Crystallization Process of TiO_2 Nanoparticles in an Acidic Solution

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Hydrolysis of titanium tetraisopropoxide followed by condensation at 30 °C yields amorphous TiO_2. Addition of nitric acid for peptization greatly accelerates the rate of amorphous to anatase conversion, resulting in an anatase with locally imperfect atomic structure. Further conversion to rutile in acidic solution has been observed and a plausible phase transformation process has been postulated.

Two of the most representative polymorphs of TiO_2, i.e., rutile and anatase, have received much interest because of their applications such as photocatalyst, optical devices, medical treatment, and environmental purifications.[1,2] In sol–gel process to prepare TiO_2, based on the hydrolysis and condensation of titanium alkoxide, the addition of acid redisperses coagulated colloid particles (peptization). It has been known that the peptization by either nitric or hydrochloric acid promotes the formation of rutile phase at a given titanium concentration.[3,4] Although the influence of acid addition on the eventual crystal structure has been studied in some literatures,[3,4] the crystallization process with the lapse of reaction time is not available. Understanding the process of crystallization is fundamental to the precise control of the polymorph type that is produced. Thus, in the present work, the evolution of TiO_2 crystal phases has been investigated as a function of reaction time by freeze-drying reaction products at selected reaction times.

Titanium tetraisopropoxide was hydrolyzed by adding an excess amount of water (water/Ti = 50) at 30 °C. Nitric acid was then added in 24 h of total reaction time for peptization (acid/Ti = 0.5). An appropriate amount of colloidal TiO_2 sol was taken from the reaction batch at different reaction intervals, followed by an immediate freeze drying in liquid nitrogen for 24 h. The quenched reaction product was characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), and Raman spectroscopy.

Figure 1 shows XRD patterns from quenched samples at varying reaction times. Before the addition of acid, no notable peaks are observed (hydrolysis/condensation time, $t_{h/c} = 10$ min and 24 h). The peak of anatase (A) appears with a trace of rutile (R) in about 12 h after the addition of acid (peptization time, $t_{pep} = 12$ h). After 24 h of reaction time, the maximum peak intensity of rutile phase increases ($250 \rightarrow 616$ counts) while that of anatase decreases ($381 \rightarrow 323$ counts).

Raman spectra from quenched samples at various reaction times are shown in Figure 2. Spectra from $t_{h/c} = 10$ min and 24 h samples exhibit a broad band between 425 and 605 cm^{-1}, which results from amorphous or highly distorted phase in the light of Ocana et al.[5] who observed similar bands at 430 and 600 cm^{-1}. Selected area diffraction pattern from the same specimen in TEM mode also showed a diffuse ring (not shown). These results indicate that XRD patterns from $t_{h/c} = 10$ min and 24 h result from the amorphous nature of the samples, not from the ultrafine nature of nanocrystals.

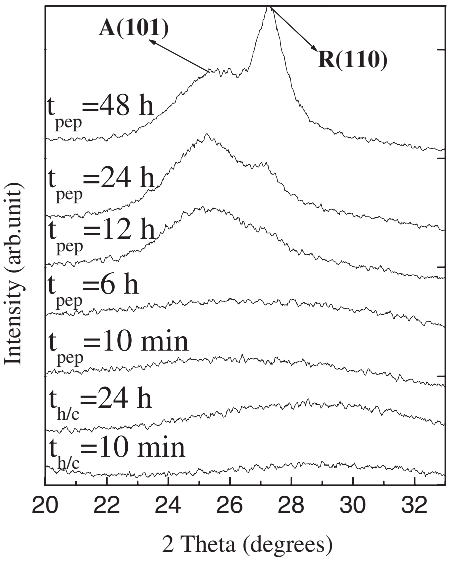

Figure 1. XRD patterns from samples at various reaction times.

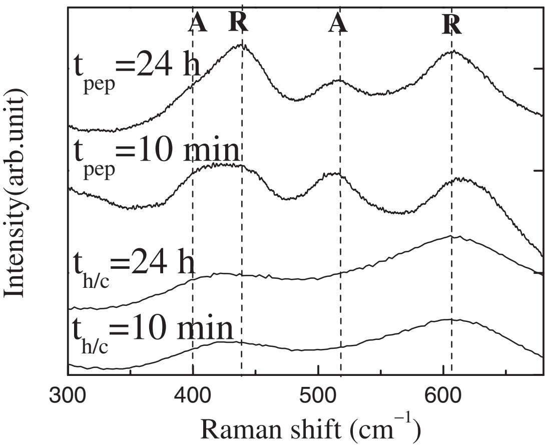

Figure 2. Raman spectra from samples at various reaction times.

For peptized samples, there is an evidence of crystalline phase in Raman spectrum even when t_{pep} is as early as 10 min, although crystalline phase appears only after t_{pep} is about 12 h in XRD (Figure 1). However, in $t_{pep} = 10$ min sample (Figure 2), the shifted Raman peaks from the position of anatase (A [A_{1g}]: 515 cm^{-1}) and rutile (R [A_{1g}]: 605 cm^{-1}) and the broad band at 400–440 cm^{-1} (A [B_{1g}] and R [E_g]) indicate that these specimens have highly distorted crystalline structure.[6] Thus, the absence of specific peaks in XRD patterns of $t_{\mathrm{pep}} =$ 10 min and 6 h samples results from such nature of TiO_2 nanocrystals. When peptization time is increased to 24 h, Raman peak positions are not shifted much, implying that the local crystal distortion is less significant. In this sample, however, the peak intensity of anatase is smaller than rutile in Raman spectrum which characterizes a local atomic arrangement. In XRD (Figure 1), which characterizes a global atomic arrangement, anatase is certainly the major phase. Thus, the local distortion in anatase does not seem to be completely eliminated before the apparent growth of rutile at $t_{\mathrm{pep}} =$ 24–48 h (Figure 1).

