Formation and Phase Transitions of Hydrated Vanadium Oxides with Layered Structures

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層状構造をもつ水和バナジウム酸化物の合成と相転移

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Hydrated vanadium oxides were prepared by hydrothermal treatment of aqueous VOSO₄ solutions. The products were found to take layered structures based on the V₂O₅ structure. Phases with the layer spacings of 7.1, 8.3, 13.2, 14.2 and 19.0 Å were obtained and a primary product was the phase with the spacing of 14.2 Å (phase I). The composition of the phase I was estimated as V₂O_{5-δ}·n H₂O (0 < δ < 0.2, 1.5 < n < 2.5). An additional phase with the spacing of 17.3 Å (phase I') was found in as-filtrated samples, which changed to the phase I by drying. The phase I transformed successively into the phases with smaller layer spacings by dehydration on heating or evacuating. The overall transitions were as follows; I' (17.3 Å) → I (14.2 Å) → Iα' (12.6 Å) → Iα (11.5 Å) → Iβ (10.0 Å) → Iγ (8.3 Å). The transition from phase I to Iβ was reversible. These layer-type phases were distinguished from V₂O₅ gels.

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1. Introduction

Layered structures have received much attention for the two-dimensional properties and intercalation phenomena as well as practical uses as catalysts and ion exchangers. The structure of V₂O₅ is regarded as a layer type and the incorporation of water molecules between the V₂O₅ layers leads to V₂O₅ gels. Thus V₂O₅ gels are of highly two-dimensional nature. V₂O₅ gels have been prepared by several methods such as polymerization of polyvanadic acid,¹⁾ gelation of vanadyl triethoxide²⁾ and quenching of molten V₂O₅ in water.³⁾ V₂O₅ gels are represented by the formula V₂O₅·n H₂O with 0 < n < 20.⁴⁾ V₂O₅ xerogel obtained by dehydration of hydrogels at RT has a formula of V₂O₅·1.6H₂O with the layer spacing of 11.55 Å which changes to V₂O₅·0.5H₂O with that of 8.75 Å above 100°C in air.⁵⁾ The contraction of the layer spacing by 2.8 Å has been attributed to the removal of monolayer of water molecules.⁵⁾ The oxidation number of vanadium in V₂O₅ gels is usually less than five, reaching to 4.9 for melt-quenched V₂O₅ gel^{6),7)} and the presence of V⁴⁺ ions has been reported to play an important role on the formation of the gels as well as the electrical properties.⁶⁾⁻⁹⁾

It is of interest to prepare crystalline phases

with layered structures analogous to V₂O₅ gels under hydrothermal conditions. In the present study, phases with layered structures were obtained by hydrothermal treatment of aqueous VOSO₄ solutions. The conditions of preparing phases with different layer spacings were examined and phase transitions induced by the dehydration and also by the subsequent hydration were observed.

2. Experimental

Hydrothermal treatment was conducted as follows. Aqueous VOSO₄ solutions with the concentrations of 4×10⁻⁴ to 4×10⁻² M were sealed in pyrex tubes and were treated in a Morey-type autoclave at 110° to 280°C for 10 to 60h. Precipitates were separated by filtration and dried in air. An average oxidation number of vanadium in the precipitate was determined by the absorptiometry on a sample dissolved in a sulfuric acid solution. Water content was obtained from a weight loss of dehydration by heating in air up to 400°C. Crystalline phases were examined by the X-ray diffraction method using CuKα radiation. High-temperature X-ray measurements were carried out using a JEOL high-temperature attachment to control temperature within ±1°C.

