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Effects of Mechanical Activation of Inorganic Gels on Their Thermal Behavior. 1. Crystallization Process of Titania Gels

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The influence of mechanical pretreatment on the crystallization from amorphous titania hydrogel to anatase was studied. The temperature of crystallization, T_{crys}, determined by the DTA exothermic peak, decreased by 18 and 44 K on grinding for 3 hr by the rotation and vibration ball-mill, respectively. Preliminary ordering of anatase in ground gels was detected by Raman spectroscopy and selected area electron diffractometry, before any X-ray diffraction peak appeared. It is suspected that the decrease in T_{crys} by mechanical activation is attributed to the above precursory ordering. By applying mechanical stress, the sudden weight loss was observed at T_{crys}. This suggests that a small amount of hydroxyl groups and NH_4^+ may block the long-range ordering of TiO_6 structural units.

Introduction

Mechanical activation for many inorganic crystalline substances has been studied. Due to the applied shear stress, the lattice is distorted and the crystallite size decreases, often leading to amorphization (*1–3*). The recrystallization from amorphous solids also takes place after prolonged grinding (*1*, *3*). Thus one of the main objects of the present study is to elucidate the change in the structure and properties of the apparently amorphous solids due to mechanical activation.

Amorphous hydrogels, prepared by the sol–gel process, have advantages over mechanically amorphized materials for the structural study, because of the relatively higher homogeneity of the former. Infrared and Raman spectroscopies are suitable for the structural analyses of the amorphous gels (*4*, *5*). A slight structural change is sensitively reflected in the thermal behavior of such gels, e.g., the change in the temperature of crystallization and dehydration, which in turn is an indication of the change in the chemical properties of gels.

Preparation of inorganic oxide materials from hydrous gels requires dehydration as well as crystallization. A decrease in the dehydration temperature on subsequent heating as a result of mechanical activation was reported for a number of metal hydrates (*6*, *7*). In some metal hydroxides or oxyhydroxides, e.g., $Al(OH)_3$ or γ-FeOOH, the dehydration or dehydroxylation takes place even during grinding in air (*6*, *8*). Similar effects of mechanical activation are expected on the hydrous inorganic gels. Hence, a practical aspect of the present study is to seek the possibility of improving the preparation methods of pure oxide materials from gels, aiming at the independent control of the crystallization and dehydra-

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tion processes by applying appropriate mechanical treatments.

Experimental

1. Materials

A total of 0.05 mole $TiCl_4$ was added into 500 cm^3 of water chilled below 286 K. A small amount of hydrolysis was detected from the slight turbidity of the solution. Then 500 cm^3 of 0.5 M NH_4OH aqueous solution was immediately mixed into the dilute sol at room temperature. The resulting gelatinous precipitate was washed and decanted repeatedly until no reaction between the washing liquid and the 0.1 M $AgNO_3$ solution was observed. The pH of the washed sol was 7.5. The filtered precipitate was dried at 323 K for 15 hr. The spongy lump was carefully ground into smaller particles with an agate mortar and further dried at 373 K and 1.3×10^3 Pa for 5 hr, resulting in the starting xerogel Ti-1. The content of Cl is 0.043 wt% according to X-ray fluorescence analysis. Ti-1 contains 0.14 mole NH_4^+ per 1 mol of TiO_2 as revealed from the elementary analysis. NH_4^+ does not seem to play any particular role in the crystallization, since the NH_4^+-free amorphous titania gel, prepared by using NaOH instead of NH_4OH, behaves almost identically to the gel obtained by NH_4OH.

2. Mechanical Activation

One-half gram of the sample Ti-1 was ground in air by a rotation ball-mill at 156 rpm with an 86.5-cm^3 polyethylene container and 40 stainless steel balls of 6.5 mm diameter. The gel Ti-1 was also ground in air by a vibration ball-mill (Glen–Creston) with the frequency 12 Hz and the amplitude 50 mm. A 50-cm^3 cylindrical agate container was filled with 0.5 g of Ti-1 and ten 10-mm agate balls. The sample ground by the rotation or vibration ball-mill for m hr was denoted with the extension tag $-\mathrm{R}m$ or $-\mathrm{V}m$, respectively.

