



SOL-GEL PREPARATION OF HIGH SURFACE AREA POTASSIUM TETRATITANATE FOR THE IMMOBILIZATION OF NUCLEAR WASTE METAL IONS

K.T. JUNG, Y.G. SHUL, J.K. MOON, W.J. OH

Department of Chemical Engineering,

Yonsei University,

Seoul, Republic of Korea

Abstract

Potassium tetratitanates ($K_2Ti_4O_9$) were synthesized by using the sol-gel method to produce ion-exchangeable materials with high surface area. The effects of mole ratios of K/Ti and H_2O /Ti were examined. $K_2Ti_4O_9$ was obtained at $740^\circ C$ by the sol-gel method, which uses a lower temperature than the melting method. After calcination at $800^\circ C$, $K_2Ti_4O_9$ exhibits a needle shape which is quite different from the shape of $K_2Ti_6O_{13}$ powder. The surface area of $K_2Ti_4O_9$ was $15\text{ m}^2/\text{g}$ by the sol-gel method after calcining at 800 C . The enhancement of BET area to $25\text{ m}^2/\text{g}$ was obtained after supercritical drying using EtOH as solvent. By using the sodium alginate method, needle type potassium titanate $10\mu\text{m}$ in length, the longest aspect ratio of 1.3×10^3 , could be obtained. There are variations in the Sr^{2+} ion exchange rate and capacity according to the preparation method. Larger BET surface area provides fast ion exchange and larger capacity for Sr^{2+} ion in the order; sol-gel process with supercritical drying > sol-gel process > melting process.

1. INTRODUCTION

Potassium titanates [$K_2O \cdot nTiO_2$ ($n=1-8$)] have cage, tunnel or layered structures, which consist of TiO_6 octahedra joined by sharing corners, edges and/or faces [1]. Among these titanates; potassium dititanate ($K_2Ti_2O_5$), potassium tetratitanate ($K_2Ti_4O_9$) and potassium hexatitanate ($K_2Ti_6O_{13}$) are well known [2-3].

Potassium tetratitanate, is used as a catalyst, filter materials, reinforcing material, heat insulator, automotive brake lining material and acoustic absorbing material as well as an ion exchanger [4,5]. When potassium ions, the ion-exchangeable sites, are replaced by protons a hydrous titanium dioxide is obtained. These hydrous titanium dioxides, which can be represented as $(H^+ \cdot H_3O)Ti_4O_9$, have a large ion exchange capacity for alkali metal ions [6], alkaline earth metal ions [7] and divalent transition metal ions [8]. These ion-exchange properties are due to the fact that hydrous titanium dioxide has exchangeable protons and hydronium ions in an interlayer structure. The acid treatment process to make crystalline hydrate titanate and the ion exchange process are well established and known to be reversible to some extent [9]. The acid treatment process and the ion exchange equation is denoted as follows:



when M means metal ion.

Some reports have been published for sorption of Sr^{2+} , Cs^+ , and other ions with sodium titanate [10]. In treating Sr^{2+} and Cs^+ , the advantage of high distribution

coefficient(K_d) value is reported at high pH; the disadvantage of this process is the slow exchange rate due to the low surface area of the powder ($< 10 \text{ m}^2/\text{g}$).

Potassium tetratitanate has been synthesized at about 900-1000°C by using a melting method and the powder has a low surface area due to the high temperature treatment. Surface area, particle size, and pore size, which have an influence on ion exchange capacity, decrease with increase of temperature. Therefore, only powder of low surface area ($\approx 10 \text{ m}^2/\text{g}$ or less) was obtained due to rapid densification of particles during the course of crystallization at this high temperature condition.

To prepare potassium tetratitanate with high surface area, the sol-gel process was found to be an excellent method since it provides many advantages over the conventional process [11]. In general, the sol-gel process is applicable to the low temperature synthesis of ceramics since the formation of an amorphous phase is promoted by the new intermediates present in a ceramic sol at low temperature. Therefore, if we make a homogeneous mixture of potassium and titanium in the sol state we can obtain a solid phase with large surface area at low temperature by suppressing the densification of a crystalline structure at high temperature. Up to now, few studies have been made on multicomponent systems. Recently, we have reported sol-gel synthesis of potassium hexatitanate to provide a large BET surface area [12].

Recently, a new process of preparing ceramic fibre by using sodium alginate has been employed by various workers [13]. This process is based on ion exchange and gelation of sodium alginate $(\text{C}_5\text{H}_7\text{O}_4\text{COONa})_x \cdot y\text{H}_2\text{O}$, which is well known as an ion exchangeable organic polymer. The alginate method does not require a ceramic powder as a starting material. In addition, the viscous solution of the sodium alginate has an advantage in that it gels in any shape such as fibre, film, and bead by ion exchange with protons or multivalent metal ions. Alumina-silica, hydroxyapatite, YBCO fibre was synthesized using this method [13].

In this study, sol-gel synthesis of potassium tetratitanate was attempted under various conditions. To enhance the surface area of potassium tetratitanate, supercritical drying was attempted for the precursor sol. Ion exchange of Sr^{2+} was tested with samples prepared by different methods; melting process, sol-gel process, and sol-gel process adopted with supercritical drying. To make long potassium titanate long fibres, synthesis of potassium tetratitanate using sodium alginate was also tested.

2. EXPERIMENTAL

The experimental scheme is shown in Fig. 1. Sol-gel reaction was carried out in a glove box under N_2 atmosphere. At first, the potassium precursor, water and catalyst were dissolved in 0.5 the theoretical amount of EtOH. Then titanium precursor dissolved in the remaining EtOH was added to partially hydrolyzed potassium alkoxide sol to make a homogeneous sol mixture. After making a homogeneous potassium-titanate sol mixture, the hydrolysis reaction proceeded and was subsequently aged at room temperature for 1-7 days to make a gelled structure. After drying the sample, it was calcined up to 800°C to obtain a crystalline potassium tetratitanate.

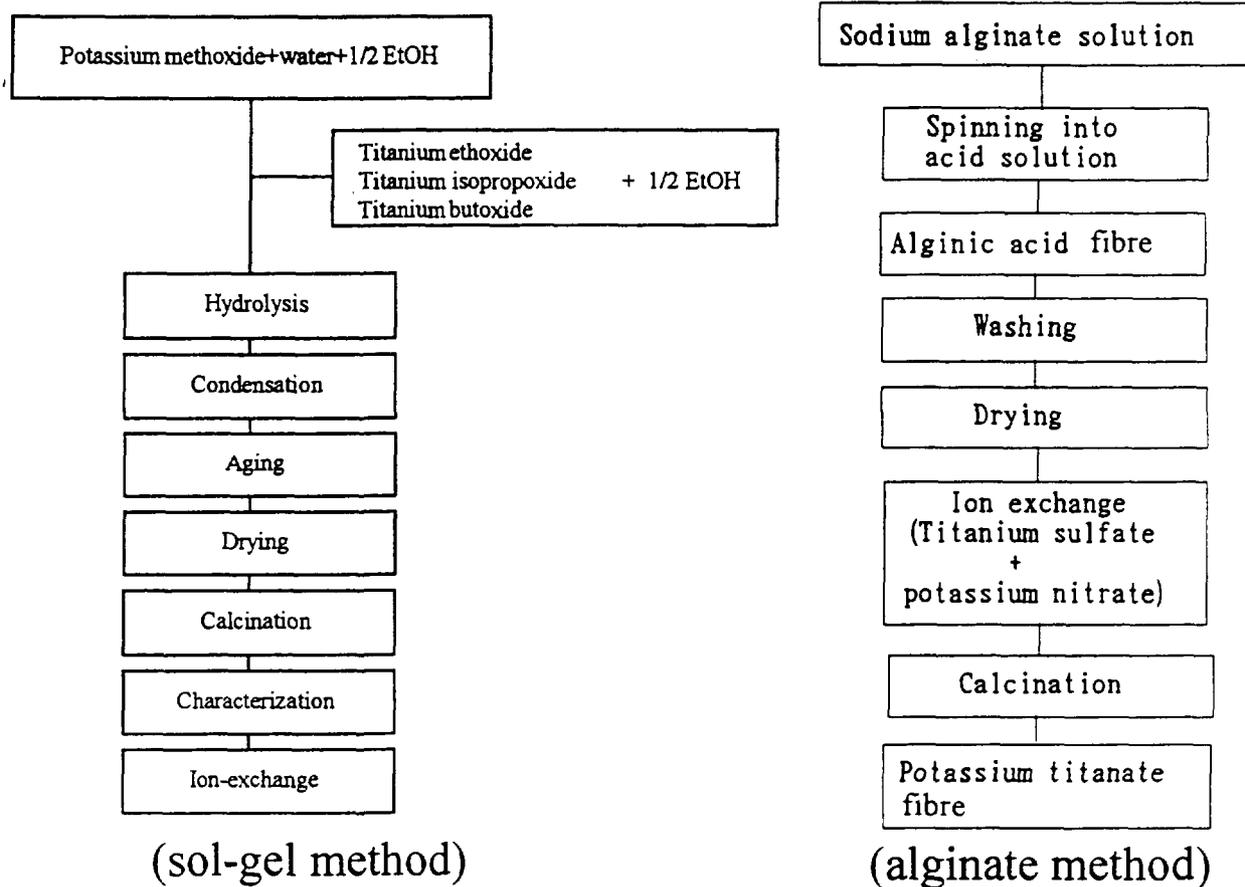


FIG. 1. Preparation of potassium titanate by sol-gel method and alginate method.

