

# Organic modification of nano-SiO<sub>2</sub> particles in supercritical CO<sub>2</sub>

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## Abstract

Organic modification of nano-SiO<sub>2</sub> particles was performed with supercritical CO<sub>2</sub> as solvent and a titanate coupling reagent NDZ-201 as the modification reagent. The surface of the nano-SiO<sub>2</sub> particles was changed after modification by the titanate coupling reagent from hydrophilic to hydrophobic. IR and thermo-gravimetric analyses indicate that the interaction between the titanate coupling reagent and the particle surface is mainly through chemical bonding. The influence of the apparent concentration of the titanate coupling reagent on the modification at 60 °C and 20.0 MPa was investigated, in which the apparent concentration is the weight percent of the titanate coupling reagent added in the supercritical solvent. The quantity of the titanate coupling reagent reacted on the particle surface reaches a maximum of  $19.81 \times 10^{-7}$  mol/m<sup>2</sup>, i.e. 1.19 molecule titanate coupling reagent/nm<sup>2</sup>, when the apparent concentration of titanate coupling reagent is 0.6% (wt).

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## 1. Introduction

Nano-SiO<sub>2</sub> particles are widely used in the fields of composite materials, biomaterials, sensors, etc. The surface of the nano-SiO<sub>2</sub> particles should be modified to achieve better dispersibility, affinity, functionality, etc. Chemical modification of the surface can enhance the dispersibility of SiO<sub>2</sub> particles in various continuous phases, change the surface activity of the SiO<sub>2</sub> particles, and bring about new surface physical and chemical characteristics. Nano-SiO<sub>2</sub> particles can be used as a DNA carrier after modification by alkoxysilanes and amines by changing the surface potential of the particles [1], and used as a fluorescence chemical sensor after modification by organic molecules with fluorescent organic chromophers [2].

There exist hydroxyl groups on the surface of inorganic oxides particles [3,4]. Chemical modification of the particle surface can be achieved through a reaction between the hydroxyl groups on the surface and modification reagents [1,2]. There are many methods of surface chemical mod-

ification, e.g. liquid methods [1,2], gaseous methods [5], mechano-chemical methods [6], etc. The methods have their disadvantages. Liquid methods need the modification reagents to be dissolved in solvents, and there are the problems of solvent recovery, and long operational procedures, high costs and severe pollution. Gaseous methods usually operate at a high temperature in order for the modification reagents to contact the particle surface in molecule form, and the reactors adopted are usually fluidized beds, fixed beds, agitating beds, etc. Gaseous methods are suitable for particles of micrometer size that do not easily agglomerate. It is difficult to achieve a uniform modification and to treat the discharge gases containing modification reagents. Mechano-chemical methods comprise mixing and grinding between the particles and modification reagents. The energy consumption in the process is high and there is probably pollution of grinding medium in the product.

Supercritical CO<sub>2</sub> is a green solvent [7,8] that has the characteristics of a high diffusion coefficient like a gas, a high solvating power like a liquid, and low viscosity, low surface tension and rapid osmosis into micro-porous materials [9–12]. When supercritical CO<sub>2</sub> is used as the solvent in a surface chemical modification process, it can carry the

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modification reagent into the void of agglomerated particles so that the modification reagent can contact with the particle surface and react with hydroxyl groups on the surface uniformly. A more uniform modification on the particle surface is achieved [13–16]. Particle modification in supercritical CO<sub>2</sub> does not lead to “caking” of the particles [13], and is especially suitable for nano-particles. The CO<sub>2</sub> solvent can be separated quickly and outright from the particles by changing the temperature and pressure. There is little or no solvent waste.

In this paper, the surface of nano-SiO<sub>2</sub> particles is modified with the titanate coupling reagent NDZ-201 in supercritical CO<sub>2</sub> as the solvent. The surface characteristics of the unmodified particles and the modified particles are evaluated. The modification state and structure of the modified particle surface are analyzed by IR absorption spectroscopy and thermogravimetric analysis. The quantity of the titanate coupling reagent chemically reacted on the particle surface is estimated from thermogravimetric analysis. The influence of the apparent concentration of the titanate coupling reagent on the modification result is also investigated.