3. Characterization

The weight loss and the heat of crystallization of gels were measured by simultaneous thermogravimetry and differential thermal analysis (Rigaku, TG–DTA), and differential scanning calorimetry (Rigaku, DSC). The thermal analyses were carried out at a heating rate of 10 K min^{-1} in a N_2 flow (200 cm^3 min^{-1}). The weight loss was conveniently expressed by the hypothetical water content, n, in TiO_2nH_2O, assuming that the liberation of H_2O and NH_3 is completed by heating titania gel above 1273 K. The species of evolved gases were identified by the mass spectrometry (VG, PC-300D), carried out simultaneously with TG–DTA (Mac Science, 2000) at a heating rate of 50 K min^{-1} under an Ar flow (200 cm^3 min^{-1}).

The morphology of the particles was observed under the transmission electron microscope (TEM) (JEOL, JEM-2000FX). The structure of gels was examined by X-ray diffractometry (XRD) (Rigaku, CN2013) and selected area electron diffractometry (SAD) (JEOL, JEM-2000FX). The vibration spectrum of each specimen diluted with KBr was measured by FT–IR spectroscopy (BIO-RAD, FTS-65). Raman spectra scattered at 90° were obtained by using the wavelength 514.5 nm of an Ar laser. These analyses were carried out at room temperture.

Results and Discussion

1. Decrease in the Temperature of Crystallization Due to Mechanical Pretreatments

The X-ray diffraction pattern of the starting sample Ti-1 was a halo as shown in Fig. 1a. The XRD pattern of the sample ground by the rotation and vibration ball-mill for 3 hr, Ti-1-R3 and Ti-1-V3, remained a halo, as shown in Figs. 1b and 1c, respectively.

DTA thermograms of titania hydrogel are shown in Fig. 2. The exothermic peaks are attributed to the crystallization of noncrys-

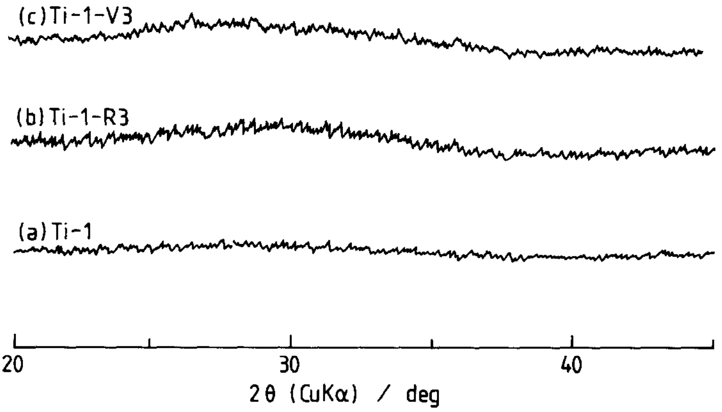


FIG. 1. XRD patterns of titania gels. (a) Ti-1, (b) Ti-1-R3, (c) Ti-1-V3.

talline titania into metastable anatase, as confirmed from the change in XRD patterns of Ti-1 with temperatures in Fig. 3. The peak temperatures of crystallization, T_{crys}, were summarized in Table I.

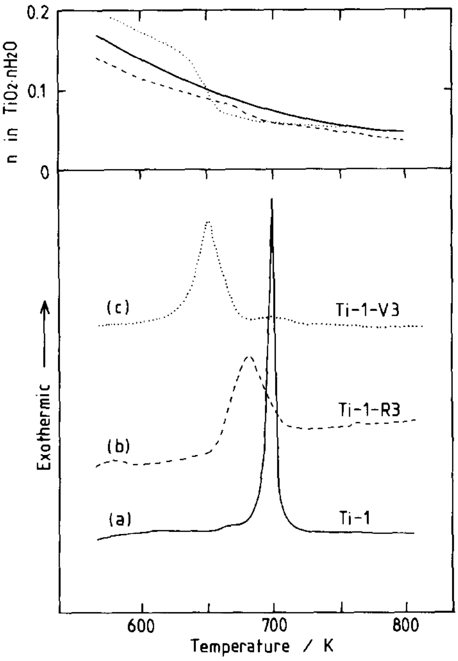


FIG. 2. DTA thermograms and the weight loss of titania gels. (a) Ti-1, (b) Ti-1-R3, (c) Ti-1-V3.