The experimental apparatus for supercritical drying (SCD) is shown in Fig. 2. As a solvent for SCD, EtOH ($T_c = 243.0^\circ\text{C}$, $P_c = 925.8$ psi) was used. Potassium tetratitanate sol was fed into the reactor (50 vol%) with EtOH solvent and the high pressure reactor was heated with a heating rate of $1^\circ\text{C}/\text{min}$ up to 300°C . When the temperature reached 300°C , the autoclave was held for 1h to ensure complete thermal equilibration (300°C , 1700 psig). After that, the pressure was decreased isothermally to atmospheric pressure by venting the solvent. To avoid condensation of solvent on the samples, the autoclave was flushed with nitrogen at atmospheric pressure from 300°C to room temperature.

An aqueous solution of 5% sodium alginate was extruded from a nozzle with a 2 mm inner diameter into 1M-HCl. The extruded sodium alginate sol gelled as an alginic acid fibre through ion exchange of its sodium ions with protons in the HCl solution, and the alginic acid fibre was rinsed 5 times in de-ionized water and then immersed in a solution of titanium sulphate and KNO_3 for more than 10 hours. The K-Ti-alginate fibre was rinsed in de-ionized water, dried at ambient temperature and then fired at 800°C for 3 hours in air.

Ion exchange experiments were executed for the kinetic measurements using a batch contact technique. 0.3g samples of potassium tetratitanate hydrate treated with 0.1M HCl were immersed in 200 mL of 0.005M strontium nitrate solution.

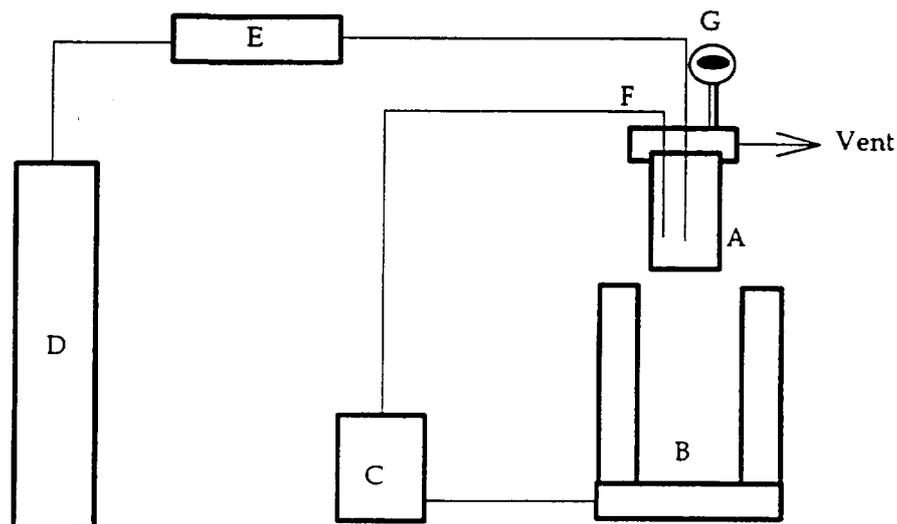


FIG. 2. *Supercritical drying apparatus.*

A: Reactor B: Furnace C: Thermocouple controller

D: Nitrogen E: Trap F: Thermocouple G: Pressure gauge

The surface area was estimated, using nitrogen adsorption, by a surface area analyzer 848 (Micrometrics Co.) and the particle size and shape of particles were observed by SEM (JEOL). To characterize thermal behavior and crystalline temperature, differential thermal analysis and thermal gravimetric analysis (TG-DTA, Thermoflex, Rigaku) of the powder were carried out. X-ray diffraction (XRD, D-Max. 3, Rigaku) was used for the identification of the crystalline phase. Strontium concentrations in the solution were determined by atomic absorption spectrometry (AAS, Perkin Elmer) using the flame technique.

3. RESULT AND DISCUSSIONS

To apply potassium titanate, which has ion exchangeable sites, for the immobilization of nuclear waste, various synthetic methods were attempted such as a melting method [9], sol-gel method [11], sol-gel method adopted with super critical drying process, and sodium alginate method.

3.1. MELTING METHOD

Potassium titanate was prepared by the reaction of titanium dioxide (rutile) and potassium carbonate. When the molar ratio K/Ti was 0.5, potassium tetratitanate was obtained at 950°C after 50 hours heating. However, potassium hexatitanate was synthesized over the temperature range 950-1050°C (K/Ti=0.3). Figure 3 shows SEM images of potassium titanate obtained by the melting method. The average length and the aspect ratio (length/diameter) of potassium tetratitanate fibre is 5 μ m and 10-15, respectively. In the case of potassium hexatitanate, the average length and the aspect ratio was smaller than that of potassium tetratitanate. Normally, those samples prepared by the melting method have a low BET surface area (< 10m²/g).

3.2. SOL-GEL METHOD

3.2.1. Synthesis of potassium tetratitanate from $\text{CH}_3\text{OK-Ti}[\text{O}(\text{CH}_2)\text{CH}_3]_4$

Figure 4 shows the TG-DTA profiles of potassium tetratitanate ($\text{K}_2\text{Ti}_4\text{O}_9$) synthesized by CH_3OK as a potassium precursor and $\text{Ti}[\text{O}(\text{CH}_2)\text{CH}_3]_4$ as a titanium precursor. Changes of TG-DTA profile are compared according to $[\text{H}_2\text{O}]/[\text{Ti}]$ ratio and drying method. In the case of (a) and (b), it is shown that weight loss was about 30% at 100-150°C and two endothermic peaks were assigned to desorption peaks of physisorbed water and chemisorbed water 100-150°C and 350-150°C, respectively. The exothermic peak at 559°C and 745°C without weight loss is due to the phase transition of amorphous powder to crystalline intermediate and intermediate to potassium tetratitanate respectively. This was proven by XRD patterns of the potassium tetratitanate after calcination at 800°C as shown in Figs. 5 and 6. This kind of low crystallization temperature was not feasible in conventional synthesis starting with solid powders. The exothermic peak (Fig. 4) at 559°C corresponds to an intermediate phase and peak at 745°C is assigned to the phase transition temperature from an intermediate to potassium tetratitanate. It proves that, unlike potassium hexatitanate, potassium tetratitanate is synthesized through an intermediate phase.

In the case of the supercritical dried sample, the weight loss was lower than that of atmospheric drying due to the extraction of water absorbed in the gel powder during the supercritical drying process and a broad exothermic peak appeared near 830°C. As shown in Fig. 7, the shape of potassium tetratitanate gel powder in the pure gel state is spherical. However, after calcination at 800°C, potassium tetratitanate is needle shaped. According to Y. Fujiki et. al [14], they synthesized potassium tetratitanate by a flux (K_2MoO_4) and cooling method at 1150°C. The size of fibres obtained was 1mm in length and 0.01mm in diameter on average. However, in our case, the fibre have a length of 0.5-5 μm and a thickness of 0.05 - 0.2 μm . The shape of the potassium tetratitanate is quite differ from the shape of potassium hexatitanate powders obtained by the melting process. Figure 8 reveals that the morphology of potassium tetratitanate changes with preparative method. In the melting method the spherical shape of potassium tetratitanate is mixed with needle shape potassium tetratitanate. The shape of potassium tetratitanate, supercritical dried process (Fig. 8 (c)), is even thinner and shorter than that from other methods(melting and sol-gel process).

