LETTER TO THE EDITOR

Transformation of Ultrafine Titanium Dioxide Particles from Rutile to Anatase at Negatively Charged Colloid Surfaces

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The phase transition of TiO_2 from rutile to anatase has not been reported below the transition temperature from anatase to rutile. This work reports the new observation that ultrafine rutile-type particles are transformed into anatase by contacting the strongly negatively charged colloid particles such as $V_2O_5 \cdot nH_2O$, MoO_3, and $H_2WO_4 \cdot nH_2O$. The weakly negatively charged particles of silica and montmorillonite did not change the structure. More active $Nb_2O_5 \cdot nH_2O$ and $Ta_2O_5 \cdot nH_2O$ reacted chemically with TiO_2 to produce new compounds. Conversely, anatase-type TiO_2 was changed into rutile by contacting with HCl solution. From these facts it is concluded that chloride ions at the interface affect to form the rutile-type TiO_2, although anatase is thermodynamically stable at low temperatures. It is concluded that the surface field of the strongly negatively charged crystalline particles in an acidic condition eases the TiO_2 article to crystallize into a thermodynamically stable one.
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INTRODUCTION

Titanium dioxide (TiO_2) has three types of crystal structures (anatase, rutile, and brookite) (1). The most common phases are anatase and rutile, the former of which is more stable with lower temperature. However, these two types can be selectively prepared at room temperature by hydrolyses of titanium salts by adding the seeds for either structure (2). When Ti–alkoxide and salts like $Ti(SO_4)_2$ and $TiCl_4$ are hydrolyzed without seeds in pure H_2O, the main particles formed are anatase. When Ti–alkoxide and $TiCl_4$ are hydrolyzed in a concentrated HCl solution (1 mol dm^{-3}), the product is a rutile-type TiO_2. This fact signifies that coordinating chemical species for Ti play an important role in deciding the crystal structure in the hydrolyzing process. It is known that anatase is transformed into rutile at temperatures around 800°C, which differ depending upon the

various perturbing parameters of (surface) free energy of particles, i.e., particle sizes (3) and impurity dosing (4). The same transition was observed by UV irradiation at room temperature (5). As far as the authors are aware, however, the rutile once formed is stable and is not transformed into anatase under ambient conditions.

The present paper reports the new finding that ultrafine rutile-type TiO_2 particles are transformed into anatase by contact with the strongly negatively charged colloid particles.

EXPERIMENTAL

Materials. Tested TiO_2 (Ti-R) was prepared by hydrolyzing titanium tetraisopropoxide (TTIP) in 1 mol dm^{-3} HCl solution and aging for more than 2 days afterward, by which ultrafine rutile-type particles were formed (6). Anatase-type TiO_2 (Ti-A) was formed by hydrolyzing TTIP in pure H_2O. The colloid particles contacted are $V_2O_5 \cdot nH_2O$ (sol-V), $HNbO_3$ (sol-Nb), $HTaO_4$ (sol-Ta), MoO_3 (sol-Mo), and H_2WO_4 (sol-W), which are strongly negative due to the polyvalency of skeletal metal ions (7). The less negative particles of Na–montmorillonite (sol-CM) and silica (sol-Si) were also tested. $V_2O_5 \cdot nH_2O$ was prepared by cation-exchange polymerization of ammonium vanadate solution (8). $HNbO_3$ and $HTaO_4$ were formed by hydrolysis of $NbCl_5$ and $TaCl_5$, respectively. These colloid particles were purified by dialysis and their concentration was adjusted to 0.15 mol dm^{-3}. Purchased MoO_3 particles (Wako Pure Chem. Ind.) was suspended in pure H_2O for sol-Mo. Sol-W was prepared conventionally by reacting HCl with Na_2WO_4 solutions and dialyzing. The sol-CM was prepared by contacting the reference clay (K–montmorillonite) supplied by Clay Science Society of Japan with NaCl solution to conduct ion-exchange reaction, followed by washing. Silica was purchased from Japan Aerosil. The latter two powders were suspended in H_2O (0.15 mol dm^{-3}) before use.

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Reactions between TiO₂ and the sols. The TiO₂ sample for all the reactions was as prepared in which HCl and the reaction product of alcohol remained. The electrodialized sample was also tested to ascertain the reactivity. The reactions were conducted by mixing the different volumes of the sols. The mixed systems including reacting sols were kept at room temperature for at least one night.