The color of the gel changed from white to grayish and yellowish from just below to just above T_{crys}. This would suggest that the oxygen vacancies increased by heating gels before the exothermic peak (*9*) and that the titania was slightly nonstoichiometric due to the existence of crystallographical shears (*10–13*). As a result of the growth of crystallites at T_{crys}, the crystallographical shears might be relaxed.

T_{crys} decreased by 18 and 44 K on rotation and vibration ball-milling, respectively, for 3 hr. According to the elementary analysis, the amount of NH_4^+ per 1 mole TiO_2 before and after vibro-milling for 3 hr was 0.14 and 0.12 mole, respectively. The net water content, calculated after subtracting the NH_4^+ content from the total weight loss, i.e., the *n* value shown in Table I, was 0.96 and 0.48 mole, respectively. This indicates that the dehydration took place more easily during grinding than during the liberation of NH_3.

Ragai compared two samples prepared by aging the hydrous titania gel under water and ammonia (*14*). According to his results, the temperature of the exothermic DTA peak, T_{crys}, of the former was higher than that of the latter; i.e., T_{crys} decreased due to the residual NH_4^+. Therefore, the decrease in T_{crys} with grinding cannot be attributed to

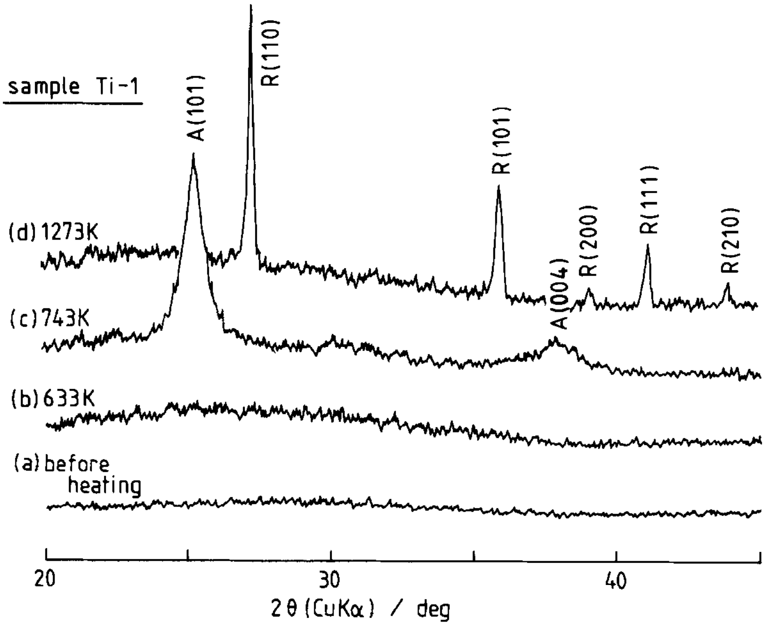


FIG. 3. Change in XRD pattern of the sample Ti-1 with temperature. (a) Before heating, (b) 633 K, (c) 743 K, (d) 1273 K. A, anatase; R, rutile.

the slight decrease in the amount of NH_4^+. The breadth of the exothermic peak, T_E-T_S, shown also in Table I, became broader on grinding gels. This means that the crystallization of the ground samples occurred more heterogeneously.

2. *Crystallization Process by Heating*

The change in the Raman spectra from the titania sol to oxide is shown in Fig. 4. Two broad bands at 450 and 700 cm^{-1} were observed for the washed sol, as shown in Fig. 4a. After drying, these bands for the xerogel Ti-1 were shifted to a lower wavenumber, i.e., 400 and 600 cm^{-1}, respectively, as shown in Fig. 4b. An additional broad band at 150 cm^{-1} was also observed for the xerogel Ti-1. All the Raman bands observed on the sol or the gel seem to belong to the Ti–O vibrations, as shown in Table II. The coordination state of threefold oxygen, OTi_3, detected in the sol and the gel, is the same as that of titanium dioxide. At least three TiO_6 structural units are needed for the OTi_3 vibrations. Therefore, the existence of

TABLE I

PROPERTIES OF TITANIA GELS

Sample	S_{BET} (m^2 g^{-1})	n^a	T_{crys} (K)	$T_E - T_S^b$ (K)	$-\Delta H_{crys}$ (kJ mole^{-1})
Ti-1	325	1.1	698	16	20.7
Ti-1-R3	77.5	0.8	680	45	19.5
Ti-1-V3	15.9	0.6	654	34	13.5

[a] n in TiO_2nH_2O.

