SiO₂ 表面吸附层中钛酸丁酯的反应过程

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摘要：研究了硅胶表面富含水吸附层中钛酸丁酯的反应过程。在不同条件的吸附相反应制备中, 首先利用分光光度计测定了乙醇体相中 Ti 含量随反应进行的变化过程。结果表明由于吸附层中钛酸丁酯的快速水解, 乙醇体相中的 Ti 含量在反应前 60 min 快速减少。钛酸丁酯与硅胶表面羟基、化学吸附层和物理吸附层中的水分子的反应活性均不相同, 这导致了 Ti 含量曲线的不同变化。EDAX 的分析结果表明温度对乙醇体相中钛酸丁酯的反应过程影响很小, 但对吸附相反应有着较为复杂的影响, Ti 含量和 TiO₂ 形貌都随着温度升高出现了两类变化。本文提出了温度对化学吸附和物理吸附的不同影响来解释样品中 Ti 含量和 TiO₂ 形貌的不同变化。

关键词：纳米反应器；钛酸丁酯反应；温度；物理吸附；化学吸附
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Reaction of Tetrabutyl Titanate in the Adsorption Layer on SiO₂ Surface

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Abstract: Reaction of tetrabutyl titanate (Ti(OBu)₄) which happened in a water-rich adsorption layer on the silica surface was studied. The change of Ti content in the alcohol bulk during reaction process of Ti(OBu)₄ was measured by spectrophotometry. The results suggested that the sharp decrease of Ti content in the first 60 min of reaction time was due to quick hydrolysis of Ti(OBu)₄ in the adsorption layer. The different reaction activity of Ti(OBu)₄ with hydroxyl group and water molecule in two kinds of the adsorption layer caused various change in Ti content curves. The EDAX results indicated that increase of temperature influenced little on reaction of Ti(OBu)₄ in the alcohol bulk, whereas, the influence of temperature on the preparation process of adsorption phase synthesis was complicated. Both the changes of Ti content and morphology of TiO₂ had two kinds of features with temperature increasing. And these different changes were explained by various effects of temperature on chemical-adsorption and physical-adsorption.

Key words: nanoreactor; reaction of tetrabutyl titanate; temperature; physical-adsorption; chemical-adsorption

0　Introduction

Synthesizing nanoparticles with maximum control over the composition and structure has recently been an interesting scientific and technological challenge[1~4].

Microreactor synthesis, like microemulsion method, is one of the remarkable methods because the significant restriction on particles size[5~8]. Adsorption Phase Synthesis (APS) is one of the latest developments of microreactor synthesis and it is effective for the prepara-

tion of various of composites with special construction. The adsorption layer formed on the surface of supports is employed as a nanoreactor in APS to prepare nanoparticles[9]. Dekany and co-workers[10~12] have been prepared several kinds of nanoparticles by APS, such as CdS, Pd nanoparticles, and so on. The authors have also synthesized TiO_2[13,14], Ag[15] and NiO[16] nanoparticles with 2~7 nm of diameter on the SiO_2 surface.

In our previous work[17~19], the volume of an adsorption layer was estimated firstly by measuring the change of water content in the bulk during the adsorption process. Then it was found that reaction of $Ti(OBu)_4$ in the adsorption layer could also be separated into two steps: hydrolysis and condensation, which was similar to that in impregnation method. However a sharp increase of Ti content on the SiO_2 surface was a special phenomenon only found in APS process. This result indicate that the reaction in micro circumstance of nanoreactor was very different from that in the bulk, which was corresponding to results in studies on other microreactors, like microemulsion, reverse microemulsion [20,21] and layer silicates[22,23].

In the preparation of TiO_2 via APS, the adsorption layer was not only used as a reactor, but also provided water molecules as the other reactants. The adsorbed water molecules on the SiO_2 surface are different from water molecules in alcohol solution and bulk water, which resulted that reaction of $Ti(OBu)_4$ in the adsorption layer was much distinguished from that in the bulk. Furthermore, the properties of adsorbed water molecules should be influenced by change of reaction

conditions, which also affected reaction of tetrabutyl titanate in the adsorption layer. In this paper, influence of evaluation of the adsorption layer, including chemical and physical adsorption layer, is studied on reaction of tetrabutyl titanate. Then the inherent mechanism which led to sharp changes of reaction products was explored.