From Figures 1 and 2, no evidence of crystalline phase is found during hydrolysis/condensation reaction until $t_{\mathrm{h/c}} =$ 24 h. Bischoff and Anderson[3] also reported similar results in XRD. However, they interpreted their XRD results from initial hydrolysis product that the crystallites were too small to be detected by XRD as crystalline. However, from the additional evidences in this work, the initial product of hydrolysis/condensation reaction is certainly amorphous. In their work, aging of the acid-free hydrolysis/condensation product for 3–5 weeks yielded crystalline (anatase and brookite) peaks in XRD. Therefore, it would be inferred that the activation energy of conversion from the highly metastable amorphous phase to the similarly metastable anatase in their work was fairly low so that the conversion was achieved even at an ambient temperature.

At initial stage of peptization, anatase phase ($t_{\mathrm{pep}} =$ 10 min in Figure 2) is crystallized from the previously formed amorphous phase ($t_{\mathrm{hc}} =$ 24 h in Figure 2). In general, the presence of acid promotes the dissolution of an amorphous phase, and thus the facilitation of amorphous to anatase transformation in the acidic solution (a low-activation energy process) is believed to be associated with the dissolution of amorphous phase and reprecipitation to anatase. The growth rate of anatase is such that a detectable amount of anatase by XRD is observed as early as 12 h of peptization time. This result is fairly fast as compared to the case of 3–5 weeks in acid-free solution.[3] Such fast growth rate is interpreted to be responsible for the local distortion of the atomic arrangement in anatase. Thus, the fast-grown anatase in the acidic solution is thermodynamically less stable as compared to a well-crystallized anatase, allowing a more suitable transformation to a stable state, e.g., rutile. Summarizing the anatase formation in acidic solution, the conversion rate of the amorphous to anatase has been greatly facilitated by the presence of acid, yielding a locally distorted atomic arrangement in anatase.

Once detectable amount of rutile by XRD is observed at $t_{\mathrm{pep}} =$ 24 h (Figure 1), rutile phase grows predominantly thereafter by decreasing anatase peak intensity, indicating that anatase transforms to rutile. In general, anatase transforms irreversibly to rutile at temperatures ranging from 400 to 1200 °C,[7,8] depending on particle sizes, crystal morphologies, and additives. This implies that the activation energy (ΔE_0) of the conversion from anatase to rutile is fairly high, inhibiting the conversion at low temperatures. It was previously pointed out that anatase could not change to rutile under low-temperature hydrothermal conditions in HCl solutions,[9] presumably owing to the lack of providing enough activation energy at a low temperature. However, our result clearly indicates a transformation of anatase to rutile even at 30 °C. Although the temperature was not as low as the one in the current work, Wu et al.[10] also reported recently that a treatment of an encapsulated sol product below 220 °C yielded transformation of anatase to rutile. Therefore, it is necessary to consider the reason why such anatase to rutile conversion could be achieved at such a low temperature in solution.

The initial pH ($\mathrm{pH_i}$) of the solutions during peptization in the current work was 0.66 and the initial concentration of Ti during hydrolysis/condensation step was about 0.02 M. In this highly acidic and titanium-dilute conditions, thermodynamically most stable Ti(IV) ionic species is $Ti(OH)_2^{2+}$.[11] In the theoretical prediction by Lencka and Riman based on the ideal solution approximation,[11] there is a solution condition ([Ti] and pH) where the order of the magnitude of the chemical potentials is $\mu_{\mathrm{r}} < \mu_{\mathrm{i}} < \mu_{\mathrm{a}}$ where μ is the chemical potential, and subscripts r, i, and a denote rutile, $Ti(OH)_2^{2+}$, and anatase, respectively.[4] In the experimental observation by Yamabi and Imai,[4] our solution condition is such a case. It is hypothesized that the presence of the metastable state i in the reaction system would reduce the activation energy from ΔE_0 (the case when the metastable state is absent in a solid-state reaction) to ΔE_1 and ΔE_2, for the two-step process in a solution. If the presence of another metastable state i lowers the activation energy as such ($\Delta E_0 > \Delta E_1$ and $\Delta E_0 > \Delta E_2$), the transformation of anatase to rutile would be achieved at a fairly reduced temperature. This low-activation-energy path involves the dissolution of anatase to the metastable phase $Ti(OH)_2^{2+}$, followed by the reprecipitation to the stable rutile phase.

In summary, amorphous TiO_2 phase forms before the peptization. Addition of acid (peptization) greatly facilitates the growth rate of anatase from amorphous phase, yielding anatase phase with a locally distorted atomic arrangement. Then, rutile phase grows via the consumption of the metastable anatase in the acidic solution. It was postulated that the presence of a thermodynamically metastable ionic species, $Ti(OH)_2^{2+}$, in the solution, provides a low-activation-energy path. Thus, the anatase to rutile transformation would be achieved even at 30 °C in the acidic solution via the dissolution of the locally imperfect anatase to form $Ti(OH)_2^{2+}$, followed by reprecipitation to rutile.

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