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Organic modification of ultrafine particles using carbon dioxide as the solvent

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Abstract

An organic modification of the surface of titanium dioxide particles precoated with SiO_2 and Al_2O_3 films in a CO_2 medium is performed, where CO_2 of different phases is used as the solvent and a titanate coupling reagent $(CH_3)_2CHOTi(OP(O)(OH)OP(O)(OC_8H_{17})_2)_3$ is the modification reagent. The results are compared with the modification carried out in a conventional organic solvent. The interaction between the functional groups of the modification reagent and the hydroxyl groups on the surface of the particles is analyzed. Experimental results indicate that the surface of particles is modified efficiently when the CO_2 solvent is in a supercritical or liquid state. The particles are remarkably changed from hydrophilic to hydrophobic by the modification. A chemical bond of $Al-O-Ti$ is likely formed between the molecules of the organic modification reagent $(CH_3)_2CHOTi(OP(O)(OH)OP(O)(OC_8H_{17})_2)_3$ and the particle surface. The actual maximum quantity order of organic modification reagent reacted on the particle surface is about 7.08×10^{-7} mol/m^2 (1.73% by weight) from thermogravimetric analysis. The organic modification process using supercritical or liquid CO_2 as the solvent has the advantages of being simple, effective, and green.

1. Introduction

Ultrafine particles have many special characteristics and are easily agglomerated. Good dispersion is the key to their performance in applications making use of their unique characteristics. The surface of inorganic ultrafine particles needs to be modified with organics when they are used in paints, as fillers, etc., to enhance their dispersion in non-aqueous systems. The methods of surface modification of inorganic ultrafine particles with organic reagents can be basically divided into dry methods and wet methods. An example of dry methods is grinding the modification reagent and the ultrafine particles together, or adding the modification reagent during the crushing process, and it is very difficult to achieve a uniform modification of the particle surface. The wet methods are the processes where the modification is carried out in an organic solvent or an aqueous solution, and there exists problems of solvent recovery, on one hand, and long operations, high costs, severe pollution, and low efficiency, on the other hand.

Carbon dioxide is a green solvent [1]. Supercritical carbon dioxide has the characteristics of a high diffusion coefficient like a gas, high solvent power like a liquid, low viscosity, low surface tension, and rapid osmosis into a microporous material [2]. In an organic modification process, the carbon dioxide used as the solvent can carry the modification reagent into the void of agglomerated particles and achieve a more uniform modification of the particle surface. Particle modification in CO_2 does not lead to "caking" of the particles. The CO_2 solvent can be separated quickly and outright from the particles by changing its phase in the modification process. There is little or no solvent waste. Obvious environmental and economic advantages would result in using a solvent that separates spontaneously, and so completely, from the desired product that traditional filtration and grinding operations are obviated [3]. The interaction of CO_2 under supercritical fluid (SCF) conditions with a fumed silica has been studied by Tripp and Combes [4] with infrared (IR) spectroscopy. It is shown that

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the physisorption of CO_2 with the isolated SiOH groups is weak. Combes et al. [5] studied the chemical modification of SiO_2 wafer surface in supercritical CO_2 with in situ infrared spectroscopy. The utility of CO_2 as a solvent for the reaction of organosilanes with silica is demonstrated with hexamethyldisilazane (HMDS) and octadecyltrichlorosilane (OTS). For HMDS, the byproduct is weakly physisorbed on the hydroxyl groups of the surface and is easily removed by evacuation or purging. Moreover, the byproduct can be completely avoided by performing the reaction at relatively low CO_2 pressures. Physisorption of OTS from SCF CO_2 occurs via a weak interaction with the surface hydroxyl groups. The amount of OTS hydrolyzed in SCF CO_2 is much lower than in traditional nonaqueous solvents. Jia and McCarthy [6] studied the chemical modification of the buried interfaces between silicon wafers and either polystyrene or poly-(methyl methacrylate) (PMMA) with the reagent (tridecafluoro-1,1,2,2-tetrahydrooctyl) dimethylchlorosilane (FDCS) using liquid and supercritical carbon dioxide as the solvent and infusing agent. Above the critical point of CO_2, FDCS reacts with surface silanols at the SiO_2/polystyrene interface to form a monolayer. Due to strong hydrogen bonding between the PMMA and the silicon substrate, modification of the SiO_2/PMMA interface is achieved to only a limited extent.