[b] The difference between the initial and the final temperatures of the exothermic peak.

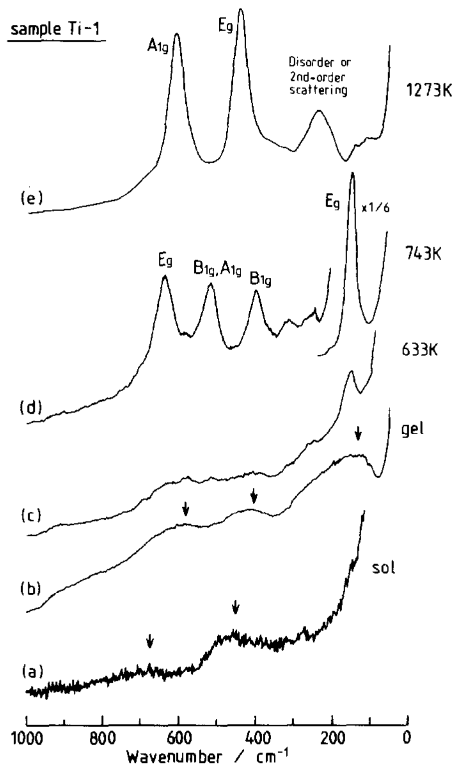


FIG. 4. Change in Raman spectrum of the sample Ti-1 with heating. (a) The sol, (b) the xerogel, (c) 633 K, (d) 743 K, (e) 1273 K.

these bands suggests that several structural units are already grouped together in the sol.

The Raman band, E_g, at 151 cm^{-1}, identical with that observed typically for anatase shown in Fig. 4d, was detected for the sample heated up to 633 K, as shown in Fig. 4c, although its XRD pattern was still a halo. The IR absorption band at 499 cm^{-1}, identical with that of anatase shown in Fig. 5c, became narrow and clear on heating up to the same temperature, as shown in Fig. 5b. The Raman band around 150 cm^{-1} and the IR band around 500 cm^{-1} for the xerogel and that heated up to 633 K thus indicate the existence of precursory ordering of anatase. At this stage, the volume of the ordered zone is obviously too small to show any XRD peaks.

The SAD pattern, shown in Fig. 6a, was mostly a halo for the sample Ti-1. However, spots were also partly detected, as shown in Fig. 6b. A SAD pattern similar to Ti-1 was observed for the sample heated up to 633 K, as shown in Fig. 6c. The interplanar spacings calculated from the location of spots on Ti-1 are similar to those of anatase, as shown in Table III. These indicate that the areas of intermediate ordering, presumably serving as embryos, or later nuclei, of the anatase phase, already preexist even in the as-dried, apparently amorphous xerogels such as Ti-1. The existence of locally ordered anatase was also observed by TEM in the amorphous titania produced by the CVD process (*17*).

3. *Mechanical Activation*

Raman spectra after mechanical treatments are shown in Fig. 7. The Raman bands for ball-milled and vibro-milled samples, Ti-1-R3 and Ti-1-V3, respectively, were identical with those of the thermally well-grown

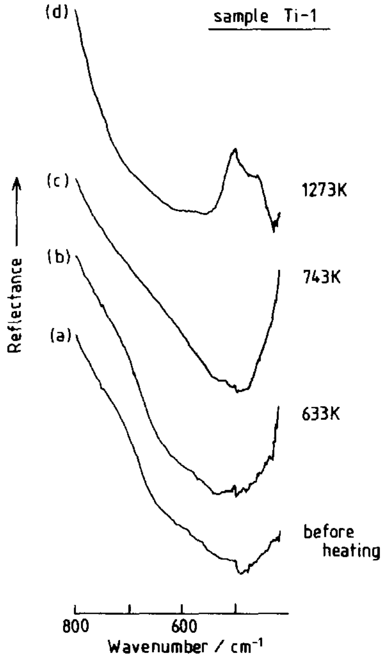
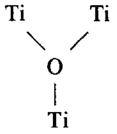


FIG. 5. Change in IR spectrum of the sample Ti-1 with temperature. (a) Before heating, (b) 633 K, (c) 743 K, (d) 1273 K.

