Synthesis of $K_2Ti_4O_9$ by the Hydrolysis of $KOH-Ti(iso-C_3H_7O)_4$ Ethanol Solution

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KOH と $Ti(iso-C_3H_7O)_4$ 混合エタノール溶液の加水分解による 四チタン酸カリウムの合成

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The precipitates with TiO_2/K_2O molar ratio=4 were obtained by hydrolysis of $KOH-Ti(iso-C_3H_7O)_4$ ethanol solution. The dried product was amorphous, and changed to a crystalline intermediate by heat-treating at about 600°C. The well grown submicron crystals of $K_2Ti_4O_9$ were obtained by heat-treatment at 1000°C for 1 h.

Key-words: Hydrolysis precipitates, Amorphous, Crystalline intermediate, Heat-treatment, $K_2Ti_4O_9$ crystals, Cation-exchanger

1. Introduction

The crystals of potassium tetratitanate $K_2Ti_4O_9$ ^{1,2)} have layer structure, and it is possible from them to obtain the hydrogen tetratitanate hydrate ($H_2Ti_4O_9 \cdot nH_2O$) by the acid treatment. These hydrated crystals are noticed to be useful for cation exchangers. In the case of melting method, $K_2Ti_4O_9$ is formed by the peritectic reaction of $K_2Ti_6O_{13}$ and melt during cooling.³⁾ This reaction proceeds slowly if the molten oxides of stoichiometric composition is cooled from high temperature and so the crystals of single phase are difficult to be obtained. It is also difficult to obtain well grown crystals by sintering the dry mixtures.

The experimental results were reported in the previous paper.³⁾ The mixed ethanol solution of metal alkoxides was hydrolyzed, and the amorphous precipitates were heat-treated at the temperature lower than the peritectic temperature and the well grown crystals of single phase $K_2Ti_4O_9$ were obtained.

In this paper, the synthesis of $K_2Ti_4O_9$ crystals was carried out by using the more stable and useful reagent KOH in place of potassium alkoxides. One of the hydrolysis products, KOH, is known to be dissolved about 29 wt% in C_2H_5OH at 28°C. However, it reacted with the hydrolysis product of titanium isopropoxide directly and the precipitates which were insoluble in the water-ethanol solution were obtained. The dried precipitates were amorphous. However, the well grown submicrometer-sized crystals of $K_2Ti_4O_9$ single phase was found to be ob-

tained by heat-treating the dried precipitates.

2. Experimentals

All chemicals used were of reagent grade and without any purification. Ethanol was treated by molecular sieve for 24 h for dehydration, and 10% KOH ethanol solution was prepared. The apparatus for hydrolysis was as same as in the previous paper.³⁾ However, the pH values of filtrates were measured after the dilution of filtrates to 1/100 to eliminate the obstruction of ethanol and by using the glass electrode pH meter HM-7E together with HM-20S (Toa Electronics Ltd.) in this paper.

The synthetic procedure of $K_2Ti_4O_9$ is as follows. $Ti(iso-C_3H_7O)_4$ was added to (1) 10 wt% $(CH_3)_3COK$ ethanol solution or (2) 10 wt% KOH ethanol solution and the mixed ethanol solutions were obtained. They were hydrolyzed by adding water-ethanol solutions (water content 9.5-63 wt%). The hydrolysis reactions were carried out at 72-75°C for 1 h by stirring and refluxing. The hydrolysis products were sealed in Teflon container and reserved in water bath at 30°C for 24 h for aging. The amounts of KOH unreacted and remained in the filtrates were estimated by the measurements of their pH values. The precipitates were dried at 100°C for 24 h. The dried precipitates were heat-treated at various temperatures. The heat-treated samples were analyzed by X-ray diffraction (XRD) to identify crystalline phases and morphological observation was carried out by scanning electron microscopy (SEM).

3. Results and discussion

3.1 The hydrolysis conditions and products

The hydrolysis reaction of the mixed alkoxides in ethanol solution is

Then the dehydration and crystallization reaction take place by drying and heat-treating.

Therefore totally

and

when KOH is used.