Titanium dioxide particles are typical inorganic ultrafine particles. Their unique physical chemistry properties and excellent pigmentary characteristics have been widely applied in paints, plastics, chemical fibers, latex, printing ink, etc. The surface of the titanium dioxide particles must be treated to passivate its photocatalysis activity and improve its dispersion in organic media. Titanium dioxide particles usually need an inorganic coating and organic modification [7]. Rutile titanium dioxide has good weather durability after it is coated with a silicon and aluminum oxide film [8], but the particle surface is still hydrophilic and the particle dispersion in nonaqueous systems is still poor, which degrades its performance in paints or as a filler. Therefore, an organic modification of the particle surface is very important for improving the particle dispersion in nonaqueous solution [9].

In this paper, carbon dioxide is used as the solvent and the surface of TiO_2 particles precoated with SiO_2 and Al_2O_3 film is modified with a titanate coupling regent, CA7. The modification results are compared with that using a conventional organic solvent. The modified and unmodified particles are evaluated through hydrophobicity tests. The state and structure of the modified particle surface are analyzed from IR absorption spectra and thermogravimetric analysis.

2. Experimental

2.1. Materials

The titanate coupling reagent $(CH_3)_2CHOTi(OP(O)(O-H)OP(O)(OC_8H_{17})_2)_3$ [isopropyl -3-(pyrropho-spboric ester-

2-octo ester)-titanate; CA7 for short] 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 (ARs) (Beijing Chemical Plant, Beijing, China). Rutile TiO_2 particles used are of technical grade (Zhenjiang Titanium Dioxide Plant, Zhenjiang, China) with an average particle diameter of 300 nm. The purity of CO_2 (Beijing Huayuan Gas, Beijing, China) used is 99.95%.

2.2. Apparatus

The experimental apparatus is schematically shown in Fig. 1. CO_2 from a gas cylinder is cooled in a cooler at a setting temperature of −10 °C, then fed into a tank with the volume of 1.5 l through a high-pressure pump. The temperature of the CO_2 in the tank can be controlled from room temperature to 300 °C within 1 °C, and the pressure can be controlled from 0 to 40 MPa within 0.1 MPa. The phase of CO_2 in the tank can be adjusted by changing the state parameters.

2.3. Sample preparation and analysis

TiO_2 particles coated with SiO_2 and Al_2O_3 films are prepared according to the methods in the literature [8]. The preparation procedures are basically described as follows. First, a dispersant is added in a slurry of 20–30% (wt) TiO_2 particles with agitating for dispersion. Second, Na_2SiO_3 solution is fed by titration into the slurry with temperature controlled at 85–90 °C. The titrated quantity of Na_2SiO_3 solution is controlled at a mass ratio of SiO_2/TiO_2 at 2–3%. After subsequently aging for 2 h, the coating of the SiO_2 film is completed. Third, $Al_2(SO_4)_3$ solution and NaOH solution are titrated in the slurry of TiO_2 particles coated
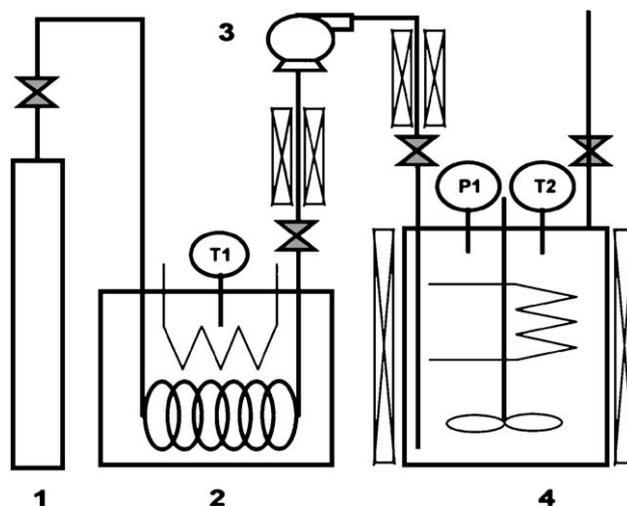