TABLE II

ASSIGNMENT OF RAMAN BANDS OF TiO_2 SOL AND GEL

Fragment	Mode	Wavenumber (cm^{-1})
O–Ti–O	Bending	144[a]
Ti–O	Stretching	900[b], 970[c]
Ti–O–Ti	Symmetric stretching	370[b], 395[c]
	Antisymmetric stretching	910[c]
	—	430[b], 570[b]

[a] The modes of bands are reported by Ohsaka (*15*).
[b] Modes reported by Bunker (*16*).
[c] Modes reported by Reichmann (*4*).

anatase shown in Fig. 4d, although no XRD peak was observed for these ground samples. The construction of TiO_6 structural units, which were already formed in gels, could have taken place because of the applied shear stress.

The IR absorption band at 638 and 639 cm^{-1} due to the lattice mode also became narrow and clear on rotation and vibration ball-milling for 3 hr, as shown in Figs. 8a and 8b, respectively. However, the position of the band for the ground samples shifted toward the direction of higher wavenumber by ca. 140 cm^{-1} from that of thermally grown anatase, 499 cm^{-1}. The color of the gel turned from white to gray on vibro-milling for 3 hr. On vibro-milling for more than 5 hr, the gel became yellow. This color change, similar to that of the thermal process, cannot mainly be attributed to the impurities introduced from the ball-mill, since the color of the milled sample did not change continuously with grinding time. The grayish gel may contain more defective nuclei of anatase formed by the applied shear stress than by heating, as shown by the higher shift of the IR band. These defective nuclei could easily grow and accomplish the long-range ordering on subsequent heating, resulting in lower T_{crys}.

TABLE III

THE INTERPLANAR SPACING d_{hkl} OF PLANE (*hkl*) ESTIMATED BY SAD SPOTS

d_{hkl} (nm)		
Gel	Anatase[a]	(*hkl*)
0.36	0.35	(101)
0.31	—	?
0.25	0.24	(103), (004), (112)
0.21	0.19	(200)
0.17	0.17	(105), (211)
0.14	0.14	(116), (220)

[a] Anatase was obtained by heating the gel Ti-1 up to 743 K.

An exothermic DTA peak was also observed for the ground samples, as already shown in Fig. 2, although the departure of H_2O and NH_3 occurred almost simultaneously. The apparent heat of crystallization, $-\Delta H_{crys}$, shown in Table I, decreased on grinding. By applying mechanical stress, the amount of H_2O and NH_3 liberated at T_{crys} increased and the extent of structural rearrangement necessary for it to crystallize into anatase decreased. In other words, the endothermic effect due to the liberation of

