Synthesis and CO₂ Absorption Property of Li₄TiO₄ as a Novel CO₂ Absorbent

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Synthesis and CO₂ absorption property of Li₄TiO₄ oxide were studied by X-ray powder diffraction and thermogravimetry. Samples were prepared by the solid state method using Li₂CO₃ and Anatase or Rutile TiO₂ as starting reagents. From the results of XRD, it was found that single phase Li₄TiO₄ can be obtained from Anatase TiO₂ and Li₂CO₃ with 1 : 2.1 molar ratio in an alumina cell in atmosphere of Ar : H₂ = 80 vol% : 20 vol% gas mixture (150 mL/min of flow rate) by heat-treatment up to 1000°C with 5°C/min of heating rate. By the results of thermogravimetry, it was found that single phase Li₄TiO₄ can absorb CO₂ in the temperature range of 300°C to 856°C, and the maximum absorption is 42 mass% at 856°C. From the results of XRD, LiTiO_x and Li₂CO₃ phases were found in the Li₄TiO₄ sample after complete CO₂ absorption. Therefore, it is supposed that following reaction occurs in the reaction process between Li₄TiO₄ and CO₂. 42 mass% of the maximum absorption could be predicted on the basis of the reaction. $\text{Li}_4\text{TiO}_4(\text{s}) + 1.5\text{CO}_2(\text{g}) \longleftrightarrow \text{LiTiO}_x(\text{s}) + 1.5\text{Li}_2\text{CO}_3(\text{s}) + (2.5-x)/2 \text{O}_2(\text{g})$ $x = 2 \sim 2.5$

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1. Introduction

It is well-known that Global Warming is quite a large problem in the world. It must be a very important and urgent challenge to solve the problem as soon as possible. This sense of urgency has been shown by the coming into effect of the Kyoto Protocol. It is thought that one of the main causes of the Global Warming is carbon dioxide CO₂ produced as one of the exhaust gases from power plants generating electricity and from other factories. Thus, it is desired to reduce the amount of the produced CO₂ gas.

However, it is difficult to reduce the amount of the CO₂ gas because it is more difficult to reduce the amount of electricity generated at present, and rather, more generation of electricity appears to be necessary for progress in developing countries. Therefore, it is important to separate CO₂ in the exhaust gases from power plant as well as the reducing the amount of produced CO₂. Therefore, effective CO₂ separation techniques or systems are desired.

Many previous superior studies^{1)–12)} have already reported on the separation techniques and systems. Researchers of Toshiba Corporation have developed a novel separation technique that employs a chemical reaction of lithium-containing oxides, such as Li₂ZrO₃ and Li₄SiO₄, with CO₂.^{5)–12)} According to these reports,^{5)–12)} it has been thought that Li₄SiO₄ is a very efficient CO₂ absorbent because 1g of Li₄SiO₄ can absorb 0.367 g of CO₂, and the absorption is supposed to depend on the following reaction (1).¹¹⁾

On the basis of the reaction, CO₂ reacts with Li₂O component of Li₄SiO₄ and changes to solid Li₂CO₃ when CO₂ is absorbed in Li₄SiO₄, and the maximum CO₂ absorption

$$\left(\frac{1 \times (\text{molecular weight of CO}_2)}{1 \times (\text{molecular weight of Li}_4\text{SiO}_4)} \times 100\% \right)$$

is theoretically estimated as 36.7 mass%, if the reaction completes. Experimental value¹¹⁾ of the maximum CO₂ absorption is consistent with 36.7 mass% of the estimated one at 700°C. Moreover, it has been confirmed that the reaction is reversible, that is, the reaction progresses in the right direction (→) below 700°C, and the left direction (←) over 700°C.

In order to find a new CO₂ absorbent, we investigated the

CO₂ absorption mechanism of Li₄SiO₄ and Li₂ZrO₃. Key point for the CO₂ absorption could be the number of Li₂O components in molecular formula. For example, Li₆CuO₄,¹³⁾ Li₅FeO₄,¹⁴⁾ and Li₄TiO₄^{15)–18)} would be more efficient CO₂ absorbents than Li₂ZrO₃ and Li₄SiO₄. According to the previous reports,^{13)–18)} Li₆CuO₄ and Li₅FeO₄ have been found as only by-products, while Li₄TiO₄ has been obtained as main product with a small amount of Li₂TiO₃. Reaction between Li₄TiO₄ and CO₂ gas has been proposed as (2) without any experimental evidence.¹⁸⁾

If this reaction really occurs, 1 mol of Li₄TiO₄ reacts with 1 mol of CO₂, that is, 1g of Li₄TiO₄ would be able to absorb 0.315 g of CO₂ corresponding to 31.5 mass%, which is smaller in the amount than that of Li₄SiO₄.