3. Results and discussion

Figure 1 shows X-ray diffraction patterns of the air-dried products taken in the reflection mode, in which appeared exclusively a series of 00ℓ peaks indicating that the phases are strongly of layer type. As seen in Fig. 1, there are phases with the layer spacings of 14.2, 8.3, 19.0, 7.1 and 13.2 Å designated as phase I, II, III, IV and V, respectively. Formation of these phases were found to be governed by VOSO_4 concentrations and reaction temperatures. Figure 2 shows a formation diagram with the parameters of VOSO_4 concentration and reaction temperature for a reaction time of 24h. In the present hydrothermal system, the average oxidation numbers of V in the products lie between four and five depending on both VOSO_4 concentrations and reaction temperatures.¹⁰⁾ That is, they become lower for higher VOSO_4 concentrations or for higher reaction temperatures and vice versa. In a fairly low concentration range of less than 20 mM, the oxidation numbers of V strongly depend on VOSO_4 concentrations rather than reaction temperatures being greater than 4. 6.¹⁰⁾ Therefore, hydrated vanadium oxides based on V_2O_5 are expected to be formed under the conditions of Fig. 2 and $\text{V}_3\text{O}_7 \cdot \text{H}_2\text{O}$ for the higher VOSO_4 concentrations. As for the degrees of hydration, lower hydrated phases are generally obtained for higher reaction temperatures and thus V_2O_5 was precipitated above 250°C. Moreover, as will be described later, the phase II, which was regarded as lower hydrated phase of the phase I, was formed at reaction temperatures higher than the phase I. As seen in Fig. 2, the phase I was obtained as single phase in a wide range of the diagram. The phases III and IV were obtained in an extremely low concentration range of less than 5 mM and hence it was unsuccessful to have an amount enough for further study. The phases II and V were usually obtained with other phases and were difficult to be separated. Therefore, the present study has been focused on the phase I. It is noticed that the effect of SO_4^{2-} ion, which is considered to be a major impurity ion in this system, on the formation of the layer-type phases, should be ruled out because these layer-type phases were also obtained in hydrothermal treatment of $\text{VO}(\text{OH})_2$ free from SO_4^{2-} ion.¹¹⁾ The morphology of the phase I is of flat plates as seen in Fig. 3 reflecting the two-dimensional feature. The composition of the phase I was estimated as $\text{V}_2\text{O}_5 \cdot \delta \cdot n \text{H}_2\text{O}$ where $0 < \delta < 0.2$ and $1.5 < n < 2.5$ depending on preparation conditions. As shown in Fig. 4, an additional layer-type phase with the spacing of 17.3 Å designated as phase I' was

Fig. 1. X-ray diffraction patterns of the phase I to V for air-dried products.

Fig. 2. Formation diagram of the hydrothermal synthesis of the phase I to V with the parameters of concentration of VOSO_4 solution and reaction temperature for reaction time of 24h.

found in as-filtrated and wet samples synthesized below 240°C. Figure 4 shows that as-filtrated samples synthesized at 170°, 240° and 260°C

adopted the phase I', the phase I' + I and the phase I, respectively, which were all changed into the phase I by drying. Therefore the phase I' is a higher hydrated form of the phase I. In order to examine the intralayer structure of the phase I, an X-ray diffraction pattern was taken in the transmission mode as shown in Fig. 5. As seen in Fig. 5, the X-ray peaks in the transmission mode well correspond to those of V_2O_5 with $h0\ell$ reflections. It indicates that the intralayer structure of the phase I is closely related to the V_2O_5 structure.

Phase transitions of the phase I induced by dehydration on heating in air were investigated by the high-temperature X-ray measurements as shown in Fig. 6. It was found that the phase I was changed successively into the phases with the layer spacings of 11.5, 10.0 and 8.3 Å designated as phase I α , I β and I γ , respectively; $I \xrightarrow{\sim 67^\circ\text{C}} I\alpha \xrightarrow{-92^\circ\text{C}} I\beta \xrightarrow{350-430^\circ\text{C}} I\gamma$. Further heating above 520°C yielded V_2O_5 . It is noteworthy that the transition from the phase I to the phase I β was reversible, i.e., the phase I β returned to the phase I on hydration while the phase I γ was

Fig. 3. SEM photograph of the phase I.

unchanged. Judging from the layer spacings and the X-ray diffraction profiles, the phase I γ seems to be the same as the phase II. So the phase II is regarded as a lower hydrated form of the phase I as mentioned above. The phase I α exhibits a resemblance to V_2O_5 xerogel ($V_2O_5 \cdot 1.6H_2O$) with respect to the layer spacing and the apparent lack

Fig. 5. X-ray diffraction patterns of the phase I taken in the reflection mode (top) and transmission mode (bottom) together with that of V_2O_5 for comparison.

