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Hydrothermal synthesis of alkali titanates from nano size titania powder

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Alkali titanates $A_2Ti_nO_{2n+1}$ (A = Li, Na, K) were synthesized by hydrothermal reaction of titania powder in an aqueous alkaline solution. A nano size titania powder of 7 nm in diameter was used as the starting material to progress the hydrothermal reaction at 100°C. In the TiO_2-LiOH-H_2O system, Li_2TiO_3 and an amorphous phase of TiO_2 were synthesized. $KTiO_2(OH)$ was synthesized as a single phase in the TiO_2-KOH-H_2O system at 125°C. Phase diagrams of the products in the TiO_2-AOH-H_2O (A = Li, K, Na) systems have been constructed in the region of AOH concentration from 0 to 50 mol · kg^{-1}-H_2O and temperature from 75 to 125°C.

1. Introduction

Alkali titanates are series of compounds with the formula $A_2Ti_nO_{2n+1}$ (A = Li, K, Na). Many kinds of alkali titanates with unique layered and tunnel crystal structures have been synthesized [1, 2]. Their physicochemical properties, such as optical properties and ionic and electronic conductivities [3–11], have been investigated on account of their application in industry as ion exchangers, electrodes for secondary batteries, filters, reinforcements, heat insulators, catalysts and so on.

The alkali titanates have been synthesized by a conventional solid state reaction or a flux method. In these methods, titania powder and alkali carbonate/alkali peroxide are used as raw materials, and the products are obtained after heating the mixture of the raw materials. The particle size and morphology of the products are difficult to control. Thus, hydrothermal synthesis is promising because this method has many operation parameters to control particle size and morphology such as temperature, time, concentration of the solution, pH, liquid-solid ratio and additives (oxidant, chelating reagents, surfactant) etc. [12–15].

In this study, alkali titanate particles were synthesized by hydrothermal reaction at a relatively low temperature of around 100°C. A nano size titania powder, with particles 7 nm in diameter, was supplied as the starting material to allow the hydrothermal reaction to take place between 75 and 125°C. Phase diagrams of the TiO_2-AOH-H_2O (A = Li, K, Na) systems have also been constructed in the region of AOH concentration from 0 to 50 mol · kg^{-1}-H_2O and temperature from 75 to 125°C.

2. Experimental procedure

A nano size titania powder TiO_2 (ST-01, Ishihara Sangyo Co., Ltd. Japan) was used. Properties of the titania are summarized in Table I.

All other reagents were commercial grade and were used in the experiments directly without any further purification. Water was deionized by the ion exchange after distillation.

The experimental procedure was as follows. Initially 0.4 g of TiO_2 powder, a certain amount of alkali hydroxide and 50 cm^3 of deionized water were put into a closed polypropylene bottle of 100 cm^3 capacity (AS ONE Co. Ltd.). The polypropylene bottle was heated in the oven up to temperature from 75 to 100°C for 2 h to progress the hydrothermal reaction. During the reaction period the bottle was kept at the autogenous saturation vapor pressure of the solution without agitation. Then, the product powder was filtered, rinsed with deionized water (LiOH and NaOH systems) or methanol (KOH system) and then dried in the open laboratory for 12 h.

The products were identified by a X-ray powder diffractometry (XRD) (Shimadzu XD-D1). The particle size and shape were analyzed using a scanning electron microscope (Hitachi S-430). Chemical analysis was carried out by ICP-AES (inductively coupled plasma atomic emission spectrometry) (SEIKO SPS-1200A) and AAS (atomic absorption spectrometry) (Shimadzu AA-6500S) after dissolving the sample in aqua regia.

3. Results and discussion

3.1. Phase diagram for the TiO_2-LiOH-H_2O system

A phase diagram of the TiO_2-LiOH-H_2O system in the region of LiOH concentration from 0 to 5 mol · kg^{-1}-H_2O and temperature from 75 to 125°C was constructed from the XRD results (Fig. 1). The XRD patterns of the products at 100°C are also shown in Fig. 2. The LiOH concentration from 0 to 5 mol · kg^{-1}-H_2O depends on the LiOH solubility in H_2O for example at 100°C, it is 7.98 mol · kg^{-1}-H_2O.