Fig. 1. Schematic diagram of the experimental apparatus. (1) CO_2 bomb; (2) cooler; (3) high-pressure pump; and (4) extracting tank.
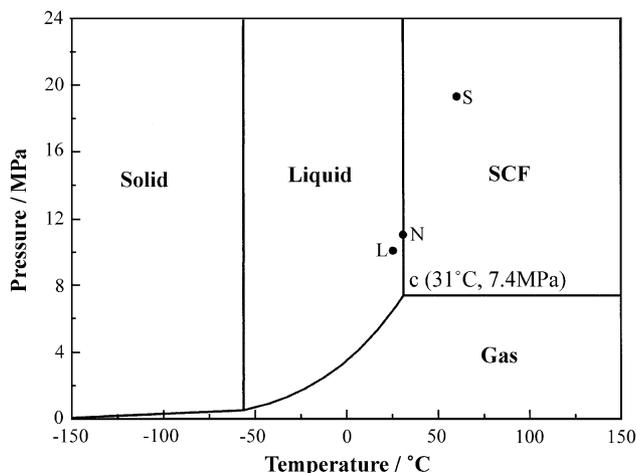
Fig. 2. States of the CO_2 solvents at experimental conditions in the phase diagram. S: 60 °C, 21.4 MPa; N: 31 °C, 11.0 MPa; L: 27 °C, 10.1 MPa.

with the SiO_2 film at the temperature of 75 °C, and a mass ratio of Al_2O_3/TiO_2 is controlled at 2–3%. After subsequently aging for 4 h, washing with deionized water, filtering, and drying at 120 °C, TiO_2 particles coated with continuous SiO_2 and Al_2O_3 films are obtained. The Brunauer–Emmet–Teller (BET) surface area of the TiO_2 particles coated with SiO_2 and Al_2O_3 film for organic modification is measured to be 18.64 m^2/g with a surface area analyzer (ASAP2010; Micromeritics Instrument, USA).

When CO_2 is used as the solvent, 50 g of TiO_2 particles precoated with the SiO_2 and Al_2O_3 films and the modification reagent CA7 are put together into the tank shown in Fig. 1, where the added quantity of coupling reagent CA7 is 4% of the weight of TiO_2 particles. This is followed by sealing the tank tightly, feeding in CO_2, raising the temperature, and pressurizing to the scheduled values. After keeping for 1 h, the agitation is stopped for the particles suspended in the CO_2 solvent settling down. Thereafter, CO_2 can be released without particle entrainment. After CO_2 release, the tank can be opened and the fine particles are taken out. The CO_2 solvents at supercritical, near-critical, and liquid state, which correspond to points S (60 °C, 21.4 MPa), N (31 °C, 11.0 MPa), and L (27 °C, 10.1 MPa), respectively, in the phase diagram of CO_2 shown as Fig. 2, are selected for organic modification.

When isopropanol is used as the solvent, CA7 (0.4 ml) is dissolved in isopropanol (20 ml) in a beaker with a constant temperature initially. This is fed to 10 g of TiO_2 particles precoated with SiO_2 and Al_2O_3 films, with stirring for 1 h,

then filtering and drying of the samples. The modification process is operated at the temperature of 60 °C and atmospheric pressure of 0.1 MPa.

The modified samples are all extracted by isopropanol for 8–9 h to remove physisorbed reagent CA7, then dried at 120 °C for 24 h. The sample numbers and their conditions are listed in Table 1.

A mixture of xylene and water, which do not mix each other, is employed to test the hydrophobic characteristics of the samples. Xylene and water of the same volume are added into a test tube to form a stable phase interface, as shown in Fig. 3. Unmodified and modified particles are, respectively, dispersed in the xylene–water system and stirred. After the mixture has stabilized, the hydrophobic characteristics can be qualitatively evaluated by inspecting the state of the floating/sinking of samples at the interface. The criterion of hydrophobic index is as follows: (1) hydrophilic: samples pass the phase interface and sink into water quickly and completely; (2) hydrophilic: samples pass the phase interface and sink into water not so quickly, but completely; (3) hydrophilic: samples float at first on the phase interface and then sink into water slowly and completely; (4) partially hydrophilic: samples float at first on the phase interface and then some particles sink into water slowly and some particles float on the phase interface; after mixing, they sink into water completely; (5) partially hydrophobic: samples float on the phase interface. After mixing for a long time, some particles still float on the phase interface; and (6) completely hydrophobic: samples float on the phase interface even with vigorous mixing for a long time. The method [9] of floating/sinking of particles in water is also used to evaluate the hydrophobic characteristics of the samples. The corresponding criteria of hydrophobic index are: (1) hydrophilic: samples sink into water quickly and completely; (2) hydrophilic: samples sink into water not so quickly, but completely; (3) hydrophilic: samples float at first and then sink into water slowly and completely; (4) partially hydrophilic: samples float at first and then sink into water slowly. Part of the powder floats on surface of water and, after agitation, sinks into water completely; (5) partially hydrophobic: samples float on the surface of water. After a long time agitation, part of the powder still floats on the surface of water; and (6) completely hydrophobic: samples float on the surface of water even with strong agitation for a long time.

