Note

Hydrothermal Synthesis of Alkali-Containing Hydrated Vanadium Oxides with Layered Structures

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層状構造をもつアリカリ含有水和バナジウム酸化物の水熱合成

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Hydrated vanadium oxides containing alkali ions were prepared by the hydrothermal treatment of VOSO_4 aqueous solutions. The products adopted layered structures with a general composition of $\text{A}_{0.3}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ($\text{A} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ and NH_4 ; $n = 0.6-1.2$). The layer spacings were around $11\text{\AA}$. They were almost unchanged for the compounds of different alkali ions. The layered structures are considered to be composed of the V_2O_5 layers intercalated with water molecules and alkali ions. Dehydration by heating or evacuation caused transitions into the phases where the layer spacings contracted by 1 to $2\text{\AA}$ leading to the values proportional to the size of alkali ions.

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1. Introduction

Hydrated vanadium oxides based on the structure of V_2O_5 adopt layered structures intercalated by water molecules. They have various layer spacings depending on the degrees of hydration. V_2O_5 gels are familiar examples of this class of compounds.¹⁾⁻⁴⁾ The present authors studied the hydrothermal synthesis of the hydrated vanadium oxides that were in regular crystalline states but not in colloidal states and also reported multi-step phase transitions in a dehydration process.⁵⁾ In the present study, the hydrated vanadium oxides containing alkali ions were prepared by a hydrothermal method. It was found that the layer spacings were nearly constant for the compounds with different alkali ions. Dehydration caused the contraction of the layer spacings to the values depending on the size of alkali ions.

2. Experimental

Hydrothermal treatment was conducted as follows. VOSO_4 aqueous solutions containing alkali ions in equimolar amounts with VOSO_4 were sealed in pyrex tubes and were reacted at 200° to

220°C for 30 h. The products were separated by filtration and were characterized by X-ray diffraction using $\text{Cu K}\alpha$ radiation, TG-DTA, absorptiometry and high-temperature X-ray measurements as described in our previous paper.⁵⁾ Alkali and nitrogen contents were measured by flame emission spectroscopy and combustion method, respectively.

3. Results and discussion

Figure 1 shows X-ray diffraction patterns of the products for Na, K, Rb, Cs and NH_4 ions. The patterns appear almost identical for the compounds with different alkali ions. Also the 001 reflections are exclusively seen in Fig. 1 indicating that the compounds are of layered structures. It should be noticed that the layer spacings are almost constant; $10.80\text{\AA}$ for Na, $10.86\text{\AA}$ for K, $10.93\text{\AA}$ for Rb, $10.92\text{\AA}$ for Cs and $10.98\text{\AA}$ for NH_4 . Thus the phases of the alkali compounds may be isostructural and are designated as the $11\text{\AA}$ phase. As shown in Fig. 2, some samples of the Na compound had the layer spacing of $13.7\text{\AA}$ in a wet state which changed to $10.80\text{\AA}$ by

Fig. 1. X-ray diffraction patterns of the alkali compounds for Na, K, Rb, Cs and NH_4 ions.

Fig. 2. X-ray diffraction patterns of the Na compounds in (a) wet and (b) dry form.

drying. That is, a more hydrated phase exists like the phase I' of the hydrated vanadium oxides in our previous paper,⁵⁾ which is called the 13.7 Å phase hereafter. As shown in Fig. 3 of an SEM picture for the Na compound, the particle shape of the alkali compounds is a thin ribbon reflecting layered structures. The compositions of the alkali compounds are listed in Table 1. They are gener-

Fig. 3. SEM picture of the Na compound.