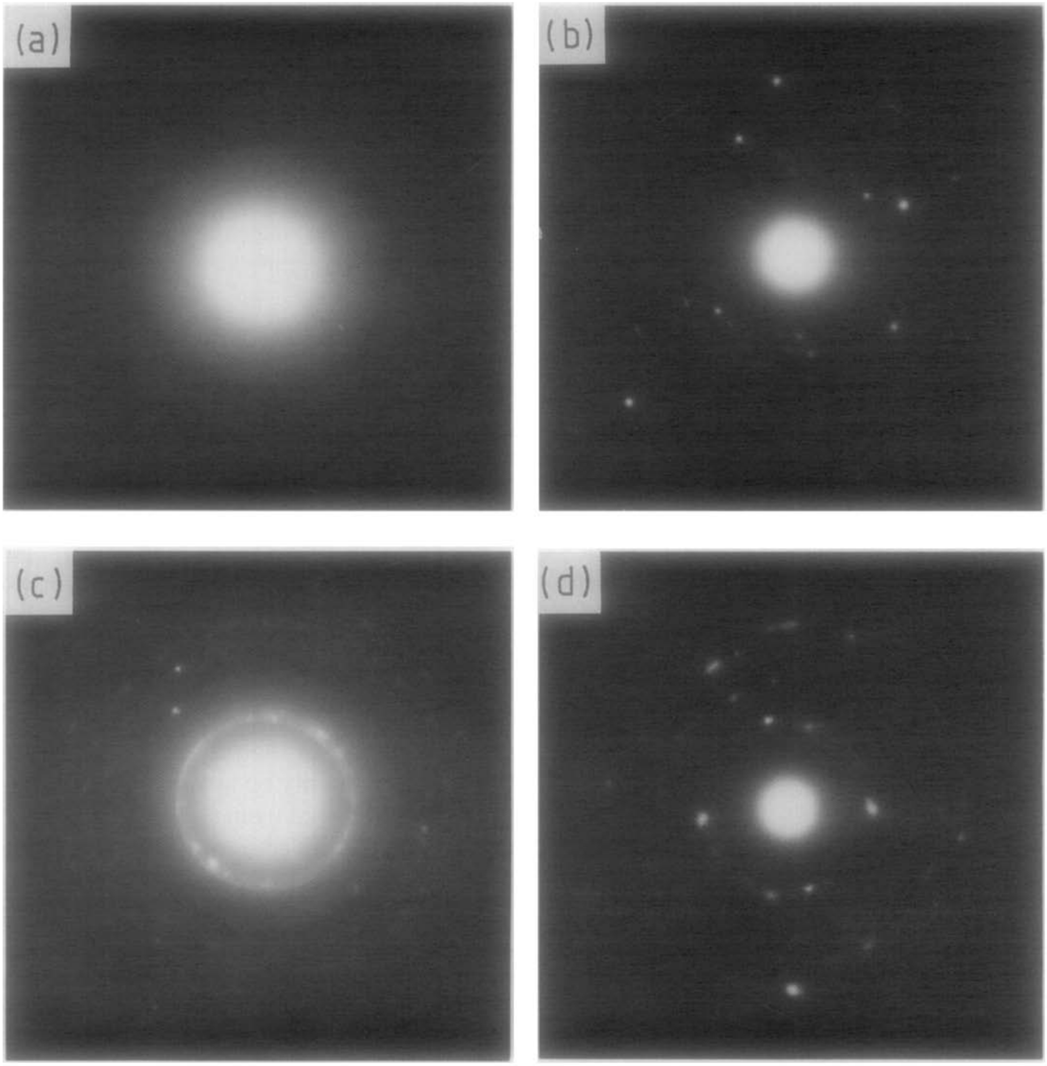


FIG. 6. Change in SAD patterns of titania gel Ti-1 with temperature. (a), (b) Before heating, (c) 633 K, (d) 743 K.

H_2O and NH_3 increased and the exothermic effect due to the crystallization decreased. As a result, the amount of the heat, $-\Delta H_{\mathrm{crys}}$, liberated from Ti-1-R3 and Ti-1-V3 was smaller than that from Ti-1.

4. Relationship between the Crystallization and the Dehydration

The weight loss, conventionally expressed by a hypothetical water content, *n*, in TiO_2nH_2O, is plotted against the temperature in Figs. 2 and 9. The sudden weight loss occurred for both of the ground samples, as shown in Fig. 2. During this sudden weight loss, not only H_2O but also NH_3 were liberated as confirmed by a simultaneous TG–DTA and mass spectrometry. There are two factors which can influence the rate of dehydration and liberation of NH_3: (i) the granulometrical properties such as the ag-

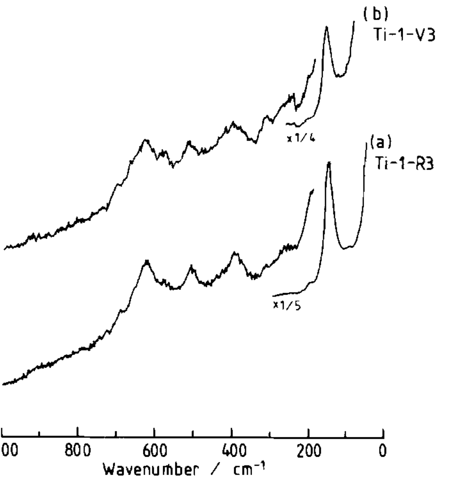


FIG. 7. Raman spectra of the ground samples. (a) Ti-1-R3, (b) Ti-1-V3.

gregate state and pore structure, and (ii) the property of chemical bonds between Ti^{4+} and OH^-.

The specific surface area, S_{BET}, was measured by N_2 adsorption, as shown in Table I. The high value of S_{BET} for untreated Ti-1 must be attributed to the large amount of micropores between primary particles, as observed by the electron micrograph in Fig. 10a. The size of the primary particle, 5–7 nm, calculated under the assumption of the uniform spheres was almost the same as that observed by TEM. The decrease in S_{BET} on mechanical treatment must be attributed to the plugging of micropores as a result of the densification of the gel particles, which actually are the agglomerates of the primary particles, as shown in Fig. 10b. The pores that disappeared were those between primary particles. The comminution of the primary particle seems unlikely.

