

# Surface Chemical Modification of Nanosized Oxide Particles with a Titanate Coupling Reagent in Isopropanol

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The function of the hydroxyl on particle surface in chemical modification in isopropanol with titanate coupling reagent CA7 was investigated. Four kinds of nanosized oxide particles: anatase TiO<sub>2</sub>, rutile TiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and monoclinic ZrO<sub>2</sub>, were used in experiments. The effects of different crystal structures of polymorph TiO<sub>2</sub> on the chemical modification, i.e., anatase and rutile TiO<sub>2</sub>, were studied. Fourier transform infrared (FTIR), X-ray photoelectron spectroscopy (XPS), and thermogravimetric (TG) analyses showed that the surfaces of anatase TiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and monoclinic ZrO<sub>2</sub> were chemically modified, and the quantities of CA7 reacted on particle surfaces were 1.66, 1.79, and 4.29 molecule nm<sup>-2</sup>, respectively. It was difficult to chemically modify rutile TiO<sub>2</sub>. The hydroxyl groups on anatase TiO<sub>2</sub> have IR adsorption bands at 3714 and 3672 cm<sup>-1</sup>. The 3714 cm<sup>-1</sup> hydroxyl reacted with CA7. The hydroxyl on rutile TiO<sub>2</sub> particle has a frequency of 3739 cm<sup>-1</sup>, but this did not react with CA7. XPS analysis showed that the binding energies of the oxygen and metal atoms on the modified oxide surfaces were increased. It was inferred that the hydroxyl group has its proton displaced to form a Me–O: species that, together with existing Me–O: on the particle surface, reacted with CA7 to form a Me–O–Ti bond.

## 1. Introduction

Nanosized oxide particles attract attention and are widely used because of their unique physical and chemical properties. However, they have large specific surface areas and agglomerate easily. Chemical modification with organic molecules can effectively prevent agglomeration and increase the dispersibility and stability of the particles in organic solvents. Functional groups are usually grafted on the particle surface during the modification to develop these special properties.<sup>1,2</sup>

The hydroxyl group on the oxide particle surface is the key species in the chemical modification. It can bond with polar molecules by forming hydrogen bonds or react with organic groups, such as alkoxy, to achieve functional modification. The structure and chemical property of the surface hydroxyl groups of Al<sub>2</sub>O<sub>3</sub> have been well-studied by IR analysis.<sup>3</sup> The hydroxyl with a vibration frequency of 3775 cm<sup>-1</sup> was found to be the most reactive<sup>3</sup> and was considered to exist in exposed zones of the surface.<sup>4</sup> Liu et al. modified the surface of hydroxyapatite particles using hexamethylene diisocyanate as a coupling reagent and showed that the surface hydroxyl groups of nanoapatite reacted with the isocyanate groups.<sup>5</sup> Bezrodna et al. investigated the molecular interactions between pyridine and anatase and rutile TiO<sub>2</sub> particles by IR spectroscopy and reported that these two different forms of TiO<sub>2</sub> have different active centers.<sup>6</sup> Layman and Hemminger investigated surface hydroxyl acidity by analyzing the interaction of organic molecules with hydroxylated ultrathin films of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.<sup>7</sup>

In this work, the modification of four kinds of nanosized oxide particles in isopropanol with the titanate coupling reagent CA7 was investigated. The chemical modification was qualitatively and quantitatively analyzed by Fourier transform infrared (FTIR), X-ray photoelectron spectroscopy (XPS), and thermogravimetric (TG) analysis. The hydroxyl states on different metal oxides as well as different crystal structures of polymorph TiO<sub>2</sub> were characterized by FTIR under vacuum, and the chemical states

of the oxygen and metal atoms on the surfaces were analyzed by XPS. A mechanism of the modification process is suggested.

## 2. Experimental Section

**2.1. Materials.** The titanate coupling reagent (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-octoester)titanate, CA7 for short] used was technical grade (First Nanjing Shuguang Chemical Plant, Nanjing, China), with a boiling point of 77 °C and a decomposition temperature of 210 °C. Isopropanol used was analytical grade (Beijing Chemical Plant, Beijing, China).  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and anatase and rutile TiO<sub>2</sub> particles used were technical grade (Zhejiang Hongsheng Material Technology Co., Ltd., Zhoushan, China). Monoclinic ZrO<sub>2</sub> particles used were technical grade (Nanjing High Technology Nano Co., Ltd., Nanjing, China). The particle diameters, specific surface areas, and surface hydroxyl densities of the particles, which were measured by Wang et al.,<sup>8</sup> are listed in Table 1.

**2.2. Procedures.** A CA7 solution was prepared by dissolving 5 mL of CA7 in 100 mL of isopropanol. The oxide particles were added into the CA7 solution in quantities where the CA7 molecules were two times that of the maximum that can be adsorbed to ensure that the particle surface can be fully modified. The maximum that can be adsorbed was estimated from an assumed CA7 monomolecular layer arrangement. The particle parameters and quantities are listed in Table 1. The reaction was carried out at 60 °C with stirring for 1 h.