1　Experimental sections

1.1　Materials

Hydrophilic colloidal silica (SiO_2) A-200 (average particle diameter is 12 nm, Specific Area is (200±25) $m^2 \cdot g^{-1}$) was obtained from Degussa (Germany). Tetrabutyl titanate was purchased from Shanghai chemical reagent co. Ltd. and used as-received. Absolute ethyl alcohol (obtained from Shanghai chemical reagent co. Ltd.) was distilled and stored over a 0.4 nm molecular sieve (SCR 4A, China).

1.2　Preparation of TiO_2 nanoparticles

1.2.1　Preparation of TiO_2 by Adsorption Phase Synthesis (APS, reaction in the water-rich adsorption layer)

0.5 gram of hydrophilic SiO_2 nanoparticles (previously pre-dehydrated and kept in a desiccator at 393 K), and 200 mL of absolute alcohol together with different volumes of water from 0 mL to 1.5 mL were added into a triflask to adsorb and stirred under different temperatures. Because of selective adsorption capacity of SiO_2, a water-rich adsorption layer formed gradually on the SiO_2 surface (Fig.1). After adsorption equilibrium (12 h), $Ti(OBu)_4$ (2.15 g) dissolved in 50 mL of ethanol
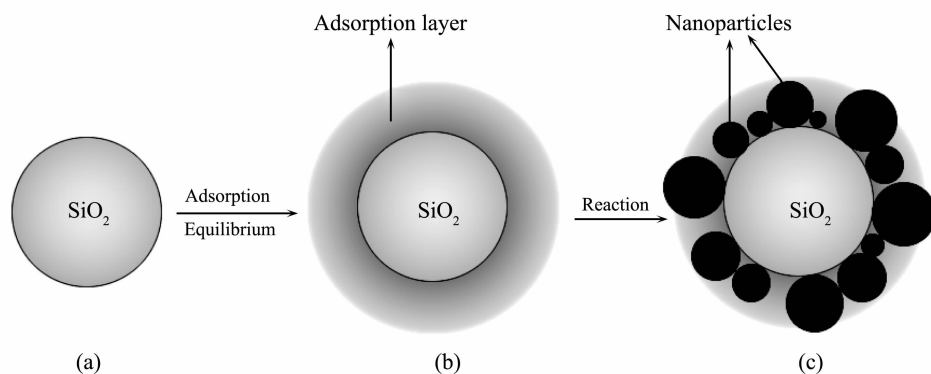
(a) Dispersion of silica in binary liquids; (b) Adsorption equilibrium; (c) Particles distribution after reaction

Fig.1　Scheme of preparation of TiO_2 in an adsorption layer

was added. The molecules of Ti(OBu)$_4$ diffused from the bulk to SiO$_2$ surface and reacted in the adsorption layer. TiO$_2$ particles were formed by hydrolysis and condensation in the adsorption layer on the silica surface. After reaction for 5 h, the product was gained by several centrifugation-redispersion-washing cycles and dried at 75~100 ℃.

1.2.2 Preparation of TiO$_2$ by Impregnation Method (IM, reaction in the alcohol bulk)

200 mL of absolute alcohol and different volumes of water from 0 mL to 1.5 mL were added into a triflask. Then Ti(OBu)$_4$ (2.15 g) dissolved in 50 mL of ethanol was added to react under different temperatures. After reacting for 4 h, 0.5 g of SiO$_2$ (previously kept in a desiccator at 393 K for 2 h) was added into the reaction system. After reaction completed (5 h), the product was gained by several centrifugation-redispersion-washing cycles and dried at 75~100 ℃.