## 2. Experimental

### 2.1. Materials

The titanate coupling reagent NDZ-201, (CH<sub>3</sub>)<sub>2</sub>CHOTi(OP(O)(OH)OP(O)(OC<sub>8</sub>H<sub>17</sub>)<sub>2</sub>)<sub>3</sub> [isopropyl-3-(pyrophosphoric ester-2-octo ester)—titanate] (for short, CA7) used is of technical grade (First Nanjing Shuguang Chemical Plant, Nanjing, China) with a boiling point of 77 °C and decomposition temperature of 210 °C. Xylene and Isopropanol used are analytical reagents (AR) (Beijing Chemical Plant, Beijing, China). The purity of the CO<sub>2</sub> (Beijing Huayuan Gas Corporation, Beijing, China) used is 99.95%. SiO<sub>2</sub> particles used are aerosol 150 (A150) with a specific surface area of 150 m<sup>2</sup>/g, and an average particle diameter about 30 nm, which are of non-porous structure, as shown in Fig. 1.

### 2.2. Apparatus

The experimental apparatus is schematically shown in Fig. 2. CO<sub>2</sub> from a cylinder is cooled in a cooler at –10 °C, and then fed into a tank of 1.5 l through a high pressure pump. The temperature of the CO<sub>2</sub> in the tank can be controlled from room temperature to 300 ± 1 °C, and the pressure can be controlled from 0 to 40 ± 0.1 MPa. The phase of the CO<sub>2</sub> in the tank can be adjusted by changing the thermodynamic state parameters. To ensure that contact between the particles and the molecules of the modification reagent occur in the supercritical fluid and to avoid direct contact between the particles and any liquid droplet of the modification reagent possibly suspended in the supercritical fluid, an annular structure made with a 300 mesh (hole size about 50 μm) sieve is placed high up in the tank, far from the bottom. The annular structure has an inner diameter of 60 mm, an external diameter of 80 mm,

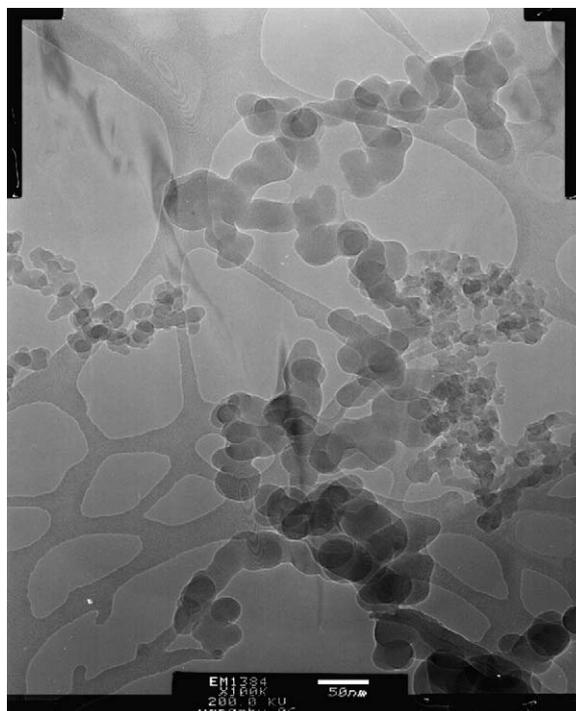


Fig. 1. TEM image of SiO<sub>2</sub>.

and a height of 80 mm, as shown in Fig. 2. The SiO<sub>2</sub> particles are very cohesive, and they are usually in loose agglomeration or form a stable structure. There are no or very little leaks of particles from the annular structure in experiments.

### 2.3. Sample preparation and analysis

SiO<sub>2</sub> particles (2.5 g) was loaded loosely in the annular structure 5, and a fixed quantity of the modification reagent CA7 was put into the bottom of the tank, see also Fig. 2. This was followed by the sealing of the tank, feeding in CO<sub>2</sub>, and increasing the temperature and pressure to the scheduled

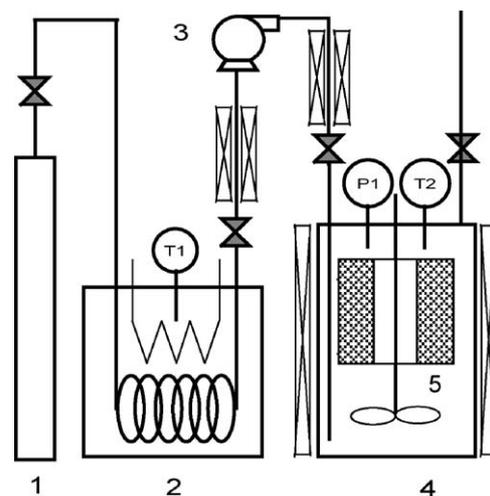


Fig. 2. Schematic diagram of the experimental apparatus (1) CO<sub>2</sub> cylinder; (2) cooler; (3) high pressure pump; (4) extracting tank; (5) reactor.