As far as the initial stage of the weight loss is concerned, it seems parallel to the initial specific surface area, S_{BET}. In the consolidated agglomerates, the water vapor and NH_3 could be entrapped in closed pores and

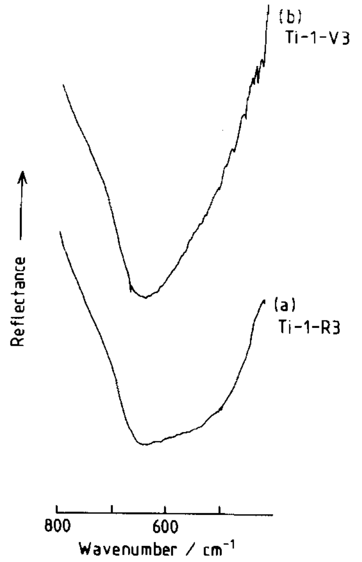


FIG. 8. IR spectra of the ground samples. (a) Ti-1-R3, (b) Ti-1-V3.

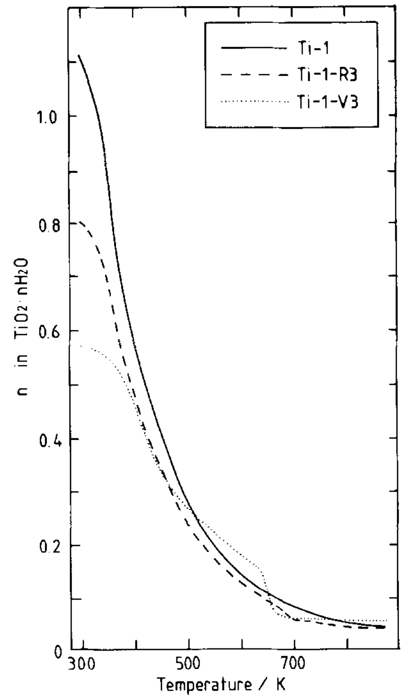
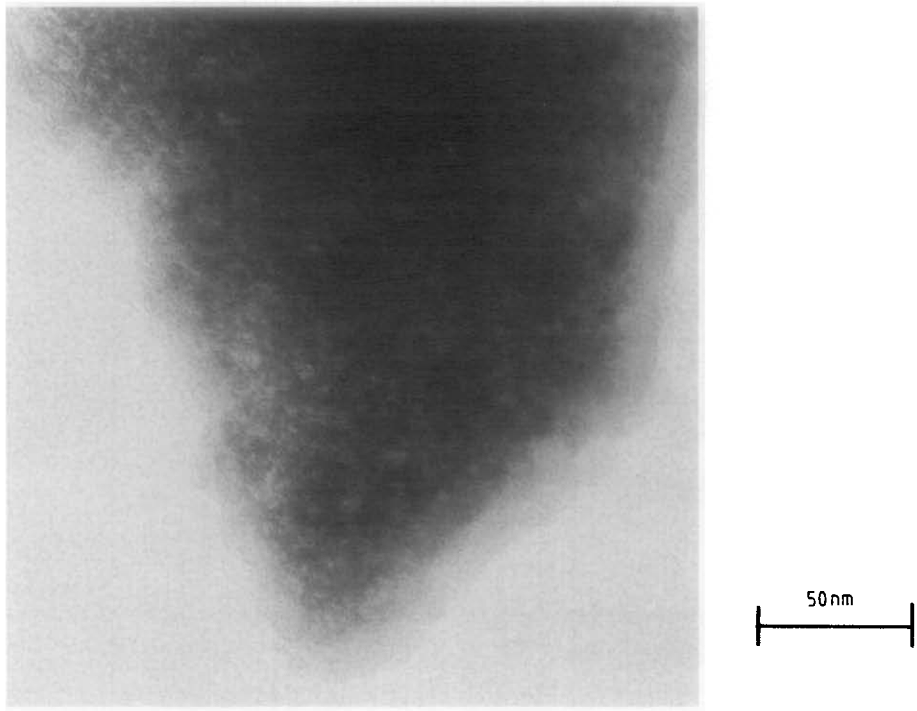


FIG. 9. Weight loss due to the dehydration of titania gels by heating at a constant rate of 10 K min⁻¹.