1.3 Characterization

1.3.1 Spectrophotometry

A standard curve of Ti content vs absorbance was estimated first by 721 spectrophotometry (shanghai, china). During the preparation process of APS, the suspension was centrifuged at different reaction time and 5 mL of the supernatant liquid was separated, followed by an evaporation of the solvent. Then the residue gained after evaporation process was dissolved in hot concentrated sulfuric acid and the solution with different Ti content was gained. Finally spectrophotometry (wavelength 390 nm) was used to measure the absorbance of the solution and Ti content in the supernatant liquid could be calculated combining with the standard curve.

1.3.2 Transmission electron microscopy (TEM)

One drop of an ultrasonic-mixed, dilute alcohol suspension of the "as-prepared" (see Section 1.2) samples was placed on a carbon-coated grid, followed by an evaporation of the solvent. Electron micrographs of the particles were taken by JEM-200CX transmission electron microscope.

1.3.3 Energy dispersive X-ray microanalysis (EDAX)

A small amount of samples were placed on a platform and compressed to flat. Then two areas of sample surface were scanned and analyzed by energy disper-

sive X-ray microanalysis (Genesis 4000) to measure Ti content on SiO$_2$.

2 Results and discussion

2.1 Measure of Ti content in the alcohol bulk during reaction

In our previous work[19], it was found that evaluation of an adsorption layer, especially formation of a physical-adsorption layer, led to great increase of Ti content on the SiO$_2$ surface after reaction finished. For further study on influence of the adsorption layer on reaction of Ti(OBu)$_4$, the change of Ti content in the alcohol bulk during reaction process was measured by spectrophotometry 721.

Fig.2 is changes of Ti content in the alcohol bulk during the reaction under different water concentrations. The first curve in Fig.2 shows that when no water added in preparation, Ti content changes slowly during whole reaction process. Whereas other four curves can all be divided obviously into two segments: Ti content decreases rapidly in the first 60 min; then changes slowly after 60 min, which is similar to the first curve.
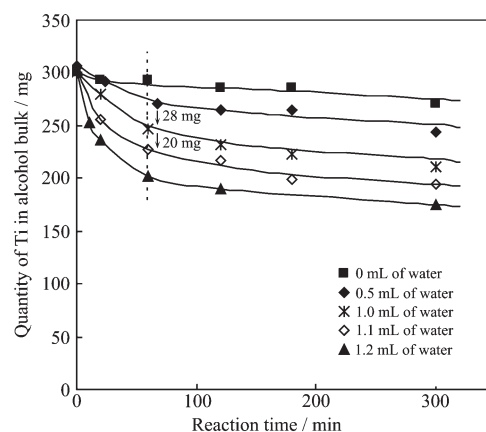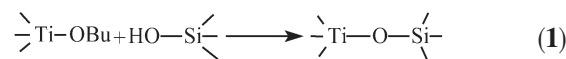

Fig.2 Dependences of Ti quantity on reaction time during APS process under different water concentrations

According to the literature[24], there were many -Si-OH distributed on the surface of hydrophilic SiO$_2$, so Ti(OBu)$_4$ could react with these -Si-OH when no water added:

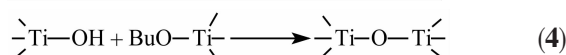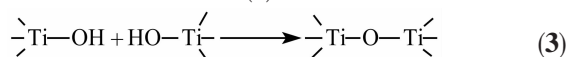$$\text{Ti—OBu} + \text{HO—Si} \longrightarrow \text{Ti—O—Si} \qquad (1)$$

This reaction was a slow-reaction, so the first Ti content curve decreased slowly.