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TABLE I Properties of the nano-size titania (ST-01)

Purity	TiO_2 93.6/wt%
Water	4.7/wt%
Type of crystal structure	anatase
Diameter	7/nm (X-ray)
Specific surface area	$300/m^2 \cdot g^{-1}$

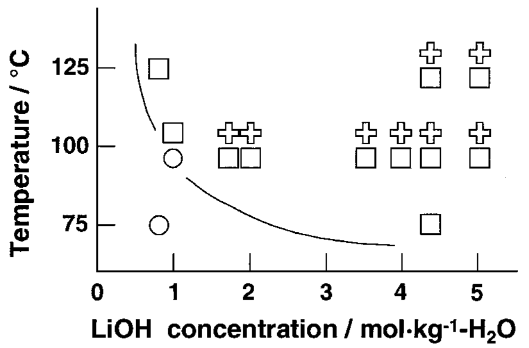

Figure 1 Phase diagram for the TiO_2-LiOH-H_2O system after hydrothermal treatment of a TiO_2 powder for 2 h at various LiOH concentrations and temperatures. ○: TiO_2, □: amorphous, and ✣: Li_2TiO_3.

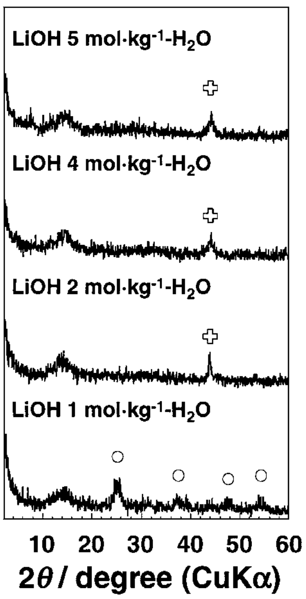

Figure 2 The XRD patterns of the products synthesized in the TiO_2-LiOH-H_2O system at 100°C.

TABLE II Chemical analyses of Li_2TiO_3 produced under different conditions

LiOH conc./mol · kg^{-1}-H_2O	Temp./°C	Time/h	Li/Ti molar ratio
–	–	–	2.00 (calc.)
2	100°C	2	0.35
4	100°C	2	0.40
5	100°C	2	0.36
5	125°C	60	0.34

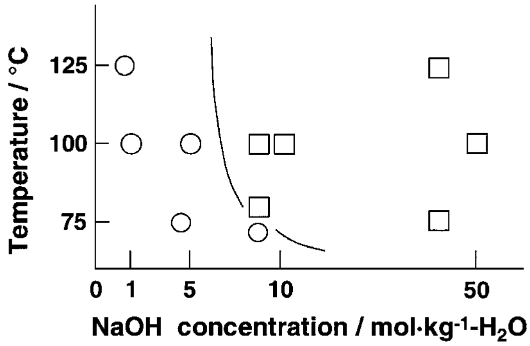

Figure 3 Phase diagram for the TiO_2-NaOH-H_2O system after hydrothermal treatment of a TiO_2 powder for 2 h at various NaOH concentrations and temperatures. ○: TiO_2 and □: amorphous.

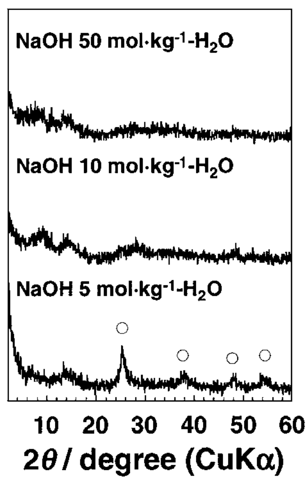

Figure 4 The XRD patterns of the products synthesized in the TiO_2-NaOH-H_2O system at 100°C.