values (60 °C, 20.0 MPa) under agitation, where the experimental temperature of 60 °C and pressure of 20.0 MPa corresponds to the typical state of supercritical CO<sub>2</sub> solvent. After operating for 1 h, the agitation was stopped. Then, CO<sub>2</sub> was released. After CO<sub>2</sub> release, the tank was opened and the SiO<sub>2</sub> particles were taken out from the annular structure 5. The time of reaching phase equilibrium in agitation state is usually shorter than 1 h from the literatures [17,18]. It is assumed that 1 h in agitation state is sufficient for the phase equilibrium and reaction.

To examine the modification state of the surface of the SiO<sub>2</sub> particles and to remove modification reagent CA7 physisorbed on the surface of SiO<sub>2</sub> particles, the modified particles were extracted by isopropanol several times with each extraction taking 24 h, and then dried at 120 °C for 24 h. Except in the reaction process, the physisorption also happens in the decompression step, a condensation of CA7 is expected while expanding the CO<sub>2</sub>, and some of CA7 molecules precipitate on the surface of SiO<sub>2</sub> particles. The condensation of CA7 does not affect the quantity of CA7 reacted with the particle surfaces, as these CA7 molecules will be removed by the extraction. A Fourier transform IR spectrometer (NICOLET 5DX, USA) was used for IR absorption spectroscopy. Thermogravimetric analysis (TGA2050, TA Instruments, USA) was used to determine the quantity of CA7 chemically reacted on the particle surface. The samples were heated from room temperature to 600 °C in nitrogen with a heating rate of 20 °C/min.

### 3. Results and discussion

#### 3.1. Hydrophobicity tests

The hydrophobic index criterion in reference [16] is used to evaluate the hydrophobic characteristics of the samples. The results are shown in Table 1. The hydrophobic index from 1 to 6 is the evaluation of the degree from hydrophilicity to hydrophobicity, index 1 corresponds to complete hydrophilicity and index 6 corresponds to complete hydrophobicity.

From Table 1, it is seen that the unmodified SiO<sub>2</sub> particles are strongly hydrophilic, while the modified SiO<sub>2</sub> particles are all strongly hydrophobic. This shows that CA7 is connected tightly onto the particle surface. Modification reagent CA7 physisorbed on the surface of SiO<sub>2</sub> particles desorbs after extraction by isopropanol for several times, while CA7

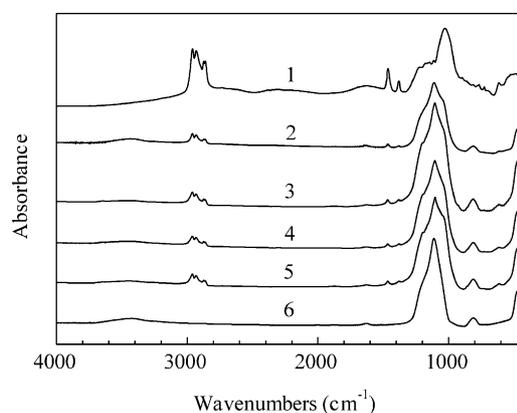


Fig. 3. IR absorption spectra of the samples. Sample no. referred to Table 1.

chemically bonded to the hydroxyl groups on the surface of particles remains on the surface of particles [16], and cannot be extracted by isopropanol, thus the particles have strong hydrophobicity.

#### 3.2. IR analysis

The IR spectra of CA7, unmodified and modified SiO<sub>2</sub> samples are shown in Fig. 3. The sample numbers are referred to Table 1. The spectra of the modified samples show characteristic absorption at 2961, 2933, 2874 and 2862 cm<sup>-1</sup>, which are the absorption peaks of the CH<sub>3</sub>- and CH<sub>2</sub>-groups of the coupling reagent CA7. This indicates that there are CA7 on the particle surface. The absorption peaks of the CH<sub>3</sub>- and CH<sub>2</sub>-groups of extracted modified samples are a little weaker than those of the non-extracted modified samples. It can be inferred that there exist not only physical adsorption between CA7 and the particle surface, but also chemical reaction. On the one hand, CA7 physisorbed is extracted out from the surface of the SiO<sub>2</sub> particles after extraction; on the other hand, CA7 chemically reacted is still bonded to the surface of the SiO<sub>2</sub> particles, thus the hydrophobic characteristics of the surface are changed.