3.2.2. Effect of K/Ti ratio

The effects of initial K/Ti ratios on the final properties of products are shown in Table 1 for different titanium alkoxides. Potassium hexatitanate converted to potassium tetratitanate on increasing the K/Ti ratio from 0.3 to 2. In this hydrolysis and condensation reaction of metal alkoxides, potassium should also act as a base catalyst to form colloid type particles instead of the polymeric types which can be observed in acid catalysis [15]. As shown in Fig. 9, the gel powder shows a spherical shape of agglomerate which should come from a colloidal type of primary particles, potassium titanate sol. When the K/Ti ratio is 2.0, the XRD patterns show potassium tetratitanate(K/Ti=0.5) as a main phase and small amount of potassium hexatitanate (K/Ti=0.3). The amount of potassium incorporation into the titanium framework is decreased as the K/Ti ratio is increased. It seems difficult to obtain pure potassium tetratitanate under these conditions because all the potassium is not incorporated with titanium ion in the sol state. The excess potassium should remain in solution or deposit on the surface of the titanium sol. It is noteworthy that the surface area of titanate gel powder

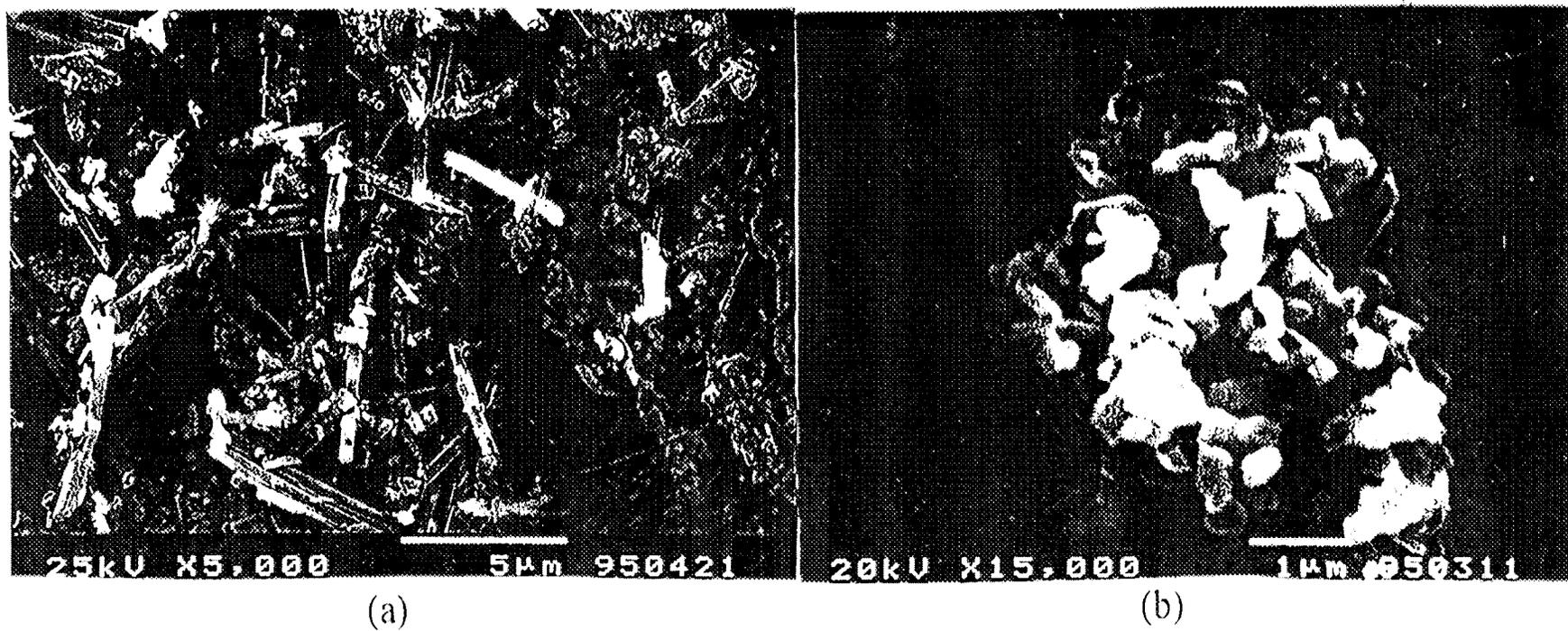


FIG. 3. SEM images of potassium titanate synthesized by melting method
(a) $K_2Ti_4O_9$ (b) $K_2Ti_6O_{13}$

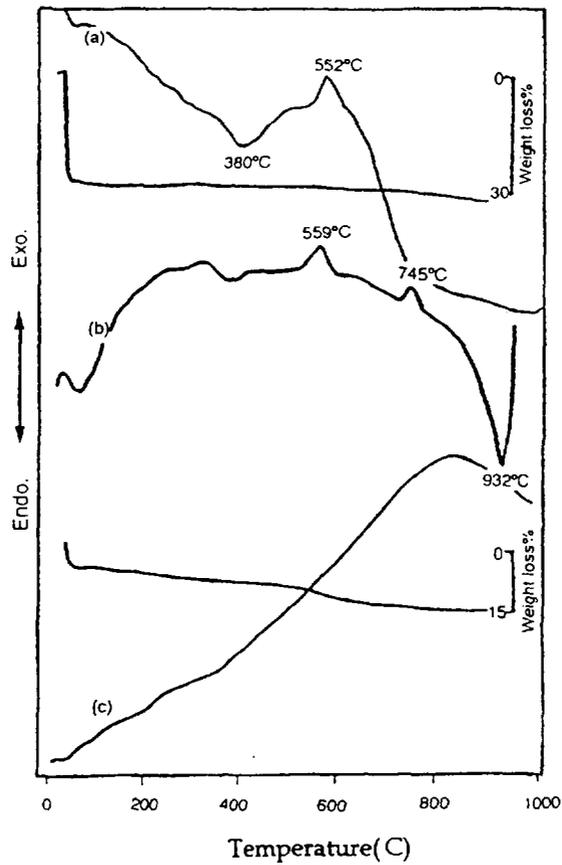


FIG. 4. TG-DTA curves of potassium titanate
 (a) $H_2O/Ti=0$ (b) $H_2O/Ti=0$
 (c) $H_2O/Ti=10$, supercritical drying

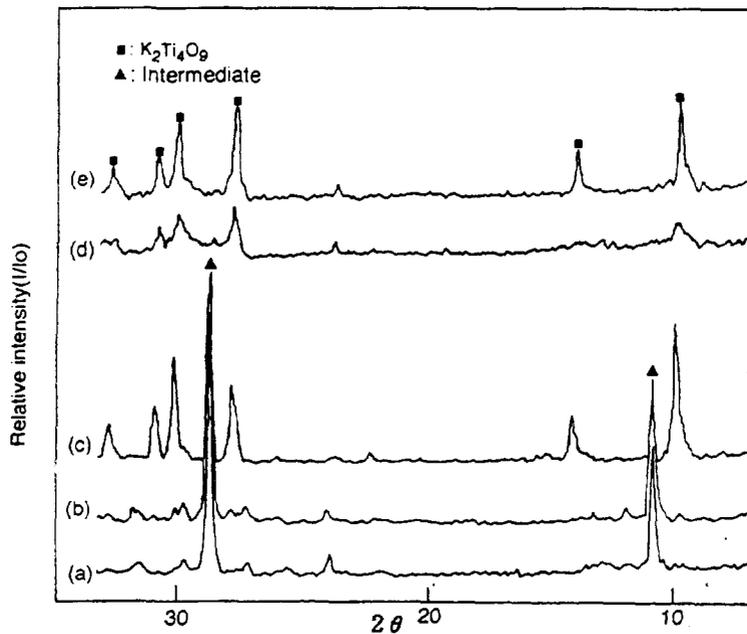


FIG. 5. Changes of XRD pattern with calcination temperature.
 ($[H_2O] \{Ti\}=0$)
 (a) after supercritical drying (300°C, 140 bar)
 (b) 700°C, 10min (c) 800°C, 1.5hrs

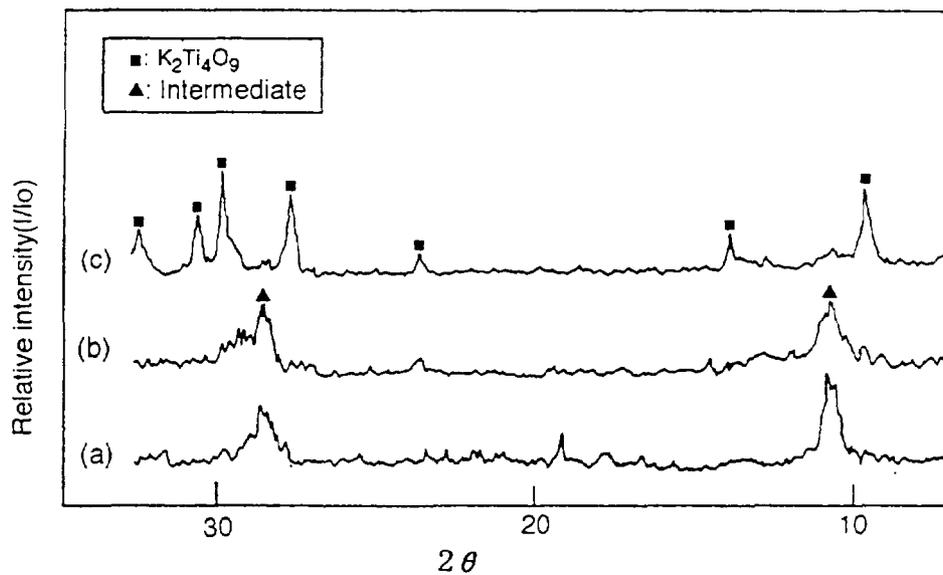


FIG. 6. Changes XRD patterns with calcination temperature ($H_2O/Ti=10$, $270^\circ C$, 118 bar)
 (a) after supercritical drying (b) $700^\circ C$, 10 min (c) $800^\circ C$, 1.5 hrs