From Eq. (1) the molar ratio of K-tert-butoxide: Ti-isopropoxide: H_2O is 1: 2: 4.5 in formular weight. On the other hand from Eq. (2) KOH: Ti-isopropoxide: H_2O is 1: 2: 3.5.

The amounts of KOH unreacted and remained in filtrate after the hydrolysis were compared in the case of using KOH with K-alkoxide ($(CH_3)_3COK$) by the experiments No. 1–5 in Table 1. The hydrolysis conditions such as the reaction temperature ($72^\circ-75^\circ C$), the total ethanol quantity ($[C_3H_5OH]/[K_2O] = 48$), the aging time (1day) and temperature ($30^\circ C$) were selected to be same. The pH values of the filtrates in sample No. 1–5 were less than or nearly equal to 7. The pH values of less than 7 were considered to be equilibrated ones by absorbing CO_2 in the atmosphere during the measurements. The ion exchanged pure water used for the dilution of the filtrates at the pH measurement showed also nearly the same value of pH. Therefore KOH quantities in these filtrates were considered to be negligible small from their pH values. These results were nearly the same when the water content was increased from molar ratio $H_2O/K_2O = 7.0$ to 74. KOH reacted with the hydrolysis product of titanium isopropoxide, and the precipitates which TiO_2/K_2O molar ratio = 4 were obtained.

3.2 Change of hydrolysis product by heat-treatment and crystal growth

The XRD pattern of the sample No. 1–5 showed nearly the same change when heat-treated at various temperatures. The typical XRD pattern of the samples prepared by using KOH was shown in Fig. 1. The only halo with maximum at about $d = 0.3$ nm ($2\theta = 29^\circ$) caused by amorphous structure was observed in the samples which were dried at $100^\circ C$ for 24 h and heat-treated at $400^\circ C$ for 1 h. The crystalline diffraction lines began to appear in the sample heat-treated at $600^\circ C$. These lines are different from those of $K_2Ti_4O_9$ (mark $\bullet$) and unknown. This

Fig. 1. XRD pattern of sample No. 2 using KOH after heat-treated at various temperatures.

○: intermediate, $\bullet$: $K_2Ti_4O_9$, $\times$: $K_2Ti_6O_{13}$

unknown crystalline phase disappears when the crystals of $K_2Ti_4O_9$ is formed by heat-treating at the higher temperature. Therefore, these diffraction lines are considered to be those of intermediate crystals (mark $\circ$). Exothermic peak corresponding to this crystallization was observed at $560^\circ-580^\circ C$ in DTA of sample No. 1–5. The mixed phases of intermediate and $K_2Ti_4O_9$ crystals were observed when heat-treated at $800^\circ C$ for 1 h. The only sharp diffraction lines of $K_2Ti_4O_9$ crystals were observed in the sample heat-treated at $1000^\circ C$ for 1 h and their intensities were much increased. Therefore the samples heat-treated at $1000^\circ C$ are confirmed to be well grow $K_2Ti_4O_9$ crystals. In the sample heat-treated at $1200^\circ C$ for 1 h, the deposition of $K_2Ti_6O_{13}$ (mark $\times$) was observed which was caused by the incongruent melting of $K_2Ti_4O_9$ by the peritectic reaction $K_2Ti_4O_9 \rightarrow K_2Ti_6O_{13} + \text{melt}$ at $1114^\circ C$. $K_2Ti_4O_9$ was identified by Dion et al.'s results⁴⁾ as shown in Table 2. The good agreement is obtained except weak diffraction lines $2.999(\text{\AA})$ and $2.749(\text{\AA})$ which are confirmed to belong to no diffraction lines possible other than $K_2Ti_4O_9$. The reason is now under investigation.

Figure 2 shows the SEM photographs of sample No. 2 which were dried at $100^\circ C$ for 24 h and heat-treated at $600^\circ C$, $800^\circ C$ and $1000^\circ C$ for 1 h respectively. The dried precipitates were amorphous and aggregated as shown in Fig. 2(a). The small angle scattering was observed in the XRD pattern of this sam-

Table 1. The conditions of hydrolysis and the identified crystalline phases after calcination.