When water was added into reaction system, two similar changes in Ti content curves, reflected different reaction rate of $Ti(OBu)_4$ with water molecules and hydroxyl groups. According to our former work[19], when an adsorption layer formed, $Ti(OBu)_4$ hydrolyzed in the adsorption layer at first:

$$\frac{\backslash}{/}Ti—OBu + H_2O \longrightarrow \frac{\backslash}{/}Ti—OH \qquad (2)$$
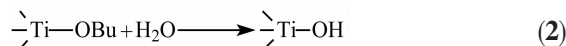
$Ti(OBu)_4$ almost hydrolyzed quickly to intermediate-products in the adsorption layer while it was added to reaction system, so Ti content in the bulk decreased sharply in the first 60 min. After hydrolysis of $Ti(OBu)_4$ finished, two reactions should happen on the SiO_2 surface besides condensation (**1**):

$$\frac{\backslash}{/}Ti—OH + HO—Ti\frac{/}{\backslash} \longrightarrow \frac{\backslash}{/}Ti—O—Ti\frac{/}{\backslash} \qquad (3)$$

$$\frac{\backslash}{/}Ti—OH + BuO—Ti\frac{/}{\backslash} \longrightarrow \frac{\backslash}{/}Ti—O—Ti\frac{/}{\backslash} \qquad (4)$$
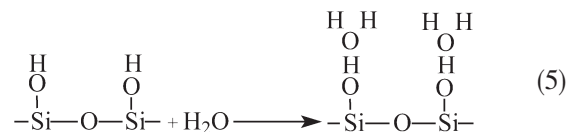
These reactions we re all slow reactions and their rates were similar to condensation (**1**), therefore Ti content in the bulk decreases slowly. And the changes of four Ti content curves after 60 min in Fig.2 almost parallel the first Ti content curve.

From the data in Fig.2, it is also found that the decrease of Ti content in first 60 min of reaction time becomes more sharply with water concentration increasing. Whereas the decreases in four Ti content curves after 60 min change little with water concentration increasing. It is notable to find that after reacting for 60 min, mass of Ti in the alcohol bulk falls sharply from 247 mg to 227 mg (decreased by 20 mg), when amount of water changes from 1.0 mL to 1.1 mL. However when quantity of water increases by 0.5 mL (from 0.5 mL to 1.0 mL), Ti content at 60 min of reaction time only decreases by 28 mg. This phenomenon indicates that there is a sharp decrease of Ti content in the alcohol bulk within scope of 1.0~1.1 mL of water (as an arrow shown in Fig.2), that is to say Ti concentration on the SiO_2 surface increases dramatically, which being consistent with the EDAX results in our former work[19].

According to literature[25] and our previous work[17,19], this sharp decrease was due to the evaluation of the adsorption layer with water concentration increasing. The evaluation of the adsorptio n layer was a gradual pro-

cess. When water molecules were adsorbed on the SiO_2 surface, a chemical-adsorption layer was formed first on the silica surface and water molecules in the chemical-adsorption layer combined strongly with surface of SiO_2 via chemical bonds.

$$
\begin{array}{c}
\quad\quad\quad\quad\quad\quad\quad\quad\; H\;H \quad\quad H\;H \\
\quad\quad\quad\quad\quad\quad\quad\quad\; O \quad\quad\quad O \\
H \quad\quad\;\; H \quad\quad\quad\quad\; H \quad\quad\; H \\
O \quad\quad\;\; O \quad\quad\quad\quad\; O \quad\quad\; O \\
-Si—O—Si- + H_2O \longrightarrow -Si—O—Si-
\end{array} \qquad (5)
$$

When water concentration was higher than the critical value[26] (like 1.1 mL of water here), a physical-adsorption layer could form. The physical-adsorption layer was a multi-molecules layer and water molecules in this layer combined with the silica surface via weak molecular force (such as hydrogen bond and van der Waals force).

Being in different state, hydroxyl groups on the silica surface, water molecules in the chemical-adsorption layer, and water molecules in the physical-adsorption layer had different reaction activity with $Ti(OBu)_4$. Condensation reaction between $Ti(OBu)_4$ and hydroxyl groups was the slowest reaction. And the hydrolysis of $Ti(OBu)_4$ with water molecules in the physical-adsorption layer was the fastest one. With increase of water concentration, the reaction of $Ti(OBu)_4$ in first 60 min became faster and Ti content in the alcohol bulk decreased more. The sharp change between 1.0 mL of water and 1.1 mL of water showed the effect of the physical adsorption layer (as shown by as an arrow in Fig.2).