A Fourier transform IR spectrometer (Nicolet 5DX, USA) is used for IR absorption spectra analysis. A thermogravimetric analysis instrument (TGA2050; TA Instru-

Table 1
Sample numbers and experimental conditions

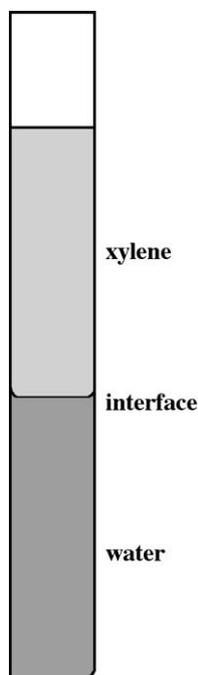| Sample number	0	1a	1b	2a	2b	3a	3b	4a	4b	5b
Modification	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Solvents	–	Supercritical CO_2		Near-critical CO_2		Liquid CO_2		Isopropanol		Supercritical CO_2
Extraction	–	No	Yes	No	Yes	No	Yes	No	Yes	Yes

Fig. 3. Testing of the hydrophobic nature of fine particles.

ments, USA) is used to determine the quantity of chemically reacted CA7 on the particle surface. The samples are heated from room temperature to 600 °C in nitrogen. The heating rate is 20 °C/min.

3. Results and discussion

3.1. Hydrophobicity tests

The results of hydrophobic tests are shown in Table 2. From Table 2, it is seen that unmodified TiO_2 particles (sample 0) are strongly hydrophilic, while modified TiO_2 particles are all strongly hydrophobic. This shows that CA7 is connected tightly onto the particle surface. The coupling reagent on the particle surface of modified samples cannot be extracted, however, although it is extracted by isopropanol for a long time. It can be inferred that a chemical bond is

likely formed between the coupling reagent CA7 and the coating layers of SiO_2 and Al_2O_3 on the surface of TiO_2. From Table 2, it is seen that the modified samples are hydrophobic, regardless of whether the modification solvent is supercritical CO_2 (sample 1), near-critical CO_2 (sample 2), liquid CO_2 (sample 3), or isopropanol (sample 4).

3.2. IR spectra analysis

The IR spectra of CA7 and unmodified and modified TiO_2 samples are shown in Fig. 4. The spectra of the modified samples show characteristic peaks of absorption at 2956, 2927, and 2860 cm^{-1}, which are the absorption
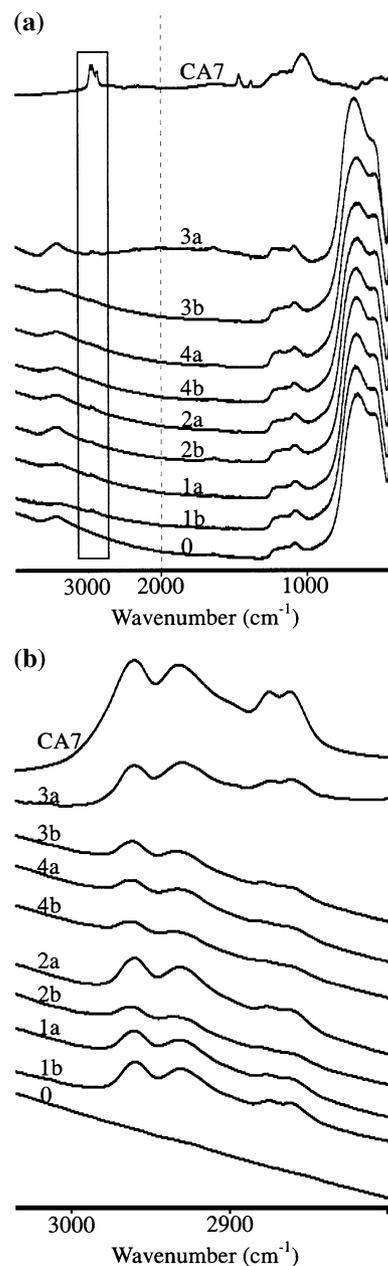

Fig. 4. IR absorption spectra of samples. (a) IR absorption spectra; and (b) local amplification of absorption peaks of CH_3 and CH_2 groups.