#### 3.3. Thermogravimetric analysis

The organic modification reagent in a nitrogen environment thermally decomposes at higher temperatures. The TG curve of CA7 is shown in Fig. 4a. In the weight loss with temperature curve, there is an inflexion point temperature at which the sample weight sharply decreases. The inflexion

Table 1  
Sample numbers and experimental results (the quantity of CA7 added is 5.4 g)

Number	1	2	3	4	5	6
Sample	CA7	SiO <sub>2</sub> -CA7 (non-extracted)	SiO <sub>2</sub> -CA7 (extracted for 24 h)	SiO <sub>2</sub> -CA7 (extracted for 24 h + 24 h)	SiO <sub>2</sub> -CA7 (extracted for 24 h + 24 h + 24 h)	SiO <sub>2</sub>
Hydrophobic index [16]	–	6	6	6	6	1
Inflexion point temperature (°C)	210	210	270	270	270	–
Remaining weight at 600 °C (%)	20.00	74.38	74.86	77.11	77.20	98.76

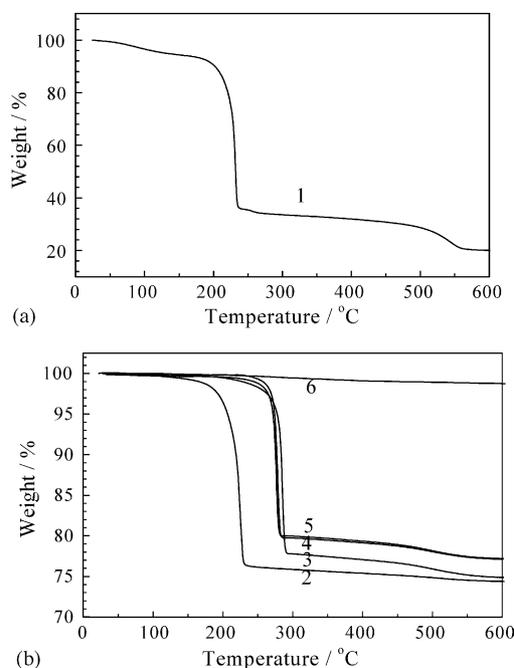


Fig. 4. Thermogravimetric curves of the samples. Sample no. referred to Table 1.

temperature is 210 °C, and corresponds to the decomposition temperature of CA7. It is deduced that CA7 begins to decompose at this temperature. Thereafter, the weight of CA7 does not decrease and the remaining weight is 20% at 600 °C.

For determining the quantity of CA7 chemically reacted with the surface of the SiO<sub>2</sub> particles, thermogravimetric analyses of unmodified and modified SiO<sub>2</sub> samples were performed. The results are shown in Fig. 4b and Table 1.

In Fig. 4b, the weight of the unmodified SiO<sub>2</sub> (sample 6) decreases slowly as the temperature increases. The remaining weight is 99.89% at 150 °C and 98.76% at 600 °C, respectively. In order to estimate the quantity of hydroxyl groups on the particle surface, it is assumed that water absorbed on the particle surface desorbs completely at 150 °C, and the weight loss above 150 °C is due to the dehydration of the hydroxyl groups on the surface. Thus, the concentration of hydroxyl groups on the surface of SiO<sub>2</sub> particles is estimated to be 1.26 mmol/g, i.e.  $8.4 \times 10^{-6}$  mol/m<sup>2</sup>. The actual concentration of the hydroxyl groups is possibly higher than that estimated from TGA, since the conditions under which the hydroxyl groups on oxide surfaces are removed completely are very severe, such as under vacuum at 800 °C [4].

There is an inflexion point temperature on the TG curves of the modified SiO<sub>2</sub> particles. When the temperature is lower than the inflexion point temperature, the weight of the modified SiO<sub>2</sub> decreases slowly, similar to the behavior of unmodified SiO<sub>2</sub>. Near the inflexion point temperature, the weight of the modified SiO<sub>2</sub> decreases rapidly. When the temperature is higher than the inflexion point temperature, the weight of the modified SiO<sub>2</sub> samples decreases slowly again, and becomes constant at about 600 °C. The inflexion point

temperature of the non-extracted modified SiO<sub>2</sub> (sample 2) is 210 °C from the TG curve in Fig. 4b, corresponding to the decomposition temperature of CA7 in Fig. 4a. It is considered that physisorbed CA7 begins to decompose at the inflexion point temperature. The inflexion point temperatures of the extracted modified SiO<sub>2</sub> (sample 3, 4 and 5) are all 270 °C from the TG curves in Fig. 4b, which is obviously higher than that of the non-extracted sample. It is concluded that CA7 chemically bonds with the surface of the particles. Due to the chemical bond formed, the decomposition temperature of CA7 bonded on the surface of the particles increases, thus the decomposition temperature of extracted modified SiO<sub>2</sub> is higher than that of pure CA7.