2.2 Temperature experiments under different water concentrations

2.2.1 Temperature experiments of impregnation method (IM)

In our former research[18], it was found that Ti content on the SiO_2 surface also changed with temperature increasing, which might be due to damage of physical-adsorption by increase of temperature. To explore this effect further, we should realize the influence of temperature on reaction of $Ti(OBu)_4$ in the alcohol bulk at first. Therefore based on the results in our former work[19], experiments of IM under two water concentrations (0.5 mL and 1.2 mL) and different temperatures (0~70 ℃) was designed. And Fig.3 is Ti content of samples by IM

under two water concentrations versus reaction temperature.

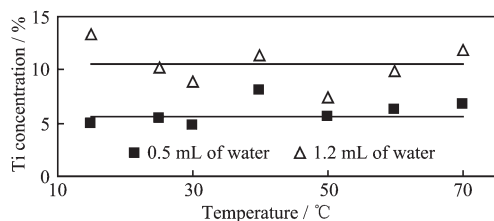Fig.3　Dependence of Ti concentrations in samples by IM on temperature

From the results by TEM in our former work[19], the morphology of samples by IM was very uneven. So there are obvious fluctuations in two Ti content curves in Fig. 3. With water concentration increasing, the fluctuation becomes more obvious due to more heterogeneous morphology. Ignoring these fluctuations, it is found that Ti content of IM samples changes little with temperature increasing and can be treated as straight lines. Therefore the change of temperature influences little on reaction of $Ti(OBu)_4$ in the alcohol bulk.

The reaction of $Ti(OBu)_4$ is exothermal[25] ($-\Delta H_h$= 19.3 kJ·mol⁻¹ under 25 ℃), which restricted and weaken the influence of temperature on condensation rate. Phenomena appeared in Fig.3 was due to the reaction features of $Ti(OBu)_4$. Increase of temperature could promote the rate of condensation and more TiO_2 could be formed in same reaction time. Therefore the reaction of $Ti(OBu)_4$ in the alcohol bulk changed little with temperature increasing.

2.2.2　Temperature experiments of adsorption phase synthesis

To investigate further different reaction of $Ti(OBu)_4$ in the chemical-adsorption layer and the physical-adsorption layer, we designed preparation experiments under different temperatures with various volume of water added　(from 0 mL to 1.5 mL). EDAX was employed to measure Ti content on the SiO₂ surface after reacting for 5 h (Fig.4).

From Fig.4, it is shown that the change of Ti content with temperature increasing can be separated into two kinds: when volume of water added is less than 1.1 mL, Ti content changes little with temperature increas-
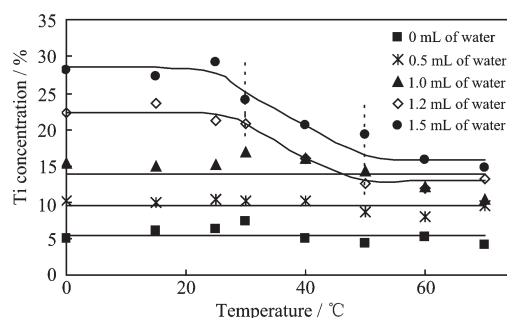

Fig.4　Dependence of Ti concentrations in all samples by APS on temperature

ing and Ti concentration curves are almost horizontal lines. While water added exceeds 1.1 mL (including 1.1 mL of water), there are sharp decreases appeared in Ti content curves with temperature rising. At low temperature, Ti concentration under two water concentration changes slightly. When temperature increases more than 30 ℃, sharp decreases appear　(the turning temperatures are all 40 ℃) and the decrement of Ti is about 50%. As temperature increases continuously, the curves become smoothly again.

Combining with the results in section 2.1 and 2.2.1, these two kinds of curves, we consider, were due to different influence of temperature on physical and chemical-adsorption. According to the results in section 2.1 and our former work[19], when amount of water added was less than 1.1 mL, there was only a chemical-adsorption layer formed on the SiO₂ surface. And the adsorption layer changed little with temperature increasing because of the stable chemical-bond. Therefore Ti concentration curves were almost straight lines　(as Ti content curves under 0 mL, 0.5 mL and 1.0 mL of water shown in Fig.4).