Table 1. Compositions of the alkali compounds.

alkali compound	composition	oxidation number of V
Na compound	$\text{Na}_{0.27}\text{V}_2\text{O}_5 \cdot 0.1 \cdot 1.17\text{H}_2\text{O}^*$	4.85
	$\text{Na}_{0.37}\text{V}_2\text{O}_4 \cdot 0.99 \cdot 1.03\text{H}_2\text{O}$	4.80
K compound	$\text{K}_{0.32}\text{V}_2\text{O}_5 \cdot 0.1 \cdot 0.91\text{H}_2\text{O}$	4.85
Rb compound	$\text{Rb}_{0.30}\text{V}_2\text{O}_5 \cdot 0.2 \cdot 0.81\text{H}_2\text{O}$	4.87
Cs compound	$\text{Cs}_{0.34}\text{V}_2\text{O}_5 \cdot 0.2 \cdot 0.67\text{H}_2\text{O}$	4.84
NH_4 compound	$(\text{NH}_4)_{0.28}\text{V}_2\text{O}_5 \cdot 0.2 \cdot 1.03\text{H}_2\text{O}$	4.88

* for the samples taking the 13.7 Å phase in a wet form.

Fig. 4. High-temperature X-ray diffraction patterns for (a) the Na compound and (b) the Cs compound.

ally expressed as $\text{A}_{0.3}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ($\text{A}=\text{Na}, \text{K}, \text{Rb}, \text{Cs}$ and NH_4 ; $n=0.6-1.2$). The oxidation number of V is around 4.85, implying that V^{5+} ions were reduced to V^{4+} by the amount of alkali ions to conserve the composition of V_2O_5 .

Figure 4 shows high-temperature X-ray patterns of the Na and Cs compounds. On the dehydration by heating, the 11 Å phases were changed into

Fig. 5. Layer spacings plotted against ionic radii for the 11Å phases and the dehydrated phases.

those with smaller layer spacings and the dehydrated phases persisted to the decomposition of the layer phases. Almost identical behavior was observed in other compounds. The dehydrated phases were also obtained by evacuation at room temperature except for the Na compound in which the dehydration proceeds at temperatures higher than in other alkali compounds. The values of the layer spacings of the dehydrated phases varied with the alkali ions; 8.95Å for Na, 9.45Å for K, 9.78Å for Rb, 10.15Å for Cs and 9.63Å for NH₄. As shown in Fig. 5, the plot of the layer spacings against ionic radii of the alkali ions⁶⁾ gives a linear relationship, that is, the layer spacings increase as the size of alkali ions becomes larger. It is concluded that the size of alkali ions

dominates the layer spacings of the dehydrated phases and as also shown in Fig. 5 this is not the case for the 11Å phase.

Layer phases of hydrated V₂O₅ containing alkali ions except Li⁺ were formed by the hydrothermal treatment. The 11Å phase and 13.7Å phase of Fig. 2 may be related to the phases of intercalated V₂O₅ gels for metallic cations reported by Livage et al.⁷⁾ They studied intercalation of various mono- and divalent cations into V₂O₅ gels and found that intercalated phases for monovalent ions had 11Å spacing and those for divalent ones 13.7Å spacing.⁷⁾ In fact, intercalation of, for example, K⁺ into the phase I of our previous paper⁵⁾ yielded the 11Å phase but the product had lower crystallinity than that by the hydrothermal method.⁸⁾ The present hydrothermal method produced well-crystallized phases suited for structure analysis and the study to elucidate the layered structures of the alkali compounds is in progress.

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References

- 1) P. Aldebert, N. Baffier, N. Gharbi and J. Livage, *Mater. Res. Bull.*, **16**, 669-76 (1981).
- 2) J. J. Legendre and J. Livage, *J. Colloid Interface Sci.*, **94**, 75-83 (1983).
- 3) J. Legendre, P. Aldebert, N. Baffier and J. Livage, *J. Colloid Interface Sci.*, **94**, 84-89 (1983).
- 4) P. Aldebert, H. W. Hasslin, N. Baffier and J. Livage, *J. Colloid Interface Sci.*, **98**, 478-83 (1984).
- 5) Y. Oka, N. Yamamoto, T. Ohtani and T. Takada, *Seramikkusu Ronbunshi*, **97**, 1441-45 (1989).
- 6) R. D. Shannon and C. T. Prewitt, *Acta Cryst.*, **B 25**, 925-46 (1969).
- 7) A. Bouhaouss, P. Aldebert, N. Baffier and J. Livage, *Rev. Chim. Miner.*, **22**, 417-26 (1985).
- 8) Y. Oka and N. Yamamoto, unpublished work.