On the other hand, among the Li–Ti–O series oxides, presence of LiTiO₂ phase¹⁹⁾ has previously been reported. We paid attention to the LiTiO₂ phase. The reaction between Li₄TiO₄ and CO₂ would be expected as follows if the reaction products are LiTiO₂ and Li₂CO₃.

On the basis of the reaction, 1 mol of Li₄TiO₄ reacts with 1.5 mol of CO₂, and the maximum value of CO₂ absorption becomes 41.5 mass% which is greater than that of Li₄SiO₄. Thus, there is a possibility that Li₄TiO₄ would be a more effective CO₂ absorbent than Li₄SiO₄ although the single phase Li₄TiO₄ has not been obtained yet.

In this paper, we report a new synthesis method to obtain the single phase Li₄TiO₄ and the novel CO₂ absorption property.

2. Experimental procedures

Samples of Li₄TiO₄ were prepared by the solid state method using Li₂CO₃ powder reagent (99.999% purity, Rare Metallic Co., LTD.), and three kinds of TiO₂ reagents as follows.

No. 1: Anatase TiO₂ (99.98% purity, Soekawa Chemicals Co., LTD.)

No. 2: Anatase TiO₂ (99.99% purity, Rare Metallic

Co., LTD.)
No. 3: Rutile TiO₂ (99.99% purity, Rare Metallic Co., LTD.)

By XRD, it was found that a small amount of Rutile TiO₂ was contained in both the No. 1 and No. 2 reagents, that is, it was difficult to get 100% Anatase TiO₂ reagent, while the No. 3 reagent consisted of 100% Rutile TiO₂.

Before these reagents were weighed for the synthesis, thermogravimetry was performed on these reagents in order to examine whether absorption moisture was contained or not in these reagents. After the thermogravimetry, these reagents were weighed in an appropriate molar ratio and mixed/ground in a mortar by hand for 1 h or by a Ball Mill Machine for 108 h. Obtained powder mixtures were heated in an alumina cell at 600–1000°C for several hours in the following atmospheres, i) 100 vol% Ar gas or ii) Ar : H₂ = 80 vol% : 20 vol% gas mixture. In order to compare CO₂ absorption property of Li₄TiO₄ with that of Li₄SiO₄ or Li₄GeO₄, Li₄SiO₄ sample was prepared at 900°C for 12 h in air from Li₂CO₃ and SiO₂ (99.99% purity, Rare Metallic Co., LTD.) with 2 : 1 molar ratio, and Li₄GeO₄ sample was prepared at 700°C for 20 h in air from Li₂CO₃ and GeO₂ (99.9999% purity, Rare Metallic Co., LTD.) with 2.02 : 1 molar ratio.

X-ray Powder diffraction (XRD) measurements to assess phase purity were carried out using a diffractometer (Rigaku Rint2100) using Cu Kα radiation. In order to examine CO₂ absorption property of the samples, weight change and DTA signal of the samples were measured by a thermo-balance (Ulvac-Riko TGD9600) when the samples were heated in a 100 vol% CO₂ atmosphere from room temperature to 1000°C with 5°C/min or 300°C/min of heating rate.

3. Result and discussion

Synthesis

According to the previous works,^{15),17)} we used following reaction (4) for the synthesis of

Li₄TiO₄, and prepared five kinds of starting powder mixtures (A1–A5) from TiO₂ and Li₂CO₃ reagents with 1 : 2 ratio. Contents of Anatase TiO₂ and Rutile TiO₂ in A1–A5 mixtures were estimated by XRD using diffraction peak intensities of (101) for the Anatase TiO₂ and (110) for the Rutile TiO₂. Results of the estimation are shown in Table 1. From the Table, it is found that we were able to get five kinds of starting powder mixtures with different contents (%) of the Anatase TiO₂ and the Rutile TiO₂, and it is noted that it was difficult to get powder mixture consisting of 100% Anatase TiO₂ with Li₂CO₃.