When volume of water reached 1.1 mL, the physical-adsorption layer was the main structure of the adsorption layer (as shown in Fig.5a). At low temperature, both chemical-adsorption and physical-adsorption existed stably and the physical adsorption layer changed slowly with temperature increasing, which influenced little on　reaction of $Ti(OBu)_4$. So Ti concentration in samples kept almost unchanged and the first flatten stage appeared in curves. When temperature increased continuously,　the　aggravation　of　molecular　motion
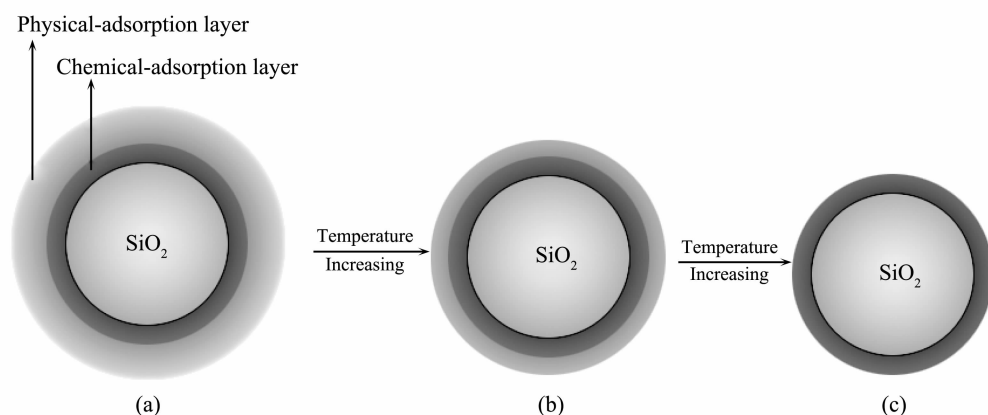
Fig.5　Scheme of the evaluation of the adsorption layer on the silica surface with temperature increasing

reached a limit, which resulted in rapid thinning of the physical-adsorption layer. The chemical-adsorption layer became main reaction site of $Ti(OBu)_4$, therefore reaction quantity lessened greatly and sharp decreases in curves appeared (the turning temperature of two curves were both 40 ℃). When temperature was very high (50 ℃ here), the physical-adsorption layer almost vanished and there was only the chemical-adsorption layer left on the silica surface. Due to the stable combination between chemical-adsorptive water and surface of SiO_2, the change of temperature affected little the adsorption layer and the nanoreactor became more stable. So the second flatten stage in curves appeared.

2.3　TEM morphology of TiO_2 gained by APS under different water concentrations and temperatures

　　Corresponding to Ti content curves in Fig.4, the morphology of TiO_2 in TEM can also be divided into two kinds. When volume of water was less than 1.1 mL, only the chemical-adsorption layer formed on the SiO_2 surface, so Ti content curves under different temperatures were almost straight lines (as shown in Fig.4) after reaction in the chemical-adsorption layer. So the morphology of all samples in TEM changes little with temperature increasing. Fig.6 is TEM pictures of samples under 1.0 mL of water gained by APS.