Sample No.	Starting Material	Hydrolysis		$[TiO_2]/[K_2O]$ mole ratio	$[H_2O]/[K_2O]$ mole ratio	$[C_2H_5OH]/[K_2O]$ mole ratio	Filtrate pH	Crystalline phase after calcined at $1000^\circ C, 1h$
		Reaction (temp/ $^\circ C$)	Aging (time/d)					
1	$(CH_3)_3COK$	72–75	1	4.0	9.0(1.0)	48	6.8	T
2	KOH	72–75	1	4.0	7.0(1.0)	48	6.3	T
3	$(CH_3)_3COK$	72–75	1	4.0	18(2.0)	48	6.6	T
4	KOH	72–75	1	4.0	28(4.0)	48	6.6	T
5	KOH	72–75	1	4.0	74(11)	48	6.7	T

a): multiples of formular ratio

T: $K_2Ti_4O_9$

Table 2. XRD analysis of sample prepared by this method.

$K_2Ti_4O_9$, Dion et al (1981) JCPDS 32-861			sample No.2 (1000°C, 1h)	
d(Å)	I/I ₁	hkl	d(Å)	I/I ₁
8.76	100	200	8.803	100
6.19	35	201	6.197	48
5.75	2	002	-----	---
4.09	1	40 $\bar{2}$	-----	---
3.95	3	20 $\bar{3}$	3.962	12
3.75	3	401	3.751	8
3.71	2	110	3.707	13
3.18	35	310	3.181	87
3.08	<1	402	-----	---
			2.999	11
2.95	35	311	2.953	97
2.88	30	004	2.884	78
2.80	1	404	-----	---
			2.749	13
2.72	20	60 $\bar{3}$	2.728	43
2.66	30	31 $\bar{3}$	2.658	71
2.62	4	312	2.618	12
2.55	<1	51 $\bar{2}$	2.555	7
2.344	3	11 $\bar{4}$	2.344	8
2.270	<1	80 $\bar{1}$	-----	---
2.186	25	512	2.188	56
2.089	25	205	2.089	55
2.047	2	71 $\bar{3}$	-----	---
1.986	2	314	1.987	10
1.895	10	020	1.895	59
1.854	2	220	1.852	7
1.838	1	405	1.837	7
1.827	2	712	1.824	9
1.752	2	91 $\bar{3}$	1.752	13
1.744	8	11 $\bar{6}$	1.742	20

ple. However, the scattering disappeared when heat-treated at 400°C for 1 h. Its SEM image was observed to be nearly same as shown in Fig. 2(a). By heat-treating at 600°C for 1 h the dried precipitates were changed to the crystalline intermediates which were investigated by the XRD analysis as shown in Fig. 1 and rather amorphous than crystalline in shape (Fig. 2(b)). They were changed to the mixture of pillar-like and plate-like crystals in shape when heat-treated at 800°C for 1 h (Fig. 2(c)). The samples heat-treated at 1000°C for 1 h were well grown pillar-like crystals of length from about 600 to 800 nm which were confirmed to be $K_2Ti_4O_9$ crystals by the XRD analysis and the plate-like crystals disappeared (Fig. 2(d)).

4. Conclusion

The synthesis of $K_2Ti_4O_9$ crystals was investigated by hydrolyzing the mixed KOH and $Ti(iso-C_3H_7O)_4$ ethanol solution and heat-treating hydrolysis product.

The results are as follows;

(1) All hydrolysis products were amorphous which were insoluble in the water-ethanol solutions when TiO_2/K_2O molar ratio=4.0.

Fig. 2. SEM photographs of the sample No. 2 heat-treated at various temperatures

(a) 100°C, 24 h; (b) 600°C, 1 h; (c) 800°C, 1 h; (d) 1000°C, 1 h; (bar=1 μm)

(2) The dried precipitates heat-treated at 600°C for 1 h were changed from amorphous to unknown intermediate crystals.

(3) The intermediate crystals were changed to well-grown $K_2Ti_4O_9$ crystals by heat-treating them at 1000°C for 1 h.

(4) No difference between of starting material $(CH_3)_3COK$ and KOH was found from the above results. Therefore, it was confirmed that the synthesis of $K_2Ti_4O_9$ crystals was possible by using KOH as well as K-alkoxide.

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