An amorphous lithium titanate was found in the range of LiOH concentration from 1 mol · kg^{-1}-H_2O at 100°C to 4.3 mol · kg^{-1}-H_2O at 75°C. When temperature and LiOH concentration increased, there was a tendency for Li_2TiO_3 formation. Note that, the broad peak at about 14° in the XRD traces is due to the sample holder which was made of glass. According to the XRD patterns, the products synthesized at LiOH concentrations above 2 mol · kg^{-1}-H_2O and temperatures above 100°C were single phase Li_2TiO_3. However, the XRD patterns in this region show very weak and broad peaks. Therefore chemical analysis was carried out by ICP-AES and AAS to examine the Li/Ti molar ratio in the products formed at 100°C and 125°C. The results are summarized in Table II.

For all samples in this experiment, the Li/Ti molar ratio was much lower than the stoichiometric value of 2. LiOH concentration, temperature and reaction time does not effect the Li/Ti molar ratio. TiO_2 anatase peaks were observed in the XRD patterns of samples calcinated at 600°C. Thus, these results suggest that a mixture of Li_2TiO_3 and amorphous TiO_2 were synthesised under the present experimental conditions.

3.2. Phase diagram for the TiO_2-NaOH-H_2O system

Fig. 3 presents the phase diagram of the products synthesized in the TiO_2-NaOH-H_2O system in the region of NaOH concentration from 0 to 50 mol · kg^{-1}-H_2O and temperature from 75 to 125°C. The XRD patterns of the products at 100°C are shown in Fig. 4.

According to the XRD patterns, TiO_2 anatase peaks decrease with increasing NaOH concentration and temperature. There is no peak in the XRD pattern of the product synthesized at a NaOH concentration of

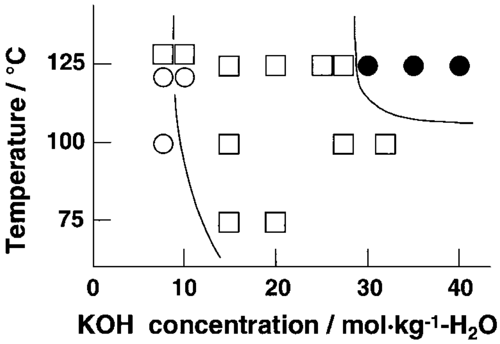

Figure 5 Phase diagram for the TiO_2-KOH-H_2O system after hydrothermal treatment of a TiO_2 powder for 2 h at various KOH concentrations and temperatures. ○: TiO_2, □: amorphous and ●: $KTiO_2(OH)$.

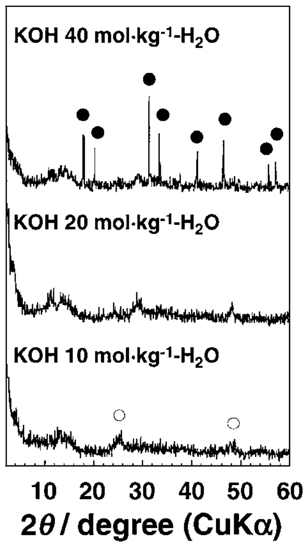

Figure 6 The XRD patterns of the products synthesized in the TiO_2-KOH-H_2O system at 125°C.

10 mol · kg^{-1}-H_2O and a temperature of 100°C. In this system, an amorphous compound was the only product except the unreacted TiO_2.

The initial TiO_2 was completely retained at a NaOH concentration of 4 mol · kg^{-1}-H_2O and a temperature of 75°C. In the TiO_2-LiOH-H_2O system discussed above, an amorphous compound was formed under this condition. Compared with the TiO_2-LiOH-H_2O system, the reactivity in the TiO_2-NaOH-H_2O system was decreased. Nevertheless, amorphous compounds were found at NaOH concentrations above 10 mol · kg^{-1}-H_2O and temperatures from 75 to 125°C. This is indicative of the high reactivity in this system since micron sized TiO_2 powder hardly reacted in these conditions.