　　When amount of water exceeded 1.1 mL, there was the physical-adsorption layer formed on the SiO_2 surface and its nature changed much with temperature increasing. So the grey of regions on the support surface both become light (Fig.7) with temperature rising, especially when temperature reaches 50 ℃, the characteristic of samples is similar to that of TiO_2 formed in the chemical-adsorption layer (as shown in Fig.6). These phenomena consist with the conclusions gained from Ti concentration curves (Fig.4).
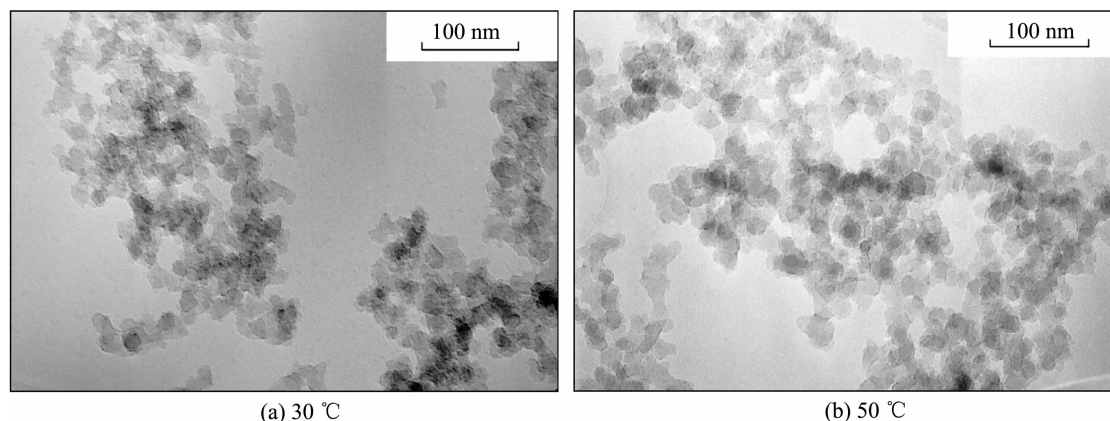

(a) 30 ℃　　　　　　　　　　　　　　　　　　　　　　　(b) 50 ℃

Fig.6　TEM photography of APS samples under 1.0 mL of water
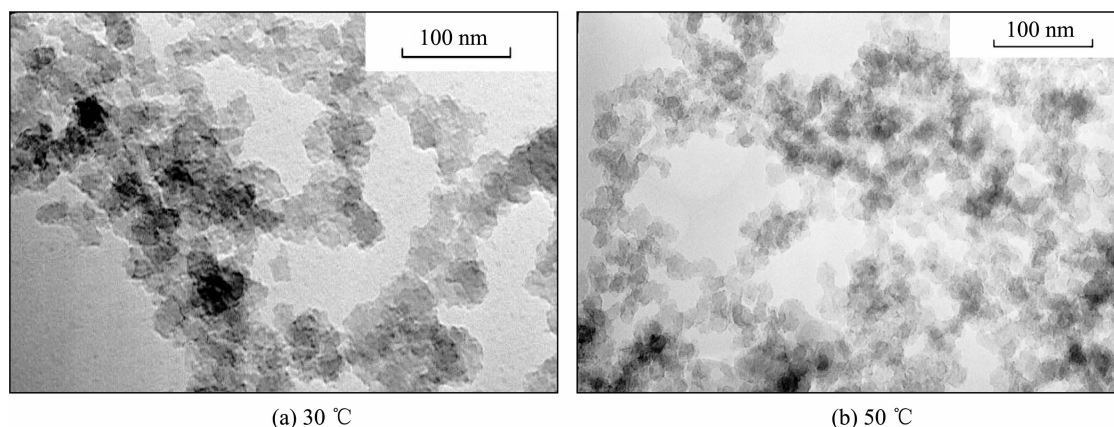
(a) 30 ℃

(b) 50 ℃

Fig.7　TEM photography of APS samples under 1.2 mL of water

3　Conclusions

The reaction of $Ti(OBu)_4$ on the SiO_2 surface changed with evaluation of the adsorption layer. With increase of water concentration in preparation, the main reactants which reacted with $Ti(OBu)_4$ changed from-Si-OH on the SiO_2 surface to water molecules in the chemical adsorption layer, then to water molecules in the physical adsorption layer. Both reaction rate and Ti concentration on the SiO_2 surface manifested a sharp increase when the physical-adsorption layer formed.

The influence of temperature on physical-adsorption and chemical-adsorption was different. Due to the stable chemical bonds, the chemical adsorption layer changed little with temperature increasing. However increase of temperature affected obviously physical adsorption. And the physical adsorption layer vanished eventually under high temperature. These vary changes of different adsorption with temperature changing caused different changes of Ti concentration on the SiO_2 surface.

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