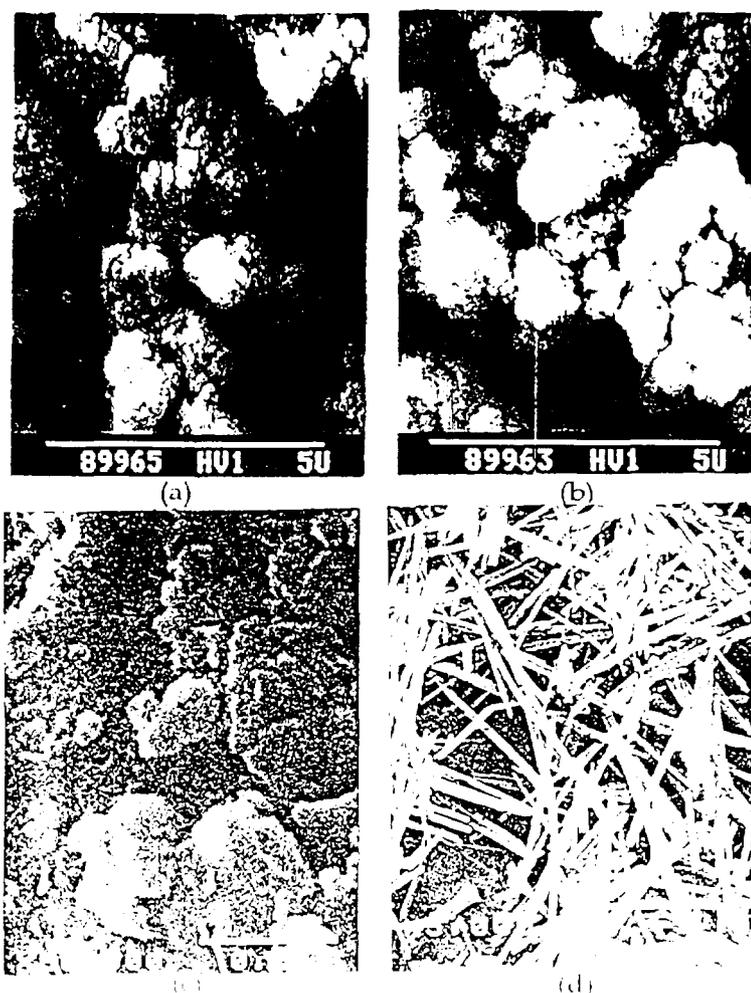
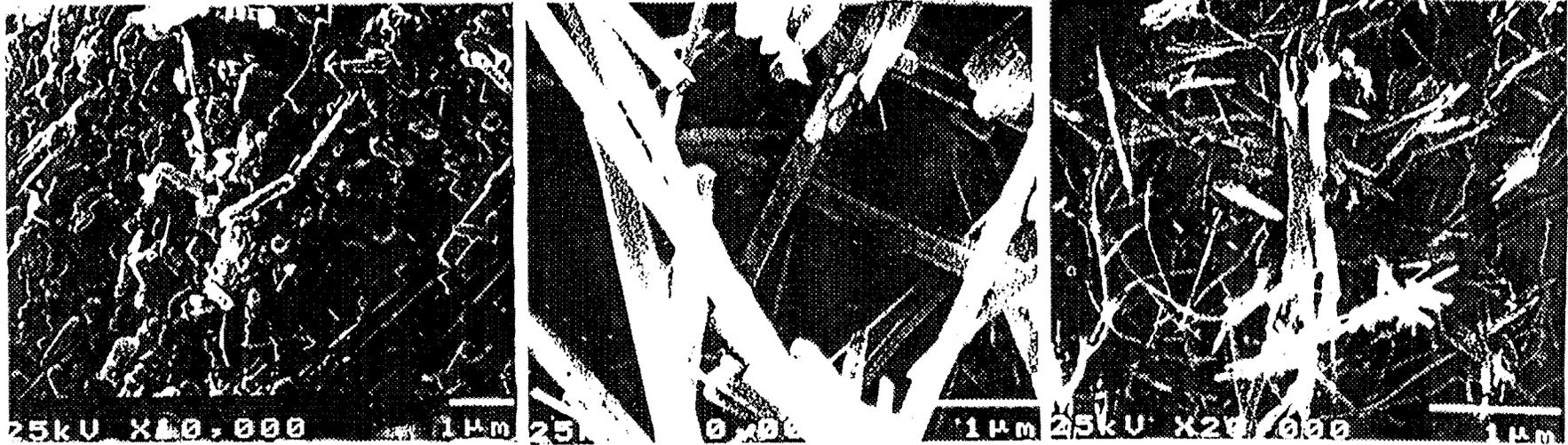


FIG. 7. SEM images of potassium titanate
 (a) $K_2Ti_6O_{13}$ gel powder (b) crystalline $K_2Ti_6O_{13}$
 (c) $K_2Ti_4O_9$ gel powder (d) crystalline $K_2Ti_4O_9$



(a)

(b)

(c)

*FIG. 8. SEM images of potassium titanate by different preparative methods
(a) melting method (b) sol-gel method (c) sol-gel method, supercritical drying*

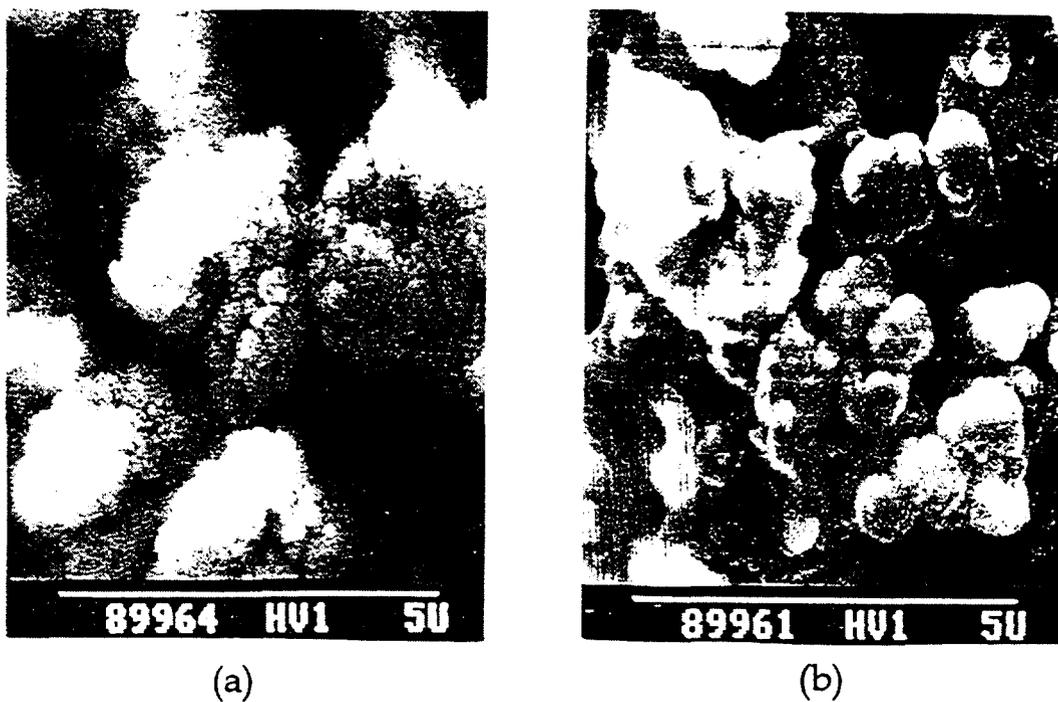


FIG. 9. SEM images of potassium titanate gel powders with different K/Ti ratios
 (a) K/Ti=0.3 (b) K/Ti=1.0

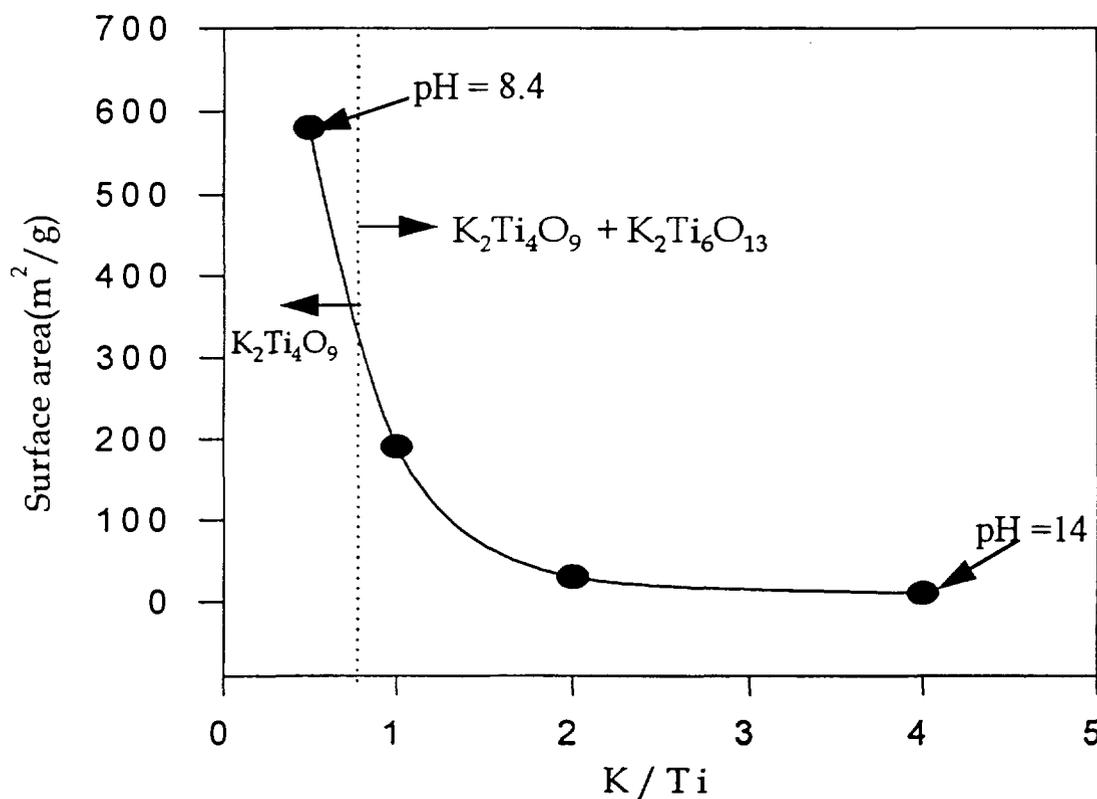


FIG. 10. Effects of K/Ti ratio on the surface area of potassium titanate gel powders.

