentration of 0.2 M, was prepared with the cation molar ratio $x=Cr^{3+}/(Zn^{2+}+Cr^{3+})$, 0.33. This mixed solution was dropped slowly into 0.2 M Na_2CO_3 aqueous solution with vigorous stirring, keeping the pH of the solution at 10.0 by addition of 2 M NaOH during precipitation. The obtained suspension was further aged at 333 K for 18 hours. The powder was separated centrifugally and washed repeatedly with deionized water, and then dried in vacuo at 318 K. The composition of the sample determined by atomic absorption and gravimetric analyses was $Zn_{0.66}Cr_{0.34}(OH)_2(CO_3)_{0.17}0.57H_2O$. The calcined samples were prepared by heating at constant temperatures between 373 and 973 K for 2 hours in the air. Through this procedure, seven samples with different calcination temperatures were obtained. By calcination, the color of the sample was changed as: purple (the original), grey (373 K), green (473 K and 573 K), black (673 K and 773 K), and dark grey (873 K and 973 K).

The XRD measurement was performed by Rigaku RAD-C diffractometer. The patterns of the calcined samples are summarized in Fig. 1. The original sample shows a typical pattern of hydrotalcite-like minerals, but the sharpness of the lines is fairly low. The samples calcined at 473 and 573 K give no significant reflection lines due to amorphous character. When the calcination temperature raised over 673 K, ZnO phase appears, in addition, a spinel $ZnCr_2O_4$ phase is apparently distinguished over 773 K. These features of structural change during thermal decomposition process is consistent with that reported by Lal et al.[4]

To study the thermal decomposition process in detail, the decomposition of CO_3^{2-} ions was examined by the TPD experiment, which was carried out under He flow (50 ml min^{-1}) with the heating rate 5 K min^{-1}. From the temperature profile of CO_2 evolution, it was found that the CO_2 gas was mainly generated between 453 and 673 K with maximum at 553 K. This is supported by an infrared absorption analysis. The measurement was performed using KBr pellets on a Perkin-Elmer 1640 model FT-IR spectrometer. In Fig. 2, the spectra of the original and the calcined samples are shown. In the IR pattern the CO_3^{2-} ions of the original sample give a strong line at 1360 cm^{-1} and a weak one at 1500 cm^{-1}. These two lines can be assigned to ν_3 (asymmetric stretching) vibration mode with perturbation due to asymmetric character of the site. In the case of the 473 K sample, it is found that the intensity of the peak at 1500 cm^{-1} increased, which was considered to be corresponding to the destruction of the layer structure. However, both absorption peaks disappeared in the spectra for the samples calcined over 673 K. This indicates that the carbonate ions are decomposed mainly at or below 573 K.

It is noteworthy that the formation of chromate species is strongly suggested in the IR spectra data. In the spectrum for the sample calcined at 573 K, an absorption peaked at 905 cm^{-1} is clearly observed, which is characteristic of CrO_4^{2-} ion. The absorption at this frequency is also observed in the spectra for all the samples calcined over 473 K. From the intensity of the peak, it seems that the 573 K sample contains the largest amount of CrO_4^{2-} ions among these samples.

In order to get another evidence of CrO_4^{2-}, we measured the UV-VIS spectra of the dissolved samples. 50 mg of the calcined samples were dissolved into 50 ml of 1 M HCl aqueous solution, then we obtained transparent yellowish solution for the samples below 573 K, whereas in case of the three samples over 673 K, about half amount of the sample in weight remained undissolved. Since, in the latter cases, the undissolved solids were insoluble even in aqua regina, we performed the analysis further using only the supernatants of

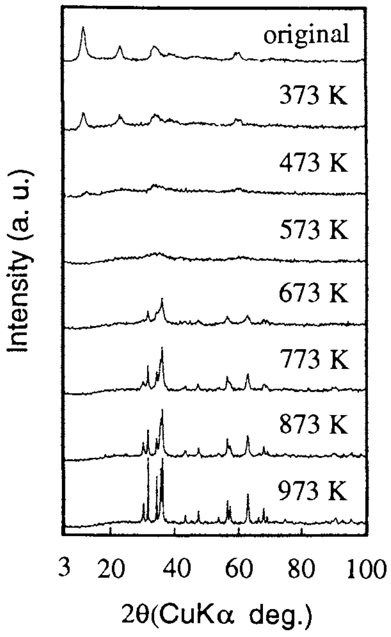

Fig. 1. XRD patterns of the calcined samples from the carbonate type Zn/Cr-LDH.