Table 2
Hydrophobic characteristics of unmodified and modified TiO_2 under different conditions

Number	Solvent	Temperature [°C]	Pressure [MPa]	Index	
				In water–xylene	In water
0	–	–	–	1	1
1b	Supercritical CO_2	60	21.4	6	6
2b	Near-critical CO_2	31	11.0	6	6
3b	Liquid CO_2	27	10.1	6	6
4b	Isopropanol	60	0.1	6	6

peaks of CH$_3$ and CH$_2$ groups of the coupling reagent CA7. This indicates that there are CA7 on the particle surface. The absorption peaks of CH$_3$ and CH$_2$ groups of extracted modified samples are a little weaker than those of non-extracted modified samples, since nonbonded and physically adsorbed CA7 are extracted after extraction by isopropanol. It can be concluded that there exist not only physical adsorption between CA7 and the particle surface, but also chemical bonding.

3.3. Thermogravimetric analysis

The organic modification reagent could oxidize or thermally decompose at higher temperatures. The TG curve of CA7 is shown in Fig. 5a. In the weight loss with temperature, there is an inflexion point temperature at which the sample weight sharply decreases. It is deduced that CA7 begins to decompose at this point. The inflexion temperature is 216 °C, and the remaining weight of CA7 is 20% at 600 °C, as shown in Table 3.

If there is modification reagent on the surface of TiO$_2$ particles, the weight of the samples will decrease with increasing temperature. The TGA results of unmodified and modified TiO$_2$ samples are shown in Fig. 5 and Table 3.

In Fig. 5b, the weight of unmodified TiO$_2$ (sample 0) decreased slowly with increasing temperature. The loss in weight is 1.96% at 600 °C, which is due to the dehydration of hydrated SiO$_2$ and hydrated Al$_2$O$_3$ of the coating layers on the surface of the TiO$_2$ particles, and adsorbed water on the surface. There is an inflexion point at a certain temperature on the TG curves of all modified TiO$_2$ particles. When the temperature is lower than the inflexion point temperature, the weight loss of modified TiO$_2$ is remarkably lower than that of unmodified TiO$_2$. When the temperature is higher than the inflexion point temperature, the weight loss of modified TiO$_2$ samples is larger than that of unmodified TiO$_2$, and the weight decreases considerably with increasing temperature. It is inferred that the modification reagent CA7 begins to decompose at the inflexion point temperature. Due to protection of the surface by the modification reagent at temperatures lower than the inflexion point temperature, the decomposition rate of hydrated SiO$_2$ and hydrated Al$_2$O$_3$ of the coating layers decreases, and the weight loss is lower than from TiO$_2$ particles without a protection of modification reagent. The modification reagent decomposes at temperatures higher than the inflexion point temperature and, at the same time, hydrated SiO$_2$ and hydrated Al$_2$O$_3$ decompose to a certain extent when they are not protected by the modification reagent, and the weight decreases more at temperatures higher than the inflexion point temperature. After that, the coating layers and the modification reagent decompose quickly with increasing temperature.

The inflexion point temperature of modified sample 1a (nonextracted) is 216 °C from the TG curve in Fig. 5b. This is the same as the inflexion point temperature of CA7. It can

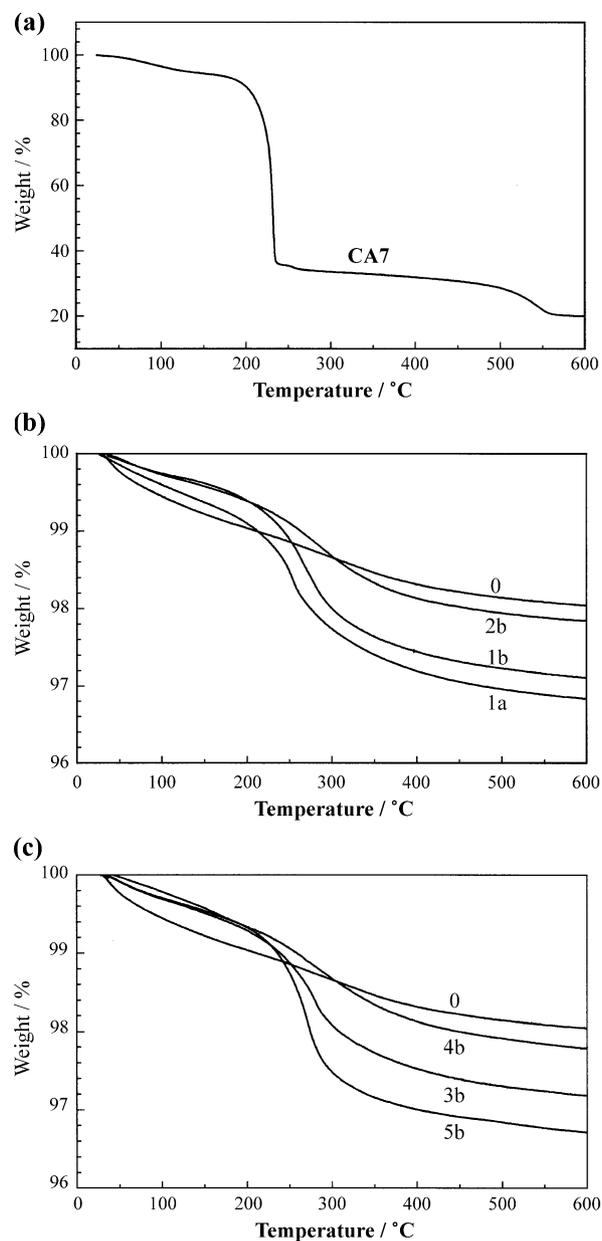Fig. 5. Thermogravimetric curves of samples. (a) CA7; (b) unmodified and modified TiO$_2$ samples; and (c) unmodified and modified TiO$_2$ samples.