dropped drastically as K/Ti ratio increased as shown in Fig. 10. When the K/Ti ratio is less than 1 more than 200m²/g area is obtained. Concurrently, when the K/Ti ratio increased, the pH of the solution increased from 8.3 (K/Ti=0.5) to 14 (K/Ti=4).

3.2.3. Effect of H₂O/Ti ratio

In the hydrolysis reaction, the H₂O/Ti ratio is an important parameter in determining the final properties of the sample because the hydrolysis reaction rate changes with water content of the solution. The titanium alkoxides are known to be sensitive to water content due to the rapid hydrolysis of titanium alkoxide in the presence of water [11]. The change of surface area of potassium titanate gel is shown in Fig. 11. It shows clearly that the large surface area of gel powder is obtained at high H₂O/Ti ratio after room temperature drying in the case of potassium hexatitanate. However, the surface area of potassium tetratitanate was not dependent on the ratio of H₂O/Ti. This is an unexpected result and we should find other ways. Among them, the supercritical drying process is one way to get a high surface area because it can minimize the liquid-vapour interfacial(capillary) force during the drying process. In Fig. 12, the surface area of the supercritical dried sample was compared with that obtained using the melting method. More than 25m²/g of surface area is obtained at 800°C by the supercritical drying.

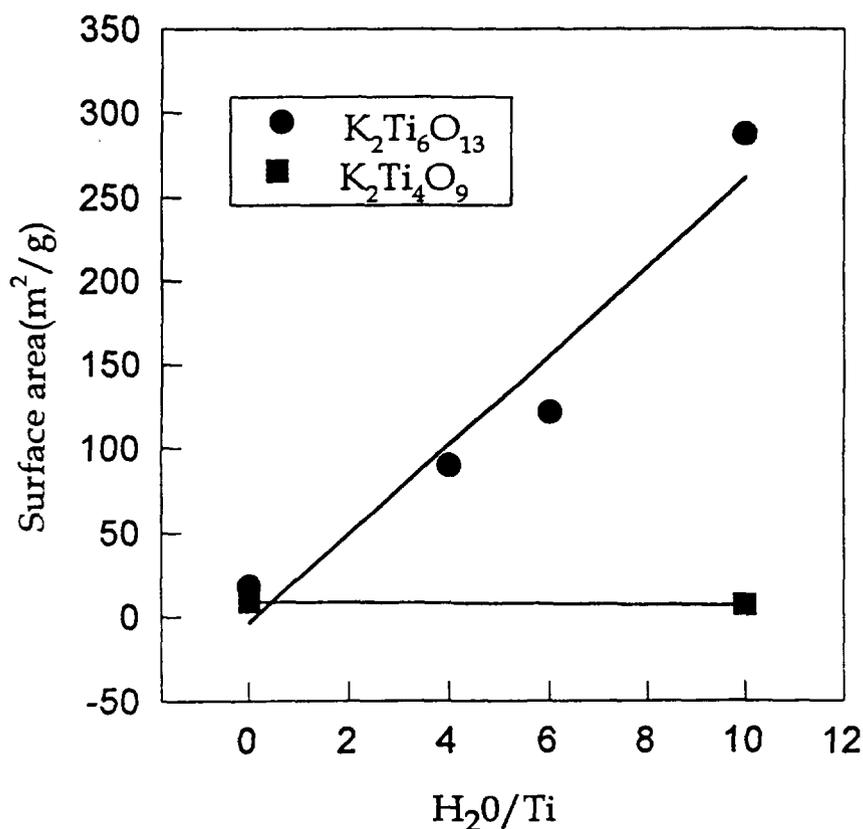


FIG. 11. Changes of surface area with H₂O/Ti in potassium titanate gel powders (25C drying)

3.2.4. Effect of titanium precursors

The effect of titanium alkoxides on the types of potassium titanates is shown in Fig. 13. The product ratio was calculated from the representative peak intensity of XRD. (200) and (001) were used as the representative planes of potassium hexatitanate and potassium tetratitanate respectively. As the alkyl chain length(R) of the titanium alkoxide increased, the potassium tetratitanates to potassium hexatitanate ratio increased at the given K/Ti ratio (=0.5). It suggests more potassium is incorporated as the chain length of alkoxide increased.

In the alkoxide system, the alcohol exchange reaction occurs readily with metal alkoxide precursors and exchange is facilitated when $\delta(\text{electrical negativity})(M) > G1$. For a series of titanium alkoxides, the alcohol exchange reaction occurs as follows:



According to Bradley et al, alcohol exchange rate decreases with the alkyl chain length, consistent with the steric effect expected for an associative S_{N} reaction mechanism. The molecular complexity of titanium alkoxide is decreased with increasing chain length of alkyl group (i.e., when R=Et, $n=2.4$; R=Pr, $n=1.4$ and R=Bu, $n=1.0$ [16]) as shown in Fig. 13. In our case, the alcohol exchange rate of Ti(OBu)_4 should be slow in comparison with Ti(OEt)_4 and Ti(OPr)_4 which may be ascribed to a steric factor of the alkyl group. Therefore, facts imply that the hydrolysis reaction of titanium alkoxide might be dependent on the chain length of alkoxide. It is possible that potassium methoxide incorporation into titanium alkoxide to form more Ti-O-K bonds before the formation of Ti-O-Ti bond is increased which increases the chain length of titanium alkoxide in the course of hydrolysis and condensation reaction. As a result, we can get a high yield of potassium incorporation into the titanium matrix (potassium tetratitanate) with Ti(OBu)_4 .

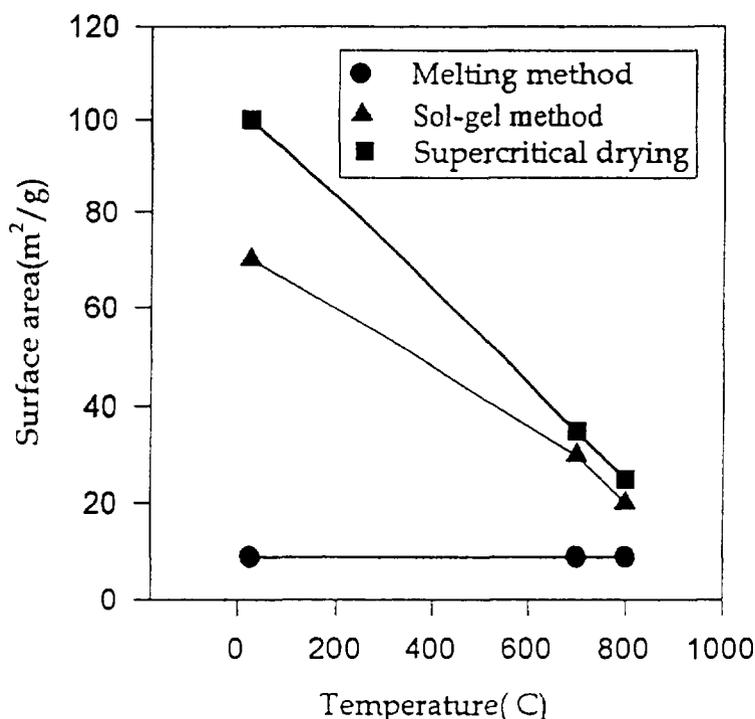


FIG. 12. Changes of surface area with calcination temperature ($\text{K}_2\text{Ti}_4\text{O}_9$, $\text{H}_2\text{O}/\text{Ti}=10$)