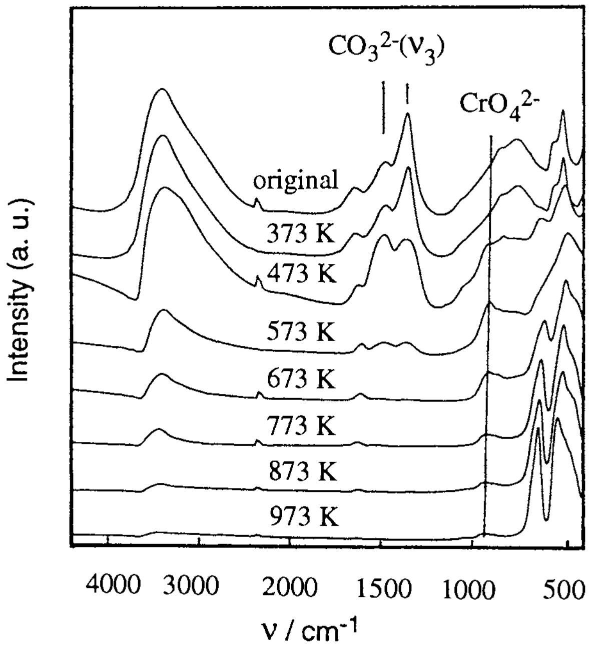

Fig. 2. FT-IR spectra of the calcined samples from the carbonate type Zn/Cr-LDH.

these three samples. The UV-VIS spectra of these solutions or supernatants showed commonly an absorption peaking at 352 nm, which can be assigned to $HCrO_4^-$ ions. However, since this peak was partially overlapped with the strong and broadened absorption of zinc ions, the chromate ions were hardly quantified. For removal of zinc ions from the solution, the pH was raised up to about 10 with addition of NaOH, then separated the precipitation by filtration. At this time, Cr^{3+} ions dissolved in the solution were also removed as hydroxide precipitates. By this procedure we obtained yellow aqueous solution of CrO_4^{2-} whose spectra showed two peaks at 272 and 369 nm.

The quantity of the extracted CrO_4^{2-} ions evaluated by the absorbance data calibrated with a standard K_2CrO_4 solution is shown in Fig. 3 as a function of the calcination temperature. In this figure, the value X stands for the mol fraction of Cr(VI) ions extracted as CrO_4^{2-} in the total Cr ions embedded in the original sample. From this figure, it is found that the 573 K sample gives the largest amount of extraction of CrO_4^{2-}, which is 18% of the Cr ions imbedded originally in the sample. This result seems consistent with that of FT-IR data shown in Fig. 2. From view point of oxidation of Cr(III) in the solid, it is also interesting that the formation of CrO_4^{2-} ions coincides with decomposition of CO_3^{2-}. Since, in case of a non-carbonate type Zn/Cr-LDH such as chloride type, the amount of CrO_4^{2-} obtained from 573 K calcined sample by the identical procedure was much less than those of the present case, it is suggested that thermal activation process including the decomposition of CO_3^{2-} may be related to oxidation of Cr ions due to some potentiality of CO_3^{2-} for oxidation.

On the other hand, oxidation of Cr(III) to Cr(VI) was clearly observed by an ESCA measurement of Cr 2p electrons. The spectra were measured using Shimadzu ESCA-K1 model. In Fig. 4, the results for all the calcined samples are summarized. The binding energy value of 576.7 eV and 579.2 eV are assigned to Cr(III) and Cr(VI) species, respectively. It is apparent that Cr(VI) is main species for the 637 K sample, while the 573