The comparison of the remaining weight of samples 2, 3, 4 and 5 at 600 °C shows that CA7 physisorbed on the surface of the particles can be removed completely by three extractions by isopropanol, in which every extraction is performed for 24 h. The quantity of CA7 physisorbed on the particle surface can be determined to be 2.82% through comparing the remaining weight at 600 °C between sample 2 and sample 5.

The quantity of CA7 chemically reacted on the particle surface can be estimated from the weights of samples at 600 °C by the method mentioned in reference [16]:

$$W_{CA7,r} = (W_0 - W_3)/(W_3 - W_1) \times 100\% \quad (1)$$

where  $W_{CA7,r}$  is the quantity of CA7 chemically reacted on the particle surface, %;  $W_0$  is the weight of unmodified particles at 600 °C, %;  $W_1$  is the weight of CA7 at 600 °C, %; and  $W_3$  is the weight of modified particles (extracted) at 600 °C, %.

For this experiment,  $W_0$ ,  $W_1$  and  $W_3$  are, respectively 98.76% (sample 6), 20.00% (sample 1) and 77.20% (sample 5) listed in Table 1. From Eq. (1),  $W_{CA7,r}$  is calculated to be 37.69%. As the specific surface area of SiO<sub>2</sub> particles is 150 m<sup>2</sup>/g and the mole weight of CA7 is 1.31 kg/mol, the amount of CA7 chemically reacted on the particle surface is  $19.18 \times 10^{-7}$  mol/m<sup>2</sup>.

### 3.4. Influence of apparent concentration of CA7

The influence of the concentration of CA7 on the quantity of CA7 chemically reacted on the surface was investigated. CA7 reacting on the particle surface and reaching phase equilibrium in supercritical CO<sub>2</sub> happen simultaneously. In the reaction process, the concentration varies with time. The phase equilibrium process results in an increasing of CA7 concentration in supercritical CO<sub>2</sub> with time. The reaction process results in a decreasing of CA7 concentration in supercritical CO<sub>2</sub> with time due to the reaction of CA7 on the particle surface. Therefore, a parameter of apparent concentration of CA7 is adopted to characterize the concentration condition of CA7, in which the apparent concentration of CA7 is the weight percent of CA7 added in the supercritical solvent. Due to the limitation of the solubility of CA7 in supercritical CO<sub>2</sub>, the apparent concentration is not the actual concentration in supercritical CO<sub>2</sub>. When the apparent

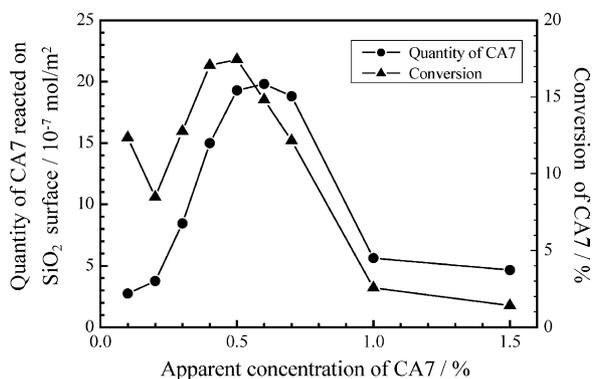


Fig. 5. The influence of apparent concentration of CA7 on the modification.

concentration is lower than the solubility, the apparent concentration equals to the actual concentration in case of phase equilibrium in the vessel. When the apparent concentration is higher than the solubility, the apparent concentration is higher than the actual concentration. The maximum load of CA7 in supercritical CO<sub>2</sub> under the temperature of 60 °C and pressure of 20 MPa is about 1.0% in our roughly measurement, so the apparent concentration of CA7 in the experiments is set from 0.1 to 1.5% for exploring its influence on modification.

The result is shown in Fig. 5, where the quantity of CA7 chemically reacted on the surface is calculated from the TGA results of the sample thrice extracted by isopropanol, as calculated by the method mentioned in Section 3.3. The reproducibility of the experimental results is verified in parallel experiments. The influence of the apparent concentration of CA7 on the reaction conversion of CA7 is also shown in Fig. 5, in which the conversion is the fraction of reacted quantity of CA7 to the added quantity of CA7.