Fig. 4. X-ray diffraction patterns of the products for as-filtrated and air-dried samples synthesized at 170°C (a), 240°C (b) and 260°C (c).

Fig. 6. High-temperature X-ray diffraction patterns of the phase I taken in air.

of 002 reflection.⁵⁾ But it has been reported⁵⁾ that $V_2O_5 \cdot 1.6H_2O$ was changed to $V_2O_5 \cdot 0.5H_2O$ with the spacing of 8.75 Å above 100°C being different from the present case, hence it is doubtful that the phase Ia is the same as the V_2O_5 xerogel. From the weight loss on heating, n in $V_2O_5 \cdot nH_2O$ was estimated to be 0.5–1.0 for the phase Ia, 0.1–0.5 for the phase Ib and 0.1 for the phase Iγ. Phase transitions of the phase I induced by dehydration were also observed in evacuation at 14°C as shown in Fig. 7. In this case, a new phase with the spacing of 12.6 Å was detected as an intermediate phase in a narrow range between the phase I and Ia, which was designated as phase Ia'. The phase Ia' was not observable in evacuation above 20°C. To sum up, the phase I was changed to the phase Ib through the phase Ia' and Ia by dehydration at 14°C and the transition was reversible. It is noted in Fig. 7 that the trace of 001 reflection of the phase I seen in (c) to (f) may be due to the phase I remaining in the portion of the sample sheet adhered to the sample holder which seemed hard to dehydrate. The weight loss by evacuation at 14°C as a

Fig. 7. X-ray diffraction patterns of the phase I taken in vacuum at 14°C for time after evacuation.

function of time is shown in Fig. 8. The weight loss curve shows a slight deflection around 3h after evacuation in the region of phase Ib. At present the origin of the deflection remains nuclear.

In conclusion, various phases of hydrated vanadium oxides with layered structure based on the V_2O_5 structure were formed under hydrothermal conditions. The phase I with the spacing of 14.2 Å was obtained as a primary product and also the phase I' with the spacing of 17.3 Å was found as a higher hydrated phase of the phase I. There were, in total, successive transitions induced by dehydration; phase I' (17.3 Å) → phase I (14.2 Å) → phase Ia' (12.6 Å) → phase Ia (11.5 Å) → phase Ib (10.0 Å) → phase Iγ (8.3 Å). The transitions from phase I to Ib were reversible for dehydration and hydration cycles. In contrast to V_2O_5 gels, the layer-type phases in the present study showed a variety of layer spacings sensitive to the degree of hydration which was rather lower than that of V_2O_5 gels. The layer-type phases gave X-ray peaks much sharper than those of V_2O_5 gels indicating that the layer-type phases adopt more regular crystalline structures. In practice, the phases with the spacings similar to those of the present layer-type phases were reported in V_2O_5 gels⁴⁾; the spacings of 14.4 and 18.7 Å may correspond to those of phase I and III, respec-

Fig. 8. Weight loss of the phase I taken in vacuum at 14°C as a function of time after evacuation.

tively. However, these phases of V_2O_5 gels are not identical with phase I or III from the following reasons. According to Ref. 4), the phase with the spacing of 14.4 Å gave six X-ray peaks of 00 l reflections in the 2θ range of 2° to 50°, whereas phase I gives seven peaks in the same 2θ range as shown in Fig. 1. Next, the phase with the spacing of 18.7 Å gave 001 and 002 reflections,⁴⁾ whereas these peaks are missing in phase III as shown in Fig. 1. Therefore, there is no phase in the present study which coincides with that of V_2O_5 gels. Moreover, the behavior of phase transitions induced by dehydration in the layer-

type phases was found to be more complicated than that of the V_2O_5 xerogels.⁵⁾ Consequently, the layer-type phases should be distinguished from V_2O_5 gels. Further study is in progress to elucidate the intralayer structures, the structures of intercalated water molecules for different layer spacings and the role of V^{4+} ion on stabilizing the layered structures.

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