First, according to the previous work,¹⁷⁾ we used 100 vol% Ar gas stream as an atmosphere for the synthesis of Li₄TiO₄. The mixtures (A1–A5) were heat-treated in 100 vol% Ar gas atmosphere at 600–1000°C for several hours. XRD was

performed on these heat-treated samples in order to identify phases in the samples. From the XRD results, it was found that main phase was Li₂TiO₃²⁰⁾ in all the samples although a small amount of Li₄TiO₄ phase was found in them. Therefore, it was confirmed that 100 vol% Ar gas atmosphere is not appropriate to obtain single phase Li₄TiO₄. We would postulate the reason not to obtain single phase Li₄TiO₄ in 100 vol% Ar gas atmosphere, as follows. We assume that Li₂CO₃ seems to melt before the reaction between TiO₂ and Li₂CO₃ completes, and it depends on difficulty of decarbonation of solid Li₂CO₃. Thus, we expected that H₂ gas would accelerate the decarbonation of Li₂CO₃, and introduced H₂ gas into atmosphere of 100 vol% Ar gas. In order to examine effects of H₂ gas on the decarbonation of Li₂CO₃, thermogravimetry was performed on the starting powder mixtures (A1–A5).

According to the reaction (4), weight of the starting powder mixtures must decrease due to the decarbonation of Li₂CO₃ when the reaction proceeds. Thus, weight decrease is an indicator of progress of the reaction. By using thermogravimetry, weight change and DTA signal of the mixtures were measured in-situ, when the mixture was heated with 5°C/min from room temperature to 1000°C in the following atmospheres, i) 100 vol% Ar gas and ii) Ar : H₂ = 80 vol% : 20 vol% gas mixture with 150 mL/min of flow rate. As a typical result, temperature dependences of weight change and DTA signal of A1 powder mixture are shown in Fig. 1. Respective weights (▲, ●) of the sample begin to decrease around 400°C in both the atmospheres, and there is almost no difference between these weight changes below 600°C in both the atmospheres. However, in the case of Ar : H₂ = 80 vol% : 20 vol% gas mixture (▲), the weight decreases drastically around 600°C and seems to saturate over 800°C, while the weight change (●) in the case of 100 vol% Ar gas is sluggish over 600°C. Moreover, in the case of 100 vol% Ar gas, a DTA signal showing an endothermal peak is found at 712°C (arrow in Fig. 1). This temperature is consistent with the melting point of Li₂CO₃. From these results, it is found that, in 100 vol% Ar gas atmosphere, Li₂CO₃ melts at 712°C and the reaction seems not to progress completely, while the reaction seems to progress almost completely in the atmosphere of Ar : H₂ = 80 vol% : 20 vol% gas mixture. These results would show that H₂ gas is effective to obtain single phase Li₄TiO₄. Therefore, we heat-treated A1–A5 powder mixtures in an alumina cell in the atmosphere of Ar : H₂ = 80 vol% : 20 vol% gas mixture with 150 mL/min of flow rate from room temperature to 1000°C with 5°C/min.

XRD was performed on these five heat-treated samples. It was found that main phase was Li₄TiO₄ although a small amount of Li₂TiO₃ or LiTiO₂ phase was detected in the samples. We measured intensities of diffraction peaks *I*(2 0 2) of Li₄TiO₄, *I*(0 0 2) of Li₂TiO₃, and *I*(2 0 0) of LiTiO₂ by XRD, and roughly estimated content of Li₄TiO₄ in these samples as

Table 1. Contents of Anatase and Rutile TiO₂ in Starting Powder Mixtures of TiO₂ and Li₂CO₃ with 1 : 2 molar ratio

Starting Powder Mixtures	A1	A2	A3	A4	A5
Kind of TiO ₂					
Anatase TiO ₂ / %	97.6	96.0	51.5	47.4	0
Rutile TiO ₂ / %	2.4	4.0	48.5	52.6	100

$$\frac{I(202)}{\{I(202) + I(002) + I(200)\}} \times 100\%.$$

The content of Li₄TiO₄ was plotted to content of Anatase TiO₂ in the starting powder mixtures A1–A5 (shown in Table 1) in Fig. 2. From the Fig. 2, it is found that the content of Li₄TiO₄ increases with the increasing of the Anatase TiO₂ content in the starting powder mixtures, and almost single phase Li₄TiO₄