After reaction, the suspension was filtered and the obtained cake was diluted in isopropanol with stirring, and then the obtained suspension was filtered again. This washing procedure was repeated 3 times. After that, the cake was extracted for 24 h to ensure that all physisorbed CA7 on the particle surface was removed and then dried at 120 °C for 24 h to give the samples for characterization.

A FTIR spectrometer (Nicolet 5DX, U.S.A.) with 2 cm<sup>-1</sup> resolution was used for sample analysis. The scans were repeated 200 times in the spectral range from 4000 to 400 cm<sup>-1</sup>. KBr was used as the mulling agent. A FTIR spectrometer (Nicolet

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**Table 1. Parameters of the Particles Used**

oxide particles	anatase TiO <sub>2</sub>	rutile TiO <sub>2</sub>	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	monoclinic ZrO <sub>2</sub>
average diameter, nm	5	40	30	10
OH density, nm <sup>-2</sup>	12.0	11.3	9.9	10.8
SSA, m <sup>2</sup> ·g <sup>-1</sup>	282	17	227	20
particle quantity, g	0.77	12.79	0.96	10.87

870, U.S.A.) with 0.125 cm<sup>-1</sup> resolution was used to characterize the surface hydroxyl frequency before and after modification. The particles were directly tableted as the sample and dehydrated at 170 °C under a vacuum of 10<sup>-3</sup> Pa for 3 h, and then the samples were analyzed under vacuum in the spectral range of 4000–3200 cm<sup>-1</sup>.

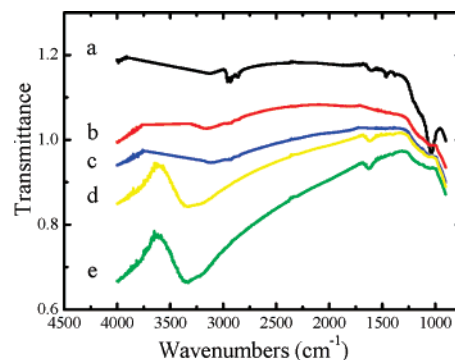
Thermogravimetric analysis was performed with a TGA2050 instrument (TA Instruments, U.S.A.) to determine the quantity of chemically reacted CA7 on the particle surface. The samples were heated from room temperature to 600 °C in nitrogen. The heating rate was 10 °C/min. An X-ray photoelectron spectrometer (Phi-Quantera, U.S.A.) with a resolution of 0.1 eV was used to determine the binding energies of the atoms on the particle surface. The excitation energy was 1486.7 eV. The analysis chamber had a vacuum of 10<sup>-9</sup> Pa.

### 3. Results and Discussion

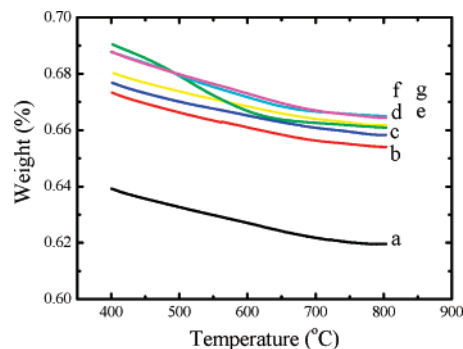
**3.1. Washing and Extraction.** The modified particle surface showed the existence of both physically and chemically adsorbed modifier. The chemically adsorbed modification is the main focus in this paper because of the important role this has in applications. Washing and extraction treatments were used to remove physically adsorbed CA7. Figure 1 shows the IR spectra of modified rutile particles extracted for different times. The nontreated sample showed the obvious characteristic bands of CA7 (see Section 3.2.1). After three washings, the characteristic bands became weaker, and after 12 h extraction, the bands vanished, i.e., CA7 was removed completely. Figure 2 shows the TG curves of modified anatase particles extracted for different times. The weight loss was the highest for the nontreated sample. The weight loss was lower after three washings. The weight loss did not change when the extraction time was >24 h, which indicated that the physically adsorbed CA7 had been completely removed. Therefore, sample treatments of three washings and 24 h extraction were used to remove physically adsorbed CA7 prior to the chemical modification analysis.

**3.2. Chemical Modification Analysis. 3.2.1. IR Analysis of Modified Particles.** The IR spectra before and after modification of the particles were analyzed. The spectra of anatase and rutile TiO<sub>2</sub> are shown in Figure 3. It can be seen from Figure 3 that the premodified anatase TiO<sub>2</sub> sample has a broad band at 3000–3500 cm<sup>-1</sup>, which can be assigned to the stretching vibrations of surface hydroxyls and adsorbed water. After washing and extraction, on modified anatase TiO<sub>2</sub>, the intensity of the surface hydroxyl and water bands were clearly decreased, and CA7 characteristic bands at 1028 cm<sup>-1</sup> (assigned to the stretching vibrations of the P=O double bond) and 2860–2960 cm<sup>-1</sup> (assigned to the stretching vibrations of C–H bonds) appeared, indicating that surface hydroxyl and water were replaced by CA7 molecules.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and monoclinic ZrO<sub>2</sub> showed the same results as anatase TiO<sub>2</sub>.