(a) Ti-1



(b)Ti-1-R3

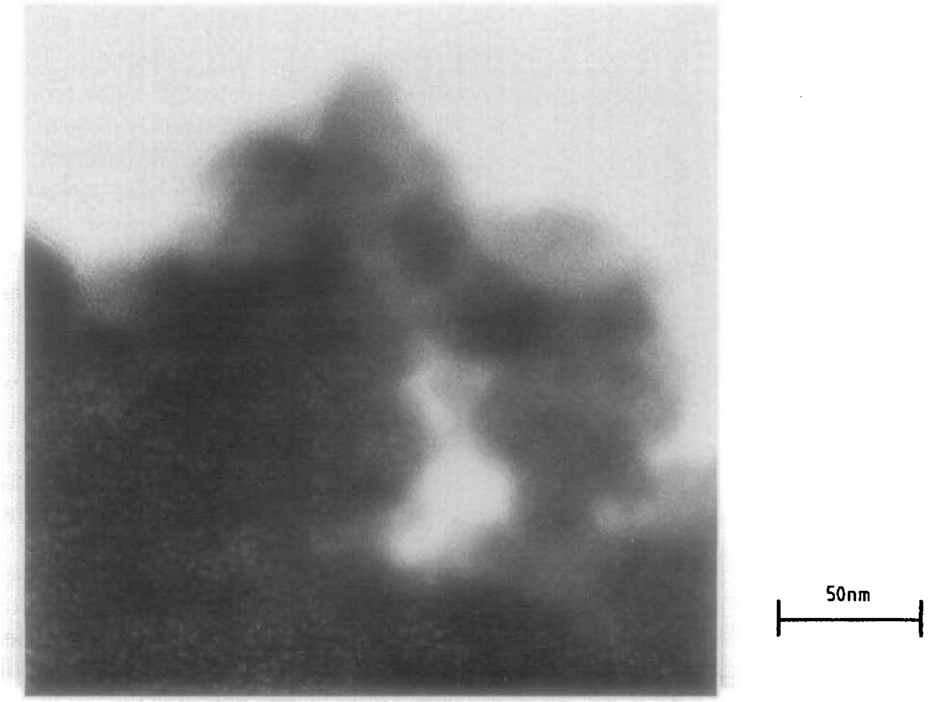


FIG. 10. Electron micrographs of titania gels. (a) Ti-1, (b) Ti-1-R3.

TABLE IV

THE CHANGE IN THE SURFACE AREA, S_{BET}, OF GELS

	S_{BET} ($\mathrm{m}^2\ \mathrm{g}^{-1}$)		
Sample	Room temperature	623 K	683 K
Ti-1	325	250	201
Ti-1-V3	15.9	25.2	21.9

their pressures may increase on heating. This might be the reason for the sudden weight loss observed for the ground gels. With closer observation, however, this kind of vapor entrapment seems unlikely, since the S_{BET} of Ti-1-V3 increased until 623 K, just before the sudden weight loss, while the S_{BET} of Ti-1-V3 decreased just after the sudden weight loss, i.e., at 683 K, as shown in Table IV.

For mechanically activated samples, the crystallization took place simultaneously with the sudden weight loss, as shown in Fig. 2. It was speculated in Section 3 that mechanical stressing promoted the aggregation of the construction unit of the anatase phase, i.e., the growth of the embryo. The decrease in T_{crys} can thus be explained by assuming an easier growth of these embryos to the potent nuclei when the material was preliminarily activated. These materials can, then, crystallize themselves before the content of H_2O and NH_3 reaches a level low enough for conventional crystallization. In other words, a small amount of hydroxyl groups and ammonium ions may have blocked the long-range ordering of structural units. The departure of H_2O and NH_3 is therefore forced to occur at T_{crys}, resulting in the sudden weight loss. In such a case, the crystallization cannot always be independent of the departure of H_2O and NH_3.

Conclusion

The decrease in the temperature of crystallization after grinding is attributed to the preliminary ordering of anatase, observed by Raman spectroscopy and electron diffractometry, even though no X-ray diffraction peak was detected. The sudden weight loss occurred simultaneously with the crystallization after mechanical activation. This suggests that a small amount of hydroxyl groups and NH_4^+ may block the long-range ordering of TiO_6 structural units.

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