Fig. 1. Temperature dependences of weight change and DTA signal of the mixture of TiO₂ and Li₂CO₃ with 1 : 2 molar ratio (A1 powder mixture), in atmosphere of 100 vol% Ar gas, and Ar : H₂ = 80 vol% : 20 vol% gas mixture.

could be obtained in A1 and A2 mixture containing Anatase TiO₂ over 95%. The results suggest that we should select 100% Anatase TiO₂ and Ar : H₂ = 80 vol% : 20 vol% gas mixture as the atmosphere. However, it is difficult to get 100% Anatase TiO₂.

In order to obtain perfect single phase Li₄TiO₄, we added excess Li₂CO₃ (5 mass% or 15 mass%) to starting powder mixture, because Li₂TiO₃ and LiTiO₂ (the undesirable extra phases) have smaller Li element than Li₄TiO₄. So, we prepared more two kinds of starting powder mixtures B1 and B2 by using Anatase TiO₂ (No. 2 reagent) and Li₂CO₃ with molar ratio of 1 : 2.1 for B1 and 1 : 2.3 for B2. Contents of Anatase and Rutile TiO₂ in these mixtures were also estimated by XRD. Results are shown in Table 2, where the result of A2 is shown again for comparison. From the Table, it is found that three powders have almost same Anatase TiO₂ content. The powders were heat-treated in an alumina cell in the atmosphere of Ar : H₂ = 80 vol% : 20 vol% gas mixture with 150 mL/min of flow rate from room temperature to 1000°C with 5°C/min of heating rate. Phases identified in the heat-treated powder samples by XRD are shown in Table 3. It is apparent that perfect single phase Li₄TiO₄ was successfully obtained in B1 and B2 samples which contained the excess Li₂CO₃. Reproducibility of the single phase obtained by this

Fig. 2. Relationship between formation of Li₄TiO₄ and Anatase TiO₂ content in the starting powder mixture.

Table 2. Contents of Anatase and Rutile TiO₂ in starting Powder Mixtures

Starting Powder Mixtures	A2 ^{*1}	B1 ^{*2}	B2 ^{*3}
Kind of TiO ₂			
Anatase TiO ₂ / %	96.0	96.1	96.0
Rutile TiO ₂ / %	4.0	3.9	4.0

^{*1} Powder Mixture of TiO₂ : Li₂CO₃ = 1 : 2 molar ratio

^{*2} Powder Mixture of TiO₂ : Li₂CO₃ = 1 : 2.1 (= 2.0 + 0.1) molar ratio

^{*3} Powder Mixture of TiO₂ : Li₂CO₃ = 1 : 2.3 (= 2.0 + 0.3) molar ratio

Table 3. Content of Li₄TiO₄ in heat-treated samples (starting powder mixtures)

Samples	A2	B1	B2
Li ₄ TiO ₄ content / %	91.2	100	100

Fig. 3. Temperature dependence of CO₂ absorption of Li₄TiO₄, Li₄SiO₄ and Li₄GeO₄ samples. The measurement was performed with 5°C/min of heating rate in atmosphere of 100 vol% CO₂.

method was confirmed. In addition, the single phase Li₄TiO₄ were not obtained in two cases: i) when flow rate of Ar : H₂ = 80 vol% : 20 vol% gas mixture was 400 mL/min, LiOH · H₂O phase was found in Li₄TiO₄ sample, ii), when flow rate of Ar : H₂ = 80 vol% : 20 vol% gas mixture was 50 mL/min, Li₂TiO₃ was found in Li₄TiO₄ sample. Next, we examined CO₂ absorption property of the single phase Li₄TiO₄ by thermogravimetry.

CO₂ Absorption Property of Li₄TiO₄

Temperature dependence of weight change of single phase Li₄TiO₄ sample was measured by the thermo-balance when the sample was heated in an alumina cell in 100 vol% CO₂ atmosphere from room temperature to 1000°C with 5°C/min of heating rate. Temperature dependences of weight change of Li₄SiO₄ and Li₄GeO₄ were measured under the same condition for comparison. The results of three samples are shown in Fig. 3, where the increase of weight corresponds with CO₂ absorption of the samples. It is found that Li₄TiO₄ begins to absorb CO₂ gas around 300°C, and absorption increases drastically at 600°C, reaching 42 mass% of the maximum value at 856°C. This temperature, 856°C is defined as the maximum temperature $T_{\max}$. Above this temperature, the sample begins to emit CO₂ gas, however, the CO₂ emission is found not to complete under 1000°C.