Crystal structure and thermal analyses. The crystal structures of the samples were analyzed by powder XRD (Rigaku
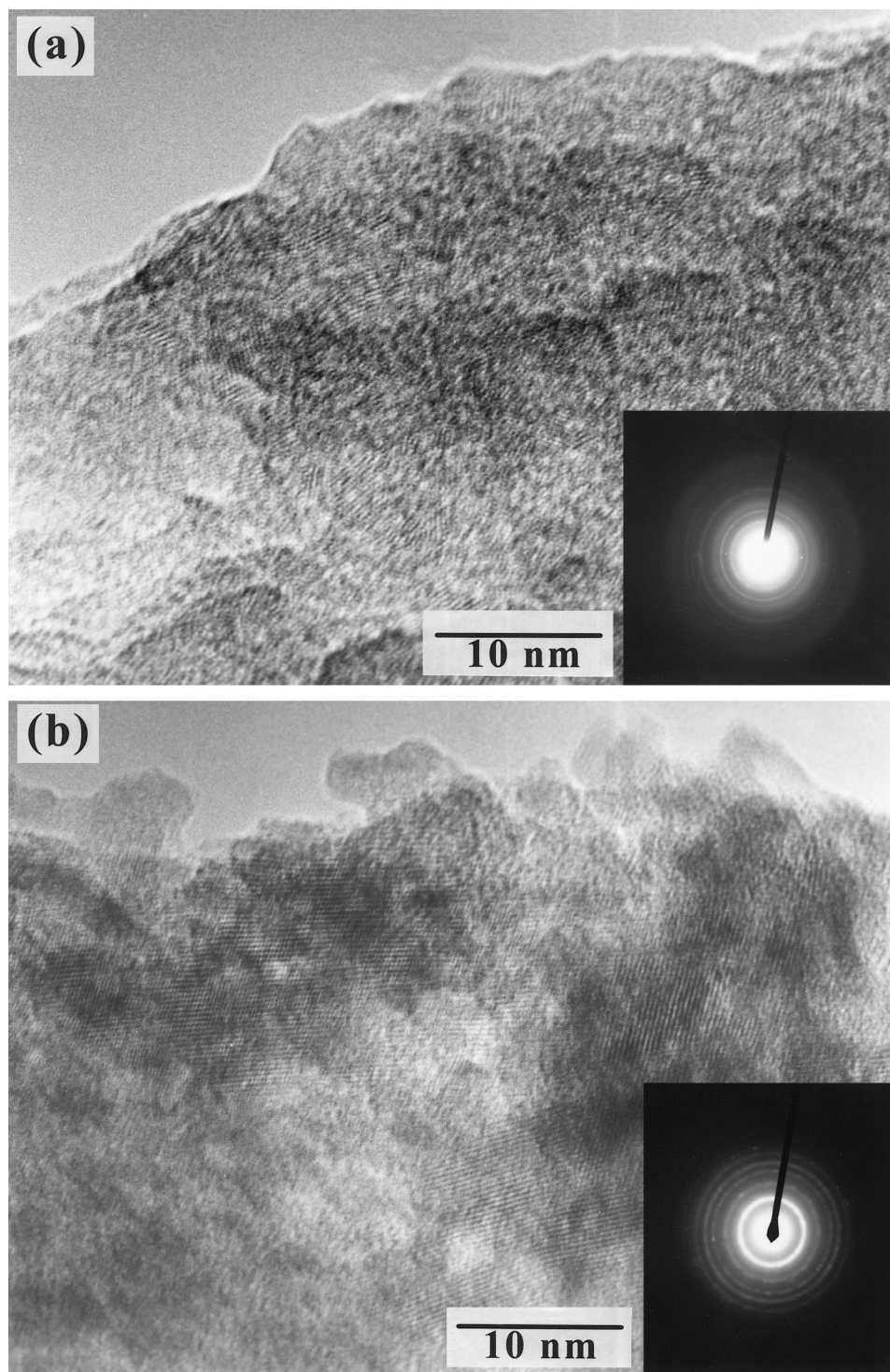

FIG. 1. Transmission electron micrographs of TiO₂ nanoparticles. (a) Ti-R; (b) Ti-R contacted with sol-V and leached with NaOH.

RAD 2R, Cu$K\alpha$) and electron microscope (Jeol JEM-2000EX).

RESULTS AND DISCUSSION

Figure 1a shows the electron micrograph of an as-prepared TiO_2 sample, Ti-R. The particle sizes are around a few nanometers. In addition to these ultrafine particles, needle-like particles (a few micrometers) were observed in a small amount, which are not shown here. The anatase-type particles (Ti-A) were ultrafine particles as well. Curve 1 in Fig. 2 and curve 1 in Fig. 3 show the XRD patterns of both samples, respectively. Curve 2 in Fig. 2 is for $V_2O_5 \cdot nH_2O$ and shows the harmonic diffraction peaks of $00l$, indicating the layered structure of the material.