be considered that CA7 physically adsorbed on the surface begins to decompose near the temperature of 216 °C. The inflexion point temperature of modified sample 1b (extracted) is 230 °C, which is higher than that of nonextracted sample. This is due to chemical bond formation between CA7 and the particle surface, so that the decomposition temperature is higher than that of pure CA7. The physically adsorbed amount of CA7 is determined to be 0.27% through comparing the difference in weight loss of the extracted sample and nonextracted sample in the TG curve at 600 °C from Fig. 5b.

The quantity of CA7 that reacted chemically with the particle surface can be estimated from the TG curve of the

Table 3
TGA results of different samples

Samples	CA7	0	1a	1b	2b	3b	4b	5b
Inflexion point temperature [°C]	216	–	216	230	228	236	230	232
Remaining weight at 600 °C [%]	20.00	98.04	96.84	97.11	97.85	97.18	97.79	96.71
CA7 reacted on particle surface [%]	–	–	–	1.21	0.24	1.11	0.32	1.73
CA7 reacted on particle surface [10^{-7} mol/m^2]	–	–	–	4.96	0.98	4.55	1.31	7.08

extracted samples. From Fig. 5b, for the unmodified TiO_2 sample at 600 °C:

$$A/M = 98.04\% \tag{1}$$

where A is the weight of nondecomposed substance, and M is the weight of unmodified TiO_2 sample.

For sample 1b (extracted) at 600 °C:

$$(A + X)/(M + Y) = 97.11\% \tag{2}$$

where X is the weight of nondecomposed substance bonded between CA7 and surface of TiO_2, and Y is the weight of CA7 that has reacted chemically.

From the TG curve of CA7:

$$X/Y = 20.00\% \tag{3}$$

From Eqs. (1)–(3), the result is:

$$Y/M = 1.21\% \tag{4}$$

that is, the quantity of CA7 that reacted with the particle surface is 1.21% by weight. As the specific surface area of particles is 18.64 m^2/g and the mole weight of CA7 is 1.31 kg/mol, the mole number of CA7 reacted on the particle surface is 4.96×10^{-7} mol/m^2. The quantity of CA7 that chemically reacted with the particle surface of other modified samples can be calculated by the same method. The results are shown in Table 3.

From Table 3, the quantities of CA7 that reacted chemically with the particle surface are quite different with the various solvents. Those would mainly depend on the essential properties of solvents, as shown in Table 4. In our rough

measurement, the solubility order is about 1.0% at a pressure of 20.0 MPa and temperature of 60 °C (supercritical), and about 0.5% at a pressure of 11.0 MPa and temperature of 30 °C (near-critical). The solubility of CA7 in liquid CO_2 solvent is generally higher than that in near-critical CO_2 solvent. These show that the initial concentrations of CA7 in the CO_2 solvents (0.17–0.18%) are all lower than their solubility in the experiments. Therefore, the solubility difference in CO_2 solvents should be not the main factor affecting the modification results. In comparing liquid (or supercritical) CO_2 and isopropanol, the densities are roughly same, but the viscosity of liquid (or supercritical) CO_2 is much lower than that of isopropanol, and the diffusivity of liquid (or supercritical) CO_2 is much higher than that of isopropanol. These differences result in the quantity of CA7 that reacted with the particle surface in liquid (or supercritical) CO_2 being remarkably higher than that in isopropanol, even though the initial concentration of CA7 in liquid (or supercritical) CO_2 (0.18%) is much lower than that in isopropanol (2.66%). Near-critical CO_2 has the same order of density, viscosity, and diffusivity as liquid (or supercritical) CO_2, but the quantity of CA7 that reacted with the particle surface is obviously less than that in liquid (or supercritical) CO_2. The reason needs to be further studied. From the modification results, it can be seen that both the supercritical and liquid CO_2 are suitable for the organic modification of particles.