It is seen from Fig. 5 that the modification results are remarkably influenced by the apparent concentration of CA7 in the modification process. The quantity of CA7 chemically reacted on the surface of the SiO<sub>2</sub> particles increases with increasing the apparent concentration of CA7, then reaches a maximum value and decreases to a steady value. When the apparent concentration of CA7 is low, CA7 can dissolve completely in the supercritical CO<sub>2</sub>, then diffuse onto the particle surface and react with the hydroxyl groups on the particle surface, and the quantity of CA7 chemically reacted on the surface of SiO<sub>2</sub> particles increases with increasing the apparent concentration of CA7. When the apparent concentration of CA7 is 0.6%, corresponding to a quantity of CA7 added of 6.6 g, the quantity of CA7 chemically reacted on the surface of SiO<sub>2</sub> reaches the maximum value of  $19.81 \times 10^{-7}$  mol/m<sup>2</sup>, i.e. 1.19 molecule/nm<sup>2</sup>. From Fig. 5 the actual solubility is probably near by 0.6%. Therefore, when the apparent concentration is higher than 0.6%, the liquid phase of CA7 probably appears in the vessel even though the phase in equilibrium. In this case, the CA7 nuclei may induce the deposition of the dissolved CA7 in supercritical CO<sub>2</sub>, resulting in the actual concentration of CA7 in supercritical CO<sub>2</sub> decrease. The CA7 nuclei increase with the apparent concentration increasing in

agitation state. Thus, the quantity of CA7 chemically reacted on the surface of SiO<sub>2</sub> particles decreases obviously when the apparent concentration exceeds a certain value. It shows that too high apparent concentration of CA7 is not favorable for the modification. The reasons for the maximum value of the quantity of CA7 chemically reacted on the particle surface with changing the apparent concentration of CA7 will be further investigated in the future.

The reaction conversion of CA7 increases first as the apparent concentration of CA7 increases, reaches a maximum value of 17.55% when the apparent concentration of CA7 is 0.5%, then decreases rapidly. The varying tendency of the CA7 conversion versus apparent concentration is also consistent with the above analysis.

Assuming a uniform distribution of hydroxyl groups on the surface, and neglecting interactions between CA7 molecules, one molecule of CA7 reacts with two hydroxyl groups according to the reaction between CA7 and the particle surface in reference [16]. The maximum quantity of CA7 chemically reacted on the particle surface is half of the concentration of hydroxyl groups on the particle surface, i.e.  $4.20 \times 10^{-6}$  mol/m<sup>2</sup>, where the concentration of hydroxyl groups is calculated from the TGA result. The maximum quantity of CA7 chemically reacted on the particle surface is also calculated to be  $4.80 \times 10^{-6}$  mol/m<sup>2</sup> according to a monolayer model of coupling reagent chemisorbed on the particle surface [16].

The maximum quantity of CA7 reacted on the particle surface is  $19.81 \times 10^{-7}$  mol/m<sup>2</sup> in the experiments, which is only about 40% of the estimated value. The reason for the discrepancy may be that the monolayer model is an ideal model that does not consider reaction dynamics. Furthermore the monolayer model is not really suitable for the surface of nanoparticles, where the particle size is very small and the interactions between coupling reagent molecules and the steric effect of organic long-chains can become intense. Molecules of the coupling reagent cannot distribute uniformly on the nanoparticle surface. Therefore, the actual quantity of coupling reagent chemically reacted on the particle surface should be determined from experiments.

#### 4. Conclusion

Chemical modification of the surface of nano-SiO<sub>2</sub> particles was performed in supercritical CO<sub>2</sub>. The surface characteristics were remarkably changed after modification by a titanate coupling reagent. The particles were changed from hydrophilic to hydrophobic. There exists not only physical adsorption of the titanate coupling reagent on the particle surface, but also chemical reaction. The modification is remarkably influenced by the apparent concentration of the titanate coupling reagent, when the temperature is 60 °C and the pressure is 20.0 MPa. When the apparent concentration of the titanate coupling reagent is 0.6%, the quantity of titanate coupling reagent reacted on the particle surface reaches a

maximum value of  $19.81 \times 10^{-7} \text{ mol/m}^2$ , i.e. 1.19 molecule titanate coupling reagent/nm<sup>2</sup>. This is about 40% of the value from a monolayer model.

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