The colloid solution of rutile particles mixed with sol-V gave the XRD pattern which does not present simply a mixture of both colloids but additional peaks for anatase-type TiO_2. In a typical case, when the mixing ratio was chosen properly (mol ratio, V:Ti = 1:1), a rather simple pattern was observed as curve 3. Leaching the mixture with NaOH aqueous solution (1 mol dm^{-3}) presented the XRD pattern of curve 4 which is exactly that for anatase. Electron microscope analysis substantiates the occurrence of the transition from rutile to anatase (Fig. 1b). $V_2O_5 \cdot nH_2O$ is a negatively charged layered material similar to the clay of montmorillonite. Yamanaka et al. reported the fact that ultrafine TiO_2 particles of around 10 Å or so are intercalated between the layers of montmorillonite and gave a blue shift of UV absorption spectrum of the TiO_2 phase (6). The latter property is characteristic of the anatase-type TiO_2. This shift seems to coincide with the phenomenon observed here as the phase transition from rutile to anatase in the system
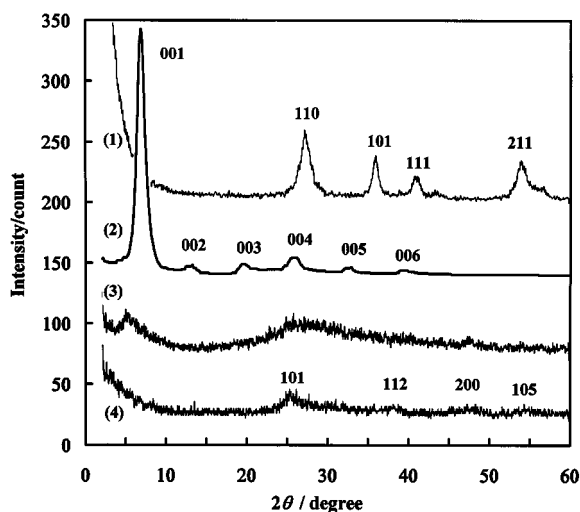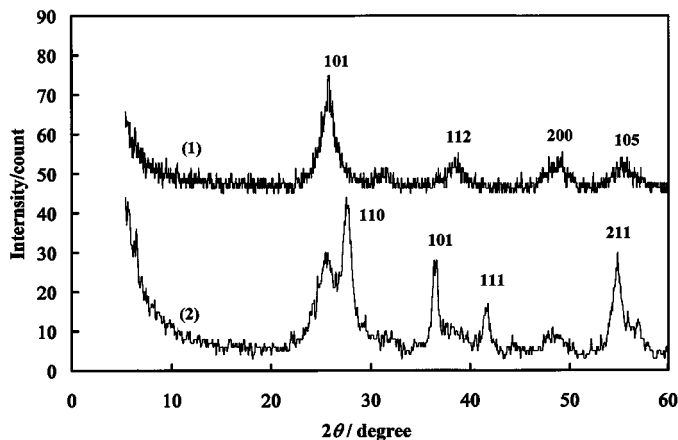

FIG. 3. XRD patterns of TiO_2. (1) Ti-A; (2) Ti-A contacted with HCl (1 mol dm^{-3}) solution. Miller indices are shown for those with rutile structure.

including $V_2O_5 \cdot nH_2O$. However, it was not possible for the present authors to find crystallographically the anatase-type TiO_2 contacted with Na–montmorillonite. A silica particle, which is negatively charged down to pH 2 and will be positive in the present system including HCl solutions (0.1–1 mol dm^{-3}), does not change the structure either.

With more negative colloid particles of sol-Mo and sol-W, phase transition from rutile to anatase was clearly demonstrated. The common property of these particles is the fact that these materials may be understood as oxo-acid. This fact leads us to expect that nonstructural oxo-acid might be concerned with the crystallization of TiO_2, but experiments using H_2SO_4, H_3PO_4, and HNO_3 did not change the crystal structure. These facts suggest the following possibility.

Under highly acidic conditions (1 mol dm^{-3} HCl) TiO_2 particles carry positive charge on the surface neutralized with counterions of Cl$^-$. As is well known, rutile-type TiO_2 has only been formed in the presence of Cl$^-$ ions in a wet system. This makes us speculate that counterions other than Cl$^-$ or chemical species like alcohols are so weak in affecting the structure that thermodynamically stable anatase is formed. The phase change in the reverse direction from anatase to rutile was successfully confirmed by contacting HCl solution (1 mol dm^{-3}) with Ti-A as shown by the XRD pattern (Fig. 3, curve 2).

With sol-Nb and sol-Ta, the TiO_2 phase has disappeared by contact, indicating the occurrence of the chemical reactions between them due to the strong reactivity.

The mechanism of the observed transitions under interfacial effect is not clear and is now being studied.

ACKNOWLEDGMENT

FIG. 2. XRD patterns of TiO_2. (1) Ti-R; (2) sol-V; (3) Ti-R contacted with sol-V; (4) Ti-R leached with NaOH after contacting with sol-V.

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