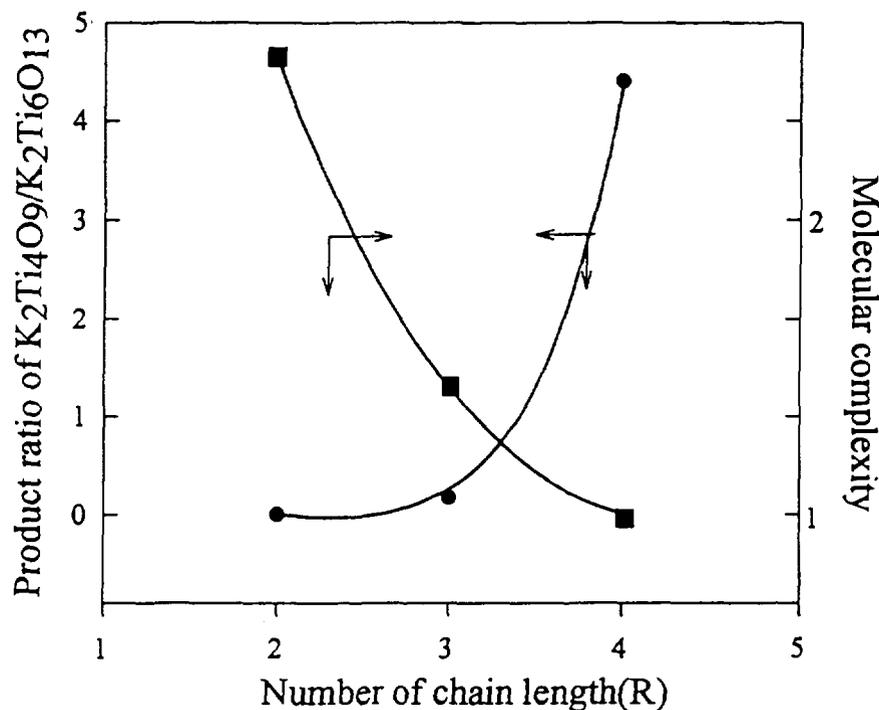


FIG. 13. Effect of alkyl chain length on the product ratio of $K_2Ti_4O_9$ to $K_2Ti_6O_{13}$ ($K/Ti=0.5$, $1000^\circ C$)

3.3. SODIUM ALGINATE METHOD

After ion exchange with metal ions, the alginic acid fibre becomes K-Ti-alginate because protons are exchanged for K and Ti ions. Figure 14 shows the changes of XRD patterns with the K/Ti ratio. We could obtain potassium titanate when the K/Ti ratio is more than 5, which is higher than that of the theoretical ratio ($K/Ti=0.3$). In the case of $K/Ti=25$, potassium tetratitanate phase is present as shown in Fig. 15 (c). This result suggests that ion selectivity for titanium ion is higher than that for potassium ion when using alginic acid [17]. These results show that a greater excess of potassium is necessary for the formation of potassium titanate in alginate and sol-gel method.

Figure 15 shows SEM images of potassium titanate after calcining the K-Ti-alginate at $800^\circ C$. The average length and thickness of potassium tetratitanate is about 2cm and $150\mu m$, respectively. The aspect ratio of this fibre is about 1.3×10^3 , which is the highest aspect ratio of potassium titanate among the various synthetic methods. This result also implies the possibility of formation of continuous fibre in the potassium titanate system.

Figure 16 shows the morphological changes of potassium tetratitanate depending on the synthetic methods. It should be noted that the needle type of potassium titanate, which has the largest length in size and the highest aspect ratio, is generated from K-Ti-alginate fibre.

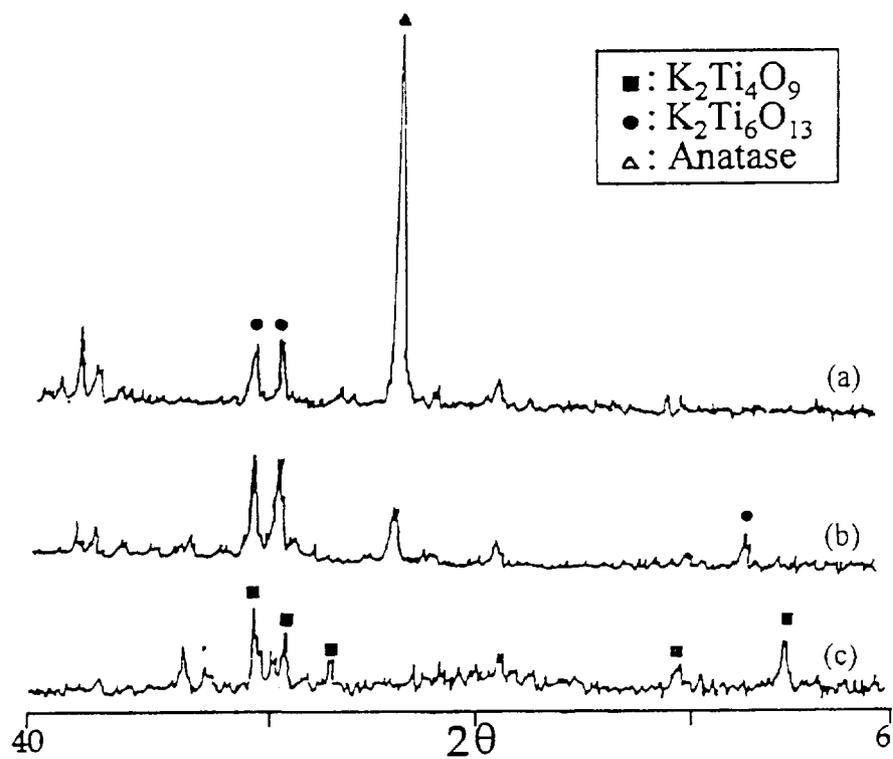


FIG. 14. Changes of XRD patterns with K/Ti ratio in alginate method.
 (a) K/Ti=5 (b) K/Ti=10 (c) K/Ti=25

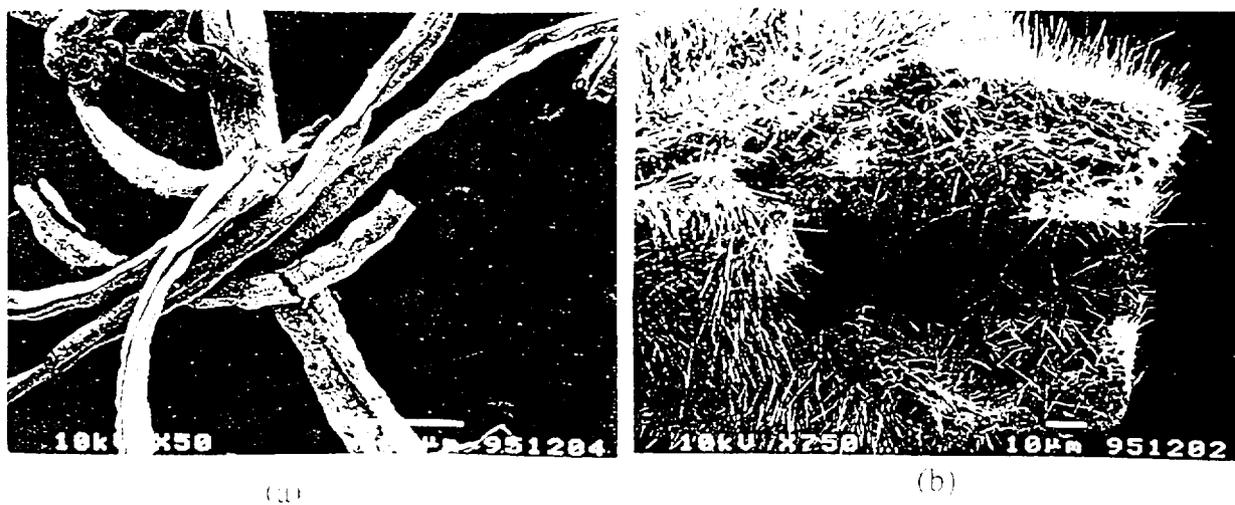


FIG. 15. SEM images of potassium tetratitanate synthesized by using alginate method (K/Ti=25, calcining at 100C).