3.3. Phase diagram for the TiO_2-KOH-H_2O system

Fig. 5 presents the phase diagram of the TiO_2-KOH-H_2O system in the region of KOH concentration from 0 to 40 mol · kg^{-1}-H_2O and temperature from 75 to 125°C. The XRD patterns of the products synthesized at 125°C are shown in Fig. 6.

The XRD pattern of the product obtained at a KOH concentration of 10 mol · kg^{-1}-H_2O and a temperature of 125°C had small peaks which resulted from the unreacted TiO_2. No peak was observed in the XRD pattern of the product synthesized at a KOH concentration of 20 mol · kg^{-1}-H_2O and a temperature of 100°C. This reveals that the unreacted TiO_2 phase tends to decrease when temperature and KOH concentration increase. An amorphous compound was found in a wide range of KOH concentrations from above 15 mol · kg^{-1}-H_2O and temperatures above 75°C to 30 mol · kg^{-1}-H_2O and a temperature of 125°C. The XRD patterns indicate that single phase $KTiO_2(OH)$ was formed at KOH concentrations above 30 mol · kg^{-1}-H_2O and a temperature of 125°C. In addition, chemical analysis was carried out by ICP-AES and AAS to examine the K/Ti molar ratio in $KTiO_2(OH)$. The results are summarized in Table III.

TABLE III Chemical analyses of $KTiO_2(OH)$ produced under different conditions

KOH conc./mol · kg^{-1}-H_2O	Temp./°C	Time/h	K/Ti molar ratio
–	–	–	1.00 (calc.)
30	125°C	2	0.95
40	125°C	2	1.00

As it can be seen, the measurements agree very closely with the stoichiometric value of 1. Therefore, the obtained product is single phase $KTiO_2(OH)$. It has been reported that single phase $KTiO_2(OH)$ was obtained in a limited region of KOH concentrations at temperature above 150°C when Ti powder of particle size smaller than 45 μm was used as the starting material [15]. Thus, it can be assumed that a nano size titania powder 7 nm in diameter enabled a hydrothermal reaction at a lower temperature.

According to the XRD patterns, TiO_2 peaks of the sample synthesized in the LiOH system at a LiOH concentration of 1 mol · kg^{-1}-H_2O and a temperature of 100°C were smaller than the some peaks in the sample before reaction. In the NaOH system, there was no peak in the XRD pattern of the compound obtained at a NaOH concentration of 10 mol · kg^{-1}-H_2O and a temperature of 100°C. For the KOH system at a KOH concentration of 10 mol · kg^{-1}-H_2O, a small TiO_2 peak remained even at a temperature of 125°C. Therefore, the reactivity of three alkaline systems is LiOH > NaOH > KOH.

3.4. Morphology of the products

The particle size and morphology of the products were investigated by SEM. The results are shown in Fig. 7.

The TiO_2 starting material (Fig. 7a), consisted of large aggregates with an average size of 1.8 μm diameter comprising nano scale grains. In the mixture of Li_2TiO_3 and amorphous TiO_2 phases (Fig. 7b) particles of size less than 1 μm in diameter existed amongst particles which had a similar size to the aggregates in the starting material. The amorphous compound in the NaOH system (Fig. 7c) also consisted of many small particles and some larger ones. The potassium hydroxy titanate $KTiO_2(OH)$ (Fig. 7d) consisted of two different kinds of particles: small ones of indefinite form and large hexagonal ones 20–30 μm in length.