Furthermore, CO_2 as a solvent has advantages over common organic liquid solvents in the organic modification process of the particles. First, CO_2 and fine particles can be separated easily and completely through pressure release while the organic liquid solvent and fine particles are difficult to separate. Second, there is no "caking" of particles in CO_2

Table 4
Thermophysical properties of various solvents

Solvent Parameters	Supercritical CO_2 60 °C, 21.4 MPa	Near-critical CO_2 31 °C, 11.0 MPa	Liquid CO_2 27 °C, 10.1 MPa	Isopropanol 60 °C, 0.1 MPa
Density [kg/m^3]	744.4 [11]	783.2 [11]	803.2 [11]	751.6 [12]
Viscosity [10^{-5} Pa s]	6.3 [11]	6.8 [11]	7.1 [11]	78.9 [12]
Mass diffusivity [10^{-8} m^2/s] [2]	∼ 1	∼ 7	–	0.02–0.2
Initial concentration of CA7 [%]	0.18	0.17	0.17	2.66

solvent; on the other hand, there is much "caking" of particles in organic liquid solvent and reshatter is required. Third, CO_2 as a green and benign solvent can be recycled.

3.4. Analysis of the modification mechanism

Previous research [4] indicates that there is only physical adsorption and no chemical reaction between CO_2 and the active groups on the surface of inorganic particles during the surface modification process when the solvent is CO_2. Thus, any chemical reaction between the modification reagent and the active groups on the surface of the inorganic particles is not effected by the presence of CO_2.

The structural formula of the titanate coupling reagent CA7 is:

$$CH_3CHO-Ti[OP-OP(OR)_2]_3 \quad R: C_8H_{17}$$
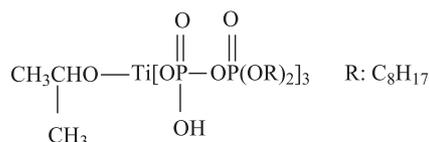
There are one isopropoxy and three organic long chains. The isopropoxy group can react with free protons on the particle surface to form a chemical bond and release isopropanol, where the free protons are from structural water, physically adsorbed water, and chemically adsorbed water on the particle surface. This leads to the modification of the particle surface. Hydroxyl groups (OH^-) on the surface of TiO_2 particles coated with SiO_2 and Al_2O_3 films react with CA7 as follows [10]:

$$(5)$$
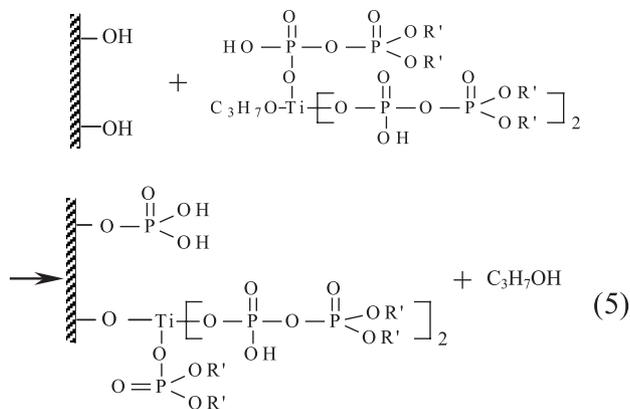
For estimating the theoretical maximum quantity of CA7 that can react with the particle surface, a monolayer model is assumed. This includes the following assumptions: First, the interactions between chemisorbed molecules in the monolayer are neglected. Second, the hydroxyl groups distribute uniformly on the surface. Third, the chemisorbed molecule is spherical with a definite diameter. Fourth, one molecule modification reagent requires x hydroxyl groups for reac-

tion. Therefore, the maximum quantity of modification reagent reacted on the particle surface is:

$$n = \frac{1}{xN_A d^2} \quad (6)$$

where n is the maximum quantity of modification reagent reacted on the particle surface [mol/m^2]; N_A is the Avogadro constant [6.022×10^{23} mol^{-1}]; x is the hydroxyl group number reacted with one molecule modification reagent; and d is the diameter of chemisorbed molecule [m]. When the chemisorbed molecules have different diameters, d is taken to the maximum of those.