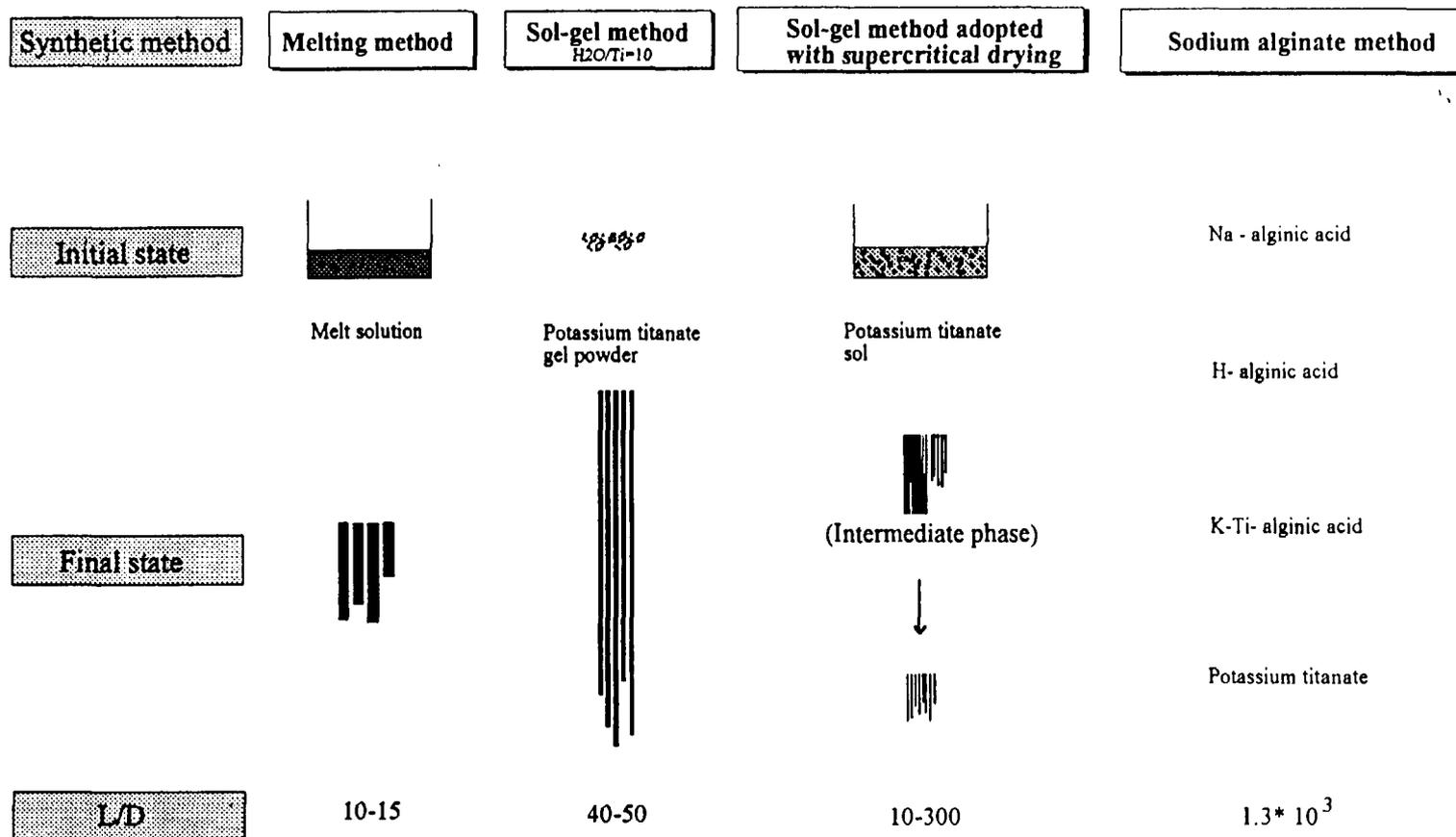


FIG. 16. Morphological changes of potassium tetratitanate depending on the synthetic methods.

3.4. ION EXCHANGE OF STRONTIUM ION

Ion exchange of strontium ions was examined for potassium titanate samples prepared by various methods. The HCl treated sample was obtained by replacing the interlayered potassium ion to proton ion and hydronium ion from the potassium tetratitanate as shown in eq. (4).



Strontium ion uptake on acid treated potassium tetratitanate as a function of time is presented in Fig. 17. Adsorption capacity depends on the pretreatment. The sample dried at 200°C shows higher Sr^{2+} ion exchange capacity (0.186 mmol/g) than that dried at 50°C (0.04 mmol/g). Figure 18 shows the degree of dispersion of acid treated potassium titanate in aqueous phase. Samples dried at 50°C are agglomerated to each other to form larger secondary particles. Therefore, degree of dispersion seems to have marked effect on ion exchange capacity.

Figure 19 shows the ion-exchange capacity of hydrous titanium dioxide as a function of pH. An increase in ion exchange capacity of hydrous titanium dioxide synthesized by the sol-gel method is observed with increasing pH. The maximum ion exchange capacity, 4.0 meq/g, was obtained at pH 12, which is highly alkaline. From the point of view of the chemical process, not only the ion exchange capacities but also the exchange rate are important parameters. Strontium ion uptake on hydrous titanium dioxide as a function of time is presented in Fig. 20. Equilibrium is attained after 10 minutes with the samples of the melting method while 5 minutes is enough to reach equilibrium with sample of the sol-gel method. The ion exchange rate of acid treated potassium tetratitanate is increased in the order; supercritical drying > sol-gel method > melting method. As for ion exchange capacity, the melting method samples are lower than those of the sol-gel method combined with the supercritical drying process.

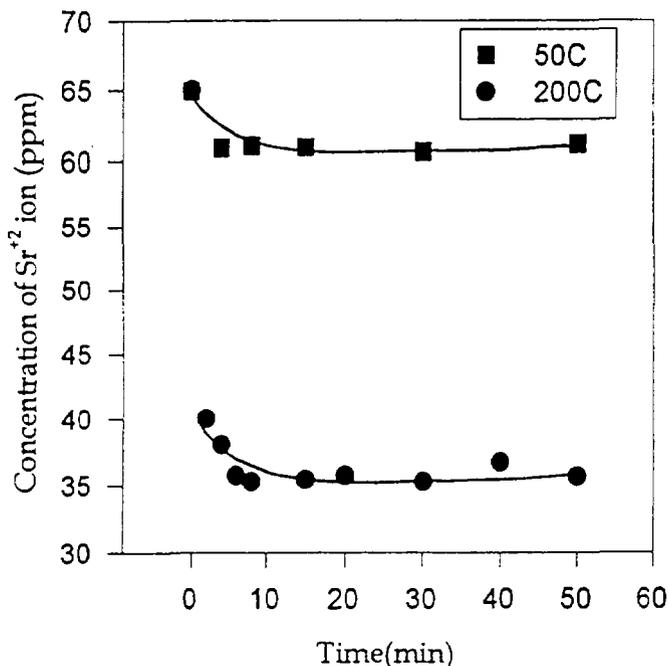
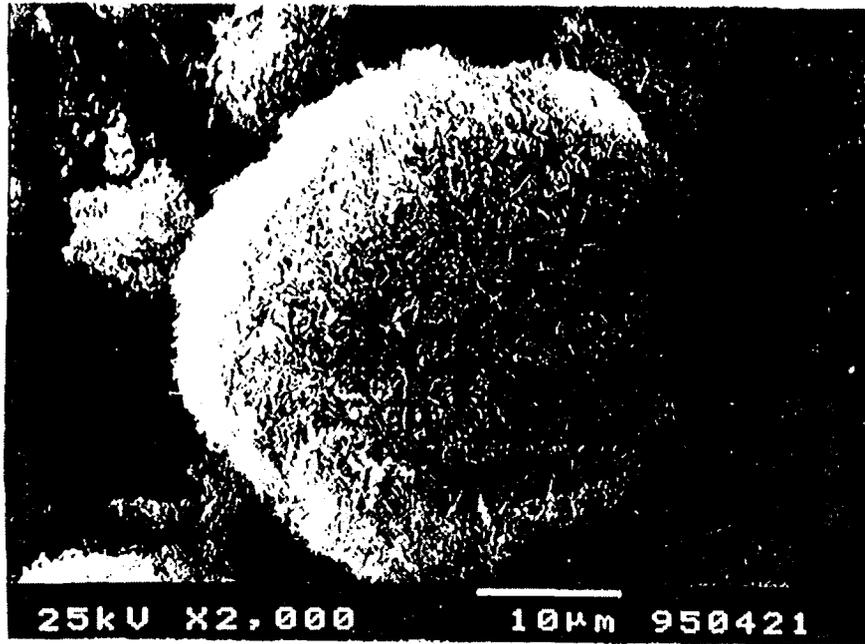
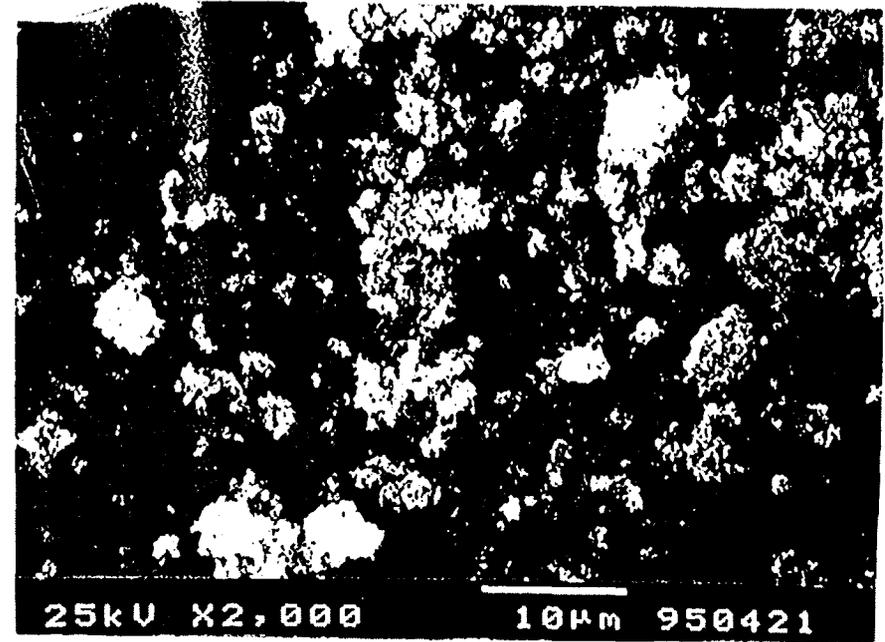