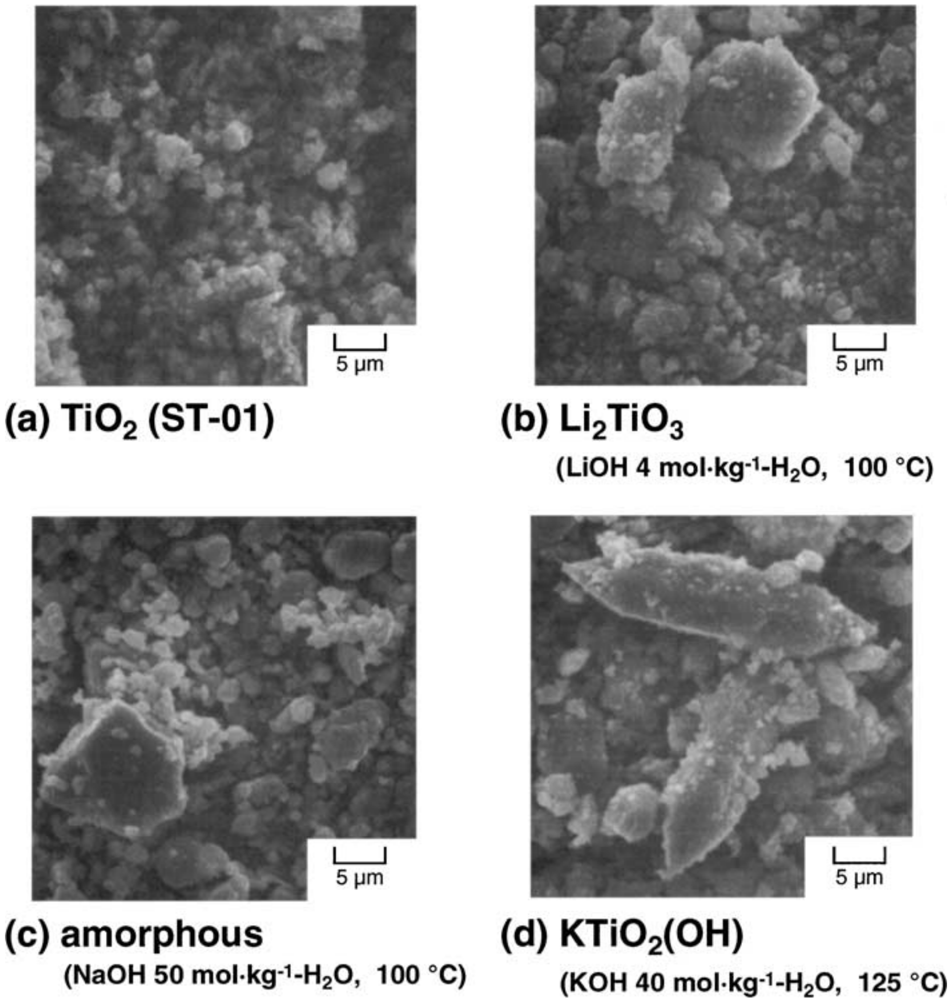

Figure 7 The SEM photographs of the products. Synthesise conditions were as follows: (a) TiO_2 raw material, (b) LiOH concentration of 4 mol · kg^{-1}-H_2O, 100°C resulting in Li_2TiO_3 and amorphous TiO_2, (c) NaOH concentration of 50 mol · kg^{-1}-H_2O, 100°C resulting in an amorphous compound and (d) KOH concentration of 40 mol · kg^{-1}, 125°C resulting in $KTiO_2(OH)$.

4. Conclusions

From the presented experimental results, the following conclusions can be made:

1. Phase diagrams for the TiO_2-AOH-H_2O systems (A = Li, Na, K) have been constructed in the region of temperature from 75 to 125°C and AOH concentration from 0 to 5, 50, 40 mol · kg^{-1}-H_2O, respectively.
2. In the TiO_2-LiOH-H_2O system, Li_2TiO_3 and an amorphous phase of TiO_2 were synthesized at LiOH concentrations above 2 mol · kg^{-1}-H_2O and temperatures above 100°C.
3. In the TiO_2-NaOH-H_2O system, only amorphous compounds could be obtained at NaOH concentrations from 10 to 50 mol · kg^{-1}-H_2O and temperatures from 75 to 125°C.
4. In the TiO_2-KOH-H_2O system, a single phase of $KTiO_2(OH)$ was synthesized at KOH concentrations above 30 mol · kg^{-1}-H_2O and a temperature of 125°C. Under this condition, small crystals of indefinite form and well-grown single crystals of hexagonal columnar form were obtained.

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