From Eq. (5), it is seen that two hydroxyl groups react with one molecule CA7, and two kinds of molecules are chemisorbed on the particle surface. One molecule diameter is twice the bond length of P—O, and the other is twice the bond length of Ti—O, neglecting steric effects of the organic long chains. The bond lengths of P—O and Ti—O are 1.76×10^{-10} and 2.08×10^{-10} m, respectively, so d is taken as 4.16×10^{-10} m. From Eq. (6), the maximum quantity of CA7 on the particle surface is calculated to be 4.80×10^{-6} mol/m^2 (i.e., 11.72% by weight).

For roughly determining the order of actual maximum quantity of coupling reagent CA7 reacted on the particle surface, the following experiment is carried out. The added quantity of coupling reagent CA7 is 20% of the TiO_2 particles by weight. The temperature of CO_2 solvent is 60 °C, and the pressure is 21.4 MPa, which is a typical state of the supercritical CO_2 solvent. The initial concentration of CA7 in the CO_2 solvent is 0.90%, which is close to the solubility of 1.0% at this condition. The reaction time is 3 h, which is supposed to be long enough for the reaction. The TGA result of the extracted modified particles (sample 5b) is shown in Fig. 5c and Table 3. The actual maximum quantity of coupling reagent CA7 reacted on the particle surface is estimated to be 7.08×10^{-7} mol/m^2 (1.73% by weight) by the same method given in Section 3.3.

The actual maximum quantity order of CA7 reacted on the particle surface is only 14.75% of the calculated value. The reasons are mainly that the assumption of the monolayer model neglects any interaction between the chemisorbed molecules, and assumes that all hydroxyl groups distribute uniformly on the particle surface. The steric effect of organic long chains is also neglected in the calculation. Actually, it is improbable that the hydroxyl groups distribute on the particle surface so uniformly that the coupling of the reagent molecules leads to uniform bonding on the surface of submicron particles, and interactions between chemisorbed molecules and the steric effect of organic long chains cannot be neglected. Furthermore, there are microholes on the particle surface where a molecule of CA7 cannot reach the internal surface and react on it. Therefore, the actual quantity of coupling reagent on the modified particle surface should be determined from experiments.

4. Conclusion

Good organic modification of the surface of TiO_2 particles precoated with SiO_2 and Al_2O_3 films is achieved using a CO_2 solvent of different phases. A chemical reaction occurs between the modification reagent CA7 and the active groups on the particle surface. The actual maximum quantity order of the modification reagent CA7 that reacts on the surface of TiO_2 particles coated with SiO_2 and Al_2O_3 films is about 7.08×10^{-7} mol/m^2 (1.73% by weight). The analysis of the mechanism of surface modification indicates that effective modification can be achieved by chemical reaction between the modification reagent and the active groups on the particle surface in a CO_2 solvent. Supercritical and liquid CO_2 are green solvents in the organic modification of inorganic particles, a recycle utilization can be achieved by using its phase transition, and there is good potential for its industrial use.

Acknowledgements

References

[1] M. Poliakoff, M.W. George, S.M. Howdle, V.N. Bagratashvili, B.X. Han, H.K. Yan, Chinese Journal of Chemistry 17 (3) (1999) 212–222.
[2] P. Subra, P. Jestin, Powder Technology 103 (1) (1999) 2–9.
[3] J.R. Combes, H.K. Mahabadi, C.P. Tripp, U.S. 5,725,987 (1998).
[4] C.P. Tripp, J.R. Combes, Langmuir 14 (26) (1998) 7350–7352.
[5] J.R. Combes, L.D. White, C.P. Tripp, Langmuir 15 (22) (1999) 7870–7875.
[6] X.Q. Jia, T.J. McCarthy, Langmuir 18 (3) (2002) 683–687.
[7] Y.L. Lin, T.J. Wang, Y. Jin, Powder Technology 123 (2–3) (2002) 194–198.
[8] A.L. Cui, T.J. Wang, Y. Jin, Chemical Journal of Chinese Universities 19 (11) (1998) 1727–1729 (Chinese).
[9] Y.L. Lin, T.J. Wang, C. Qing, J. Yang, Y. Jin, Chemical Journal of Chinese Universities 22 (1) (2001) 104–107 (Chinese).
[10] F.S. Li, Ultra-Fine Powder Technology, National Defence Industry Press, Beijing, 2000 Chinese.
[11] http://webbook.nist.gov/chemistry/fluid/.
[12] G.Q. Liu, L.X. Ma, J. Liu, Handbook of Physical Property Data of Chemistry and Chemical Engineering, Organic Volume, Chemical Industry Press, Beijing, 2002 Chinese.