FIG. 17. Changes of Sr^{2+} ion concentration with ion exchange period. ($\text{H}_2\text{O}/\text{Ti}=10$)



(a)



(b)

*FIG. 18. SEM images of acid treated $K_2Ti_4O_9$,
(a) drying at 50C (b) drying at 200C*

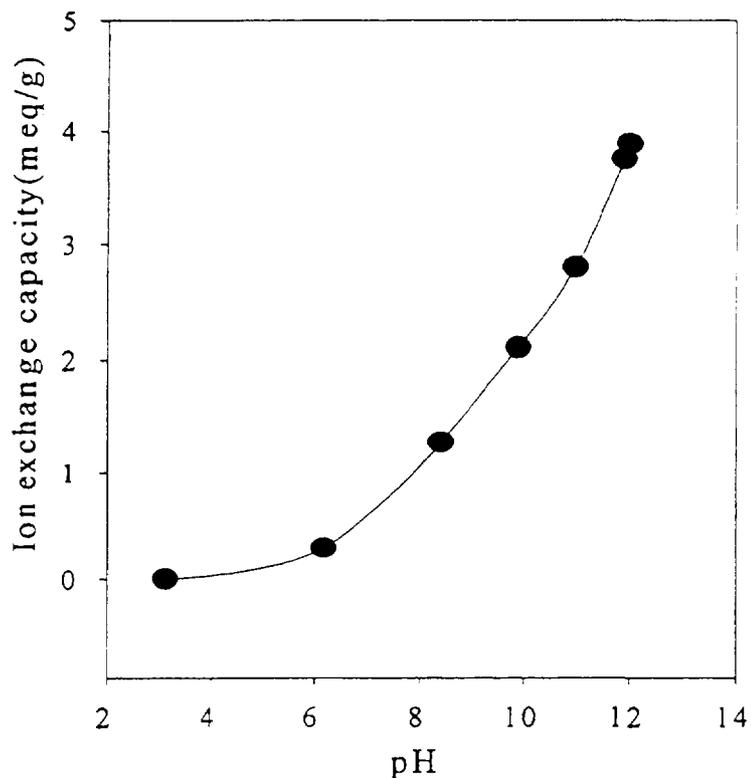


FIG. 19. Changes of strontium ion exchange capacity of hydrous titanium dioxide with pH

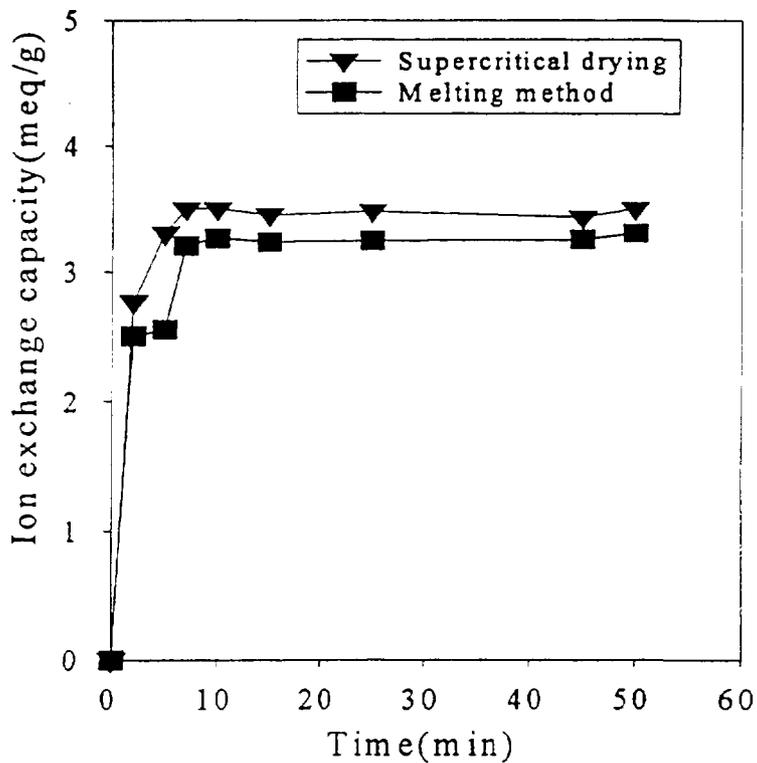


Fig. 20. Changes of Sr ion exchange capacity of hydrous titanium dioxide with preparative method as a function of time

This shows the advantages of the sol-gel process against the melting method. Namely, one can enlarge the BET surface area and change the morphology of potassium titanate using sol-gel process conditions.

To confirm the phase change behavior of exchanged sample, the strontium ion exchanged sample was calcined up to 1000°C. Figure 21 shows the change of XRD patterns of the strontium ion exchanged sample with calcination. At 1000°C, anatase, rutile, and strontium titanate were present. This shows that the following reactions proceed during the thermal process with the sintering of exchanged sample.

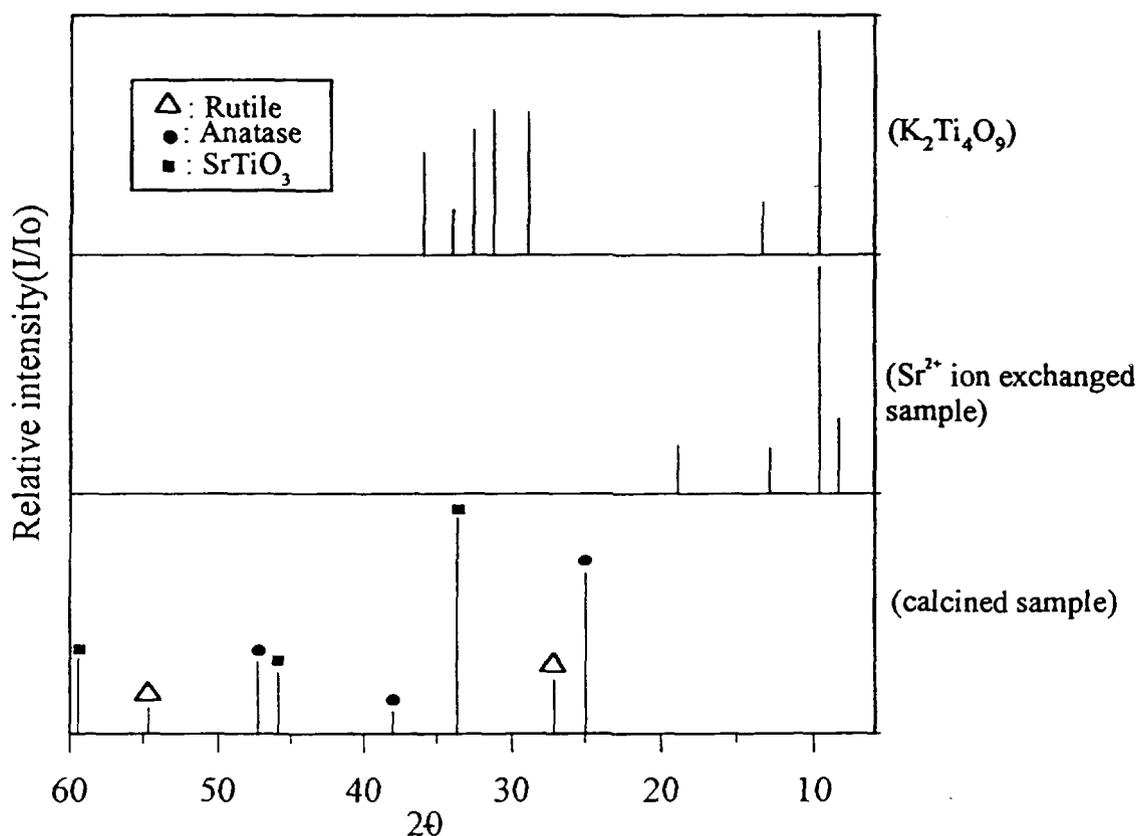
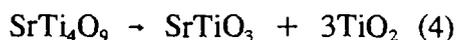


FIG. 21. Phase change behaviours of strontium ion exchanged sample after calcination at 1000°C.

4. CONCLUSIONS

- (1) In this experiment potassium tetratitanates with high surface area about 25 m²/g were obtained at 800°C by using a sol-gel process combined with supercritical drying.
- (2) The morphology and aspect ratio of potassium tetratitanate were varied depending on the preparation method. The sodium alginate method provided the largest aspect ratio.
- (3) The greater BET area of potassium titanate provides more rapid ion exchange and a greater ion exchange capacity for the immobilization of a nuclear waste metal ion (Sr²⁺).

TABLE I. EFFECT OF TITANIUM PRECURSORS ON THE FORMATION OF POTASSIUM TITANATES

Mole ratio of CH ₃ OK/Ti	Ti(OC ₃ H ₅) ₄	Ti(OCH(CH ₃) ₂) ₄	Ti(OCH ₃) ₃ CH ₃) ₄
20	20	20	20
20	20	20	20
20	20	20	20
20	20	20	20
20	20	20	20

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