On the other hand, Li₄SiO₄ and Li₄GeO₄ begin to absorb CO₂ gas around 500°C, and the CO₂ absorption increases drastically at 600°C, reaching 36.7 mass% or 26.7 mass% of the maximum value around 700°C respectively (So, $T_{\max}$ = 700°C), and above this temperature the samples begin to emit CO₂ gas. In these cases, it is found that the CO₂ emission completes almost under 1000°C. From all the results, it is found that region of CO₂ absorption of Li₄TiO₄ is wider than those of Li₄SiO₄ and Li₄GeO₄, and the maximum value of CO₂ absorption of Li₄TiO₄ is greater than those of Li₄SiO₄ and Li₄GeO₄. However, Li₄TiO₄ can hardly emit CO₂ than Li₄SiO₄ and Li₄GeO₄. The difference between $T_{\max}$ of Li₄TiO₄, Li₄SiO₄ and Li₄GeO₄ seems to depend on the difference between equilibrium temperatures for those CO₂ absorption reactions.

As mentioned previously, the maximum CO₂ absorption 36.7 mass% of Li₄SiO₄ can be estimated by the reaction (1). Equally, 26.7 mass% of Li₄GeO₄ can be estimated on the basis of following reaction (5).

Fig. 4. XRD profile of Li₄TiO₄ sample after complete CO₂ absorption.

However, the maximum CO₂ absorption 42 mass% of Li₄TiO₄ can not be explained by the reaction (2) because the maximum CO₂ absorption is estimated as 31.5 mass% on the basis of the reaction (2). For the reason, we performed XRD on the sample after complete CO₂ absorption. The result is shown in Fig. 4. From the Fig. 4, it is apparent that Li₂CO₃ and LiTiO_x¹⁹⁾ phases are found, but Li₂TiO₃ phase is not found in the sample. Therefore, the reaction between Li₄TiO₄ and CO₂ would be described as follows.

On the basis of the reaction, we could estimate the maximum value of CO₂ absorption to be from 41.5 mass% to 47.3 mass% depending on x . These values are almost consistent with 42 mass% of our experimental data. It seems that x value depends on chemical valence of Ti ion. It is not apparent, at present, whether the chemical valence of the Ti ion is +3 or +4.

Next, we tried to measure weight change of Li₄TiO₄, Li₄SiO₄ and Li₄GeO₄ when three samples were heated in 100 vol% CO₂ atmosphere from room temperature to 1000°C with 300°C/min of very fast heating rate. The fast heating rate could allow to find difference between the reaction rates of the three samples. The results are shown in Fig. 5. The very drastic weight increase around 650°C–700°C for Li₄TiO₄ seems to show that the rate of CO₂ absorption of Li₄TiO₄ is much faster than those of Li₄SiO₄ and Li₄GeO₄, and that Li₄SiO₄ and Li₄GeO₄ can hardly absorb CO₂ enough with the very fast heating rate.

4. Conclusion

We studied synthesis and CO₂ absorption property of single phase Li₄TiO₄ by the solid state reaction method and thermogravimetry. Single phase Li₄TiO₄ can be obtained from Anatase TiO₂ and Li₂CO₃ with 1 : 2.1 or 1 : 2.3 molar ratio in atmosphere of Ar : H₂ = 80 vol% : 20 vol% gas mixture (150 mL/min of flow rate) by heat-treatment up to 1000°C with 5°C/min of heating rate. Thermogravimetry shows that single phase Li₄TiO₄ can absorb CO₂ gas in the temperature range of 300°C to 856°C, and the maximum absorption is 42 mass% at 856°C. By the results of XRD, it was found that the following

Fig. 5. Temperature dependence of weight change of Li₄TiO₄, Li₄SiO₄ and Li₄GeO₄. The measurement was performed with 300°C/min of very fast heating rate in atmosphere 100 vol% CO₂.

reaction occurs in reaction process between Li₄TiO₄ and CO₂.

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