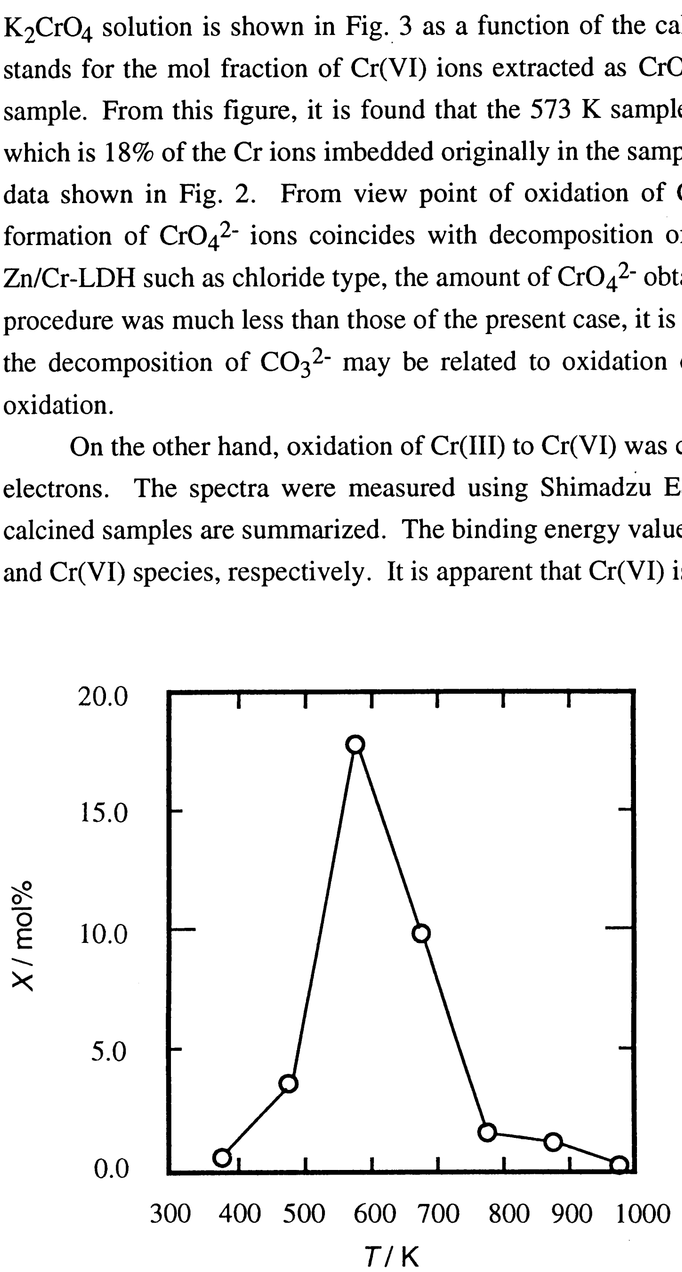

Fig. 3. The fraction of Cr(VI) ions extracted as CrO_4^{2-} from the calcined samples into aqueous solution.

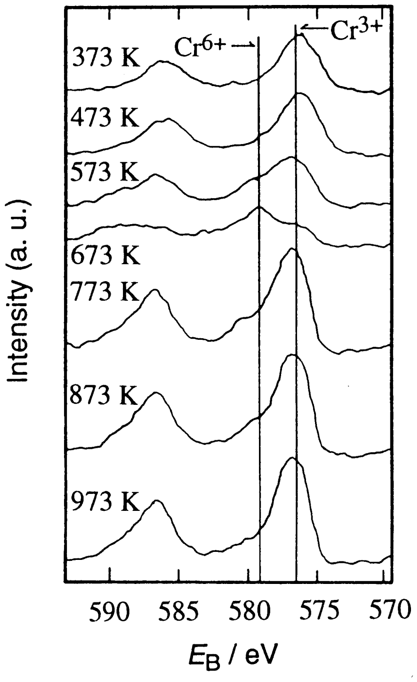

Fig. 4. ESCA spectra of Cr 2p region in the calcined samples from the carbonate type Zn/Cr-LDH.

K and 473 K sample showed the small amount of Cr(VI). When raising the calcination temperature over 773 K, Cr(VI) ions are reduced again forming a spinel phase, $ZnCr_2O_4$.

An ESCA measurement reflects only the surface layers with thickness of 10 nm, more or less. In order to examine the change in valence of Cr ions in the bulk, we measured EPR spectra. The result revealed that the sample calcined at 673 K was EPR-silent whereas the other samples gave significant signals. This fact suggests that the oxidation of Cr(III) to Cr(VI) species occurs not only in the surface layers but also in the bulk of this sample. Taking account of a fact that about half amount of the sample calcined at 673 K remained undissolved in the extraction experiment, the fraction of total oxidized Cr ions is probably larger than that presented in Fig. 3. To determine quantitatively, however, the total amount of the oxidized Cr ions, some other experimental methods should be applied. For this purpose, we are studying further this system by iodometry.

From above results, it is concluded that CrO_4^{2-} ions are formed in the relatively low temperature region from 473 to 773 K with maximum value of 18% of Cr ions embedded in the sample at around 573 K, whereas, in case of the 673 K sample, it was suggested from ESCA experiment that larger amount of Cr ions were oxidized to Cr(VI).

Oxidation of Cr(III) to Cr(VI) species in zeolite like framework at 693 and 843 K has been reported.[5] In addition a fact that the surface Cr(III) species is easily oxidized by oxygen on porous silica gel has been recognized in the field of catalyst preparation. However, the formation of Cr(VI) species during thermal decomposition process of Cr containing LDH has not been reported in literature. Comparing the oxidation process in zeolite like framework, following features should be pointed out: (1) the temperature at which the Cr ions are oxidized is rather lower, (2) the oxidation occurs not under pure oxygen but in the air, and (3) the formation of free chromate ions is associated with the decomposition of carbonate ions. Although the mechanism for the oxidation has not been clear, it may be considered that the thermal decomposition may provide many Cr ions with unsaturated bonds, having high activity for incorporation of dioxygen molecules from air.

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