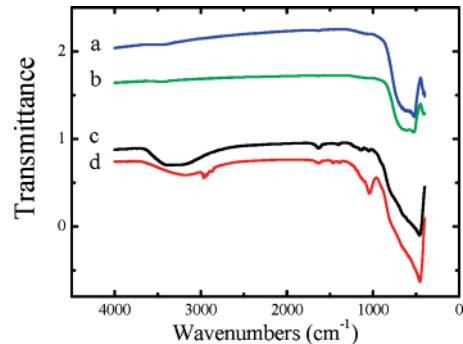
However, the postmodified rutile TiO<sub>2</sub> had almost the same IR spectrum as the premodified sample and the characteristic bands of CA7 could hardly be seen, indicating that CA7 was only physically adsorbed on rutile TiO<sub>2</sub> surface and was easily removed by washing and extraction. It indicates that, even for



**Figure 1.** IR spectra of modified rutile TiO<sub>2</sub> after different treatments: (a) none, (b) 3 washings, (c) 3 washings and 3 h extraction, (d) 3 washings and 6 h extraction, and (e) 3 washings and 12 h extraction.



**Figure 2.** TG curves of modified anatase TiO<sub>2</sub> after different treatments: (a) none, (b) 3 washings, (c) 3 washings and 3 h extraction, (d) 3 washings and 6 h extraction, (e) 3 washings and 12 h extraction, (f) 3 washings and 24 h extraction, and (g) 3 washings and 48 h extraction.



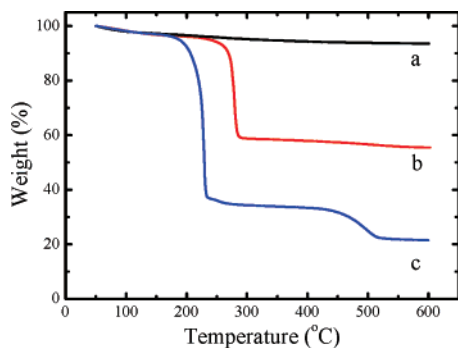
**Figure 3.** IR spectra of TiO<sub>2</sub>: (a) premodified rutile, (b) postmodified rutile, (c) premodified anatase, and (d) postmodified anatase.

**Table 2. Atomic Composition on the Particle Surface**

atom, %	anatase TiO <sub>2</sub>		rutile TiO <sub>2</sub>		$\gamma$ -Al <sub>2</sub> O <sub>3</sub>		monoclinic ZrO <sub>2</sub>	
	pre-	post-	pre-	post-	pre-	post-	pre-	post-
O	63.13	71.60	64.79	58.80	89.98	77.49	36.58	62.97
Ti	36.87	19.66	35.21	41.20	0.00	9.75	0.00	13.11
Al					10.02	6.21		
Zr							63.42	16.31
P	0.00	8.74	0.00	0.00	0.00	6.55	0.00	7.61

the same metal oxide TiO<sub>2</sub>, different crystal structures bring about different modification results.

**3.2.2. Atomic Composition of the Particle Surface.** The atomic compositions of O, Ti, and P on the pre- and postmodified surfaces were analyzed by XPS. Table 2 shows that P atoms were present on the postmodified surface of anatase TiO<sub>2</sub>. The amount of Ti decreased and O increased because the atomic ratio of Ti/O in CA7 is 1:22, which is much less than the ratio of 1:2 in TiO<sub>2</sub>. Ti and P were present on the postmodified



**Figure 4.** TG curves of CA7, pre- and post-anatase TiO<sub>2</sub>: (a) premodified anatase, (b) postmodified anatase, and (c) CA7.

**Table 3.** TG Analysis of the Quantities of Chemical Modification

particle	anatase TiO <sub>2</sub>	γ-Al <sub>2</sub> O <sub>3</sub>	monoclinic ZrO <sub>2</sub>
W <sub>0</sub> , %	94.01	93.23	99.51
W <sub>2</sub> , %	57.36	59.46	87.17
W <sub>CA7</sub> , %	101.72	88.56	18.74
density, nm <sup>-2</sup>	1.66	1.79	4.29

surfaces of γ-Al<sub>2</sub>O<sub>3</sub> and monoclinic ZrO<sub>2</sub>. However, P was not seen on modified rutile TiO<sub>2</sub>, and the O and Ti atomic ratio was hardly changed. This showed that CA7 had successfully modified the surfaces of anatase TiO<sub>2</sub>, γ-Al<sub>2</sub>O<sub>3</sub>, and monoclinic ZrO<sub>2</sub> but hardly modified the surface of rutile TiO<sub>2</sub>, which is the same result as with the FTIR analysis.

**3.2.3. Quantity of Chemical Modification.** Figure 4 shows the thermogravimetric curves of CA7 on pre- and postmodified anatase TiO<sub>2</sub> particles. It can be seen from Figure 4 that CA7 on the postmodified anatase TiO<sub>2</sub> decomposed at 280 °C, which is much higher than that of CA7. This indicated that a strong bond was formed between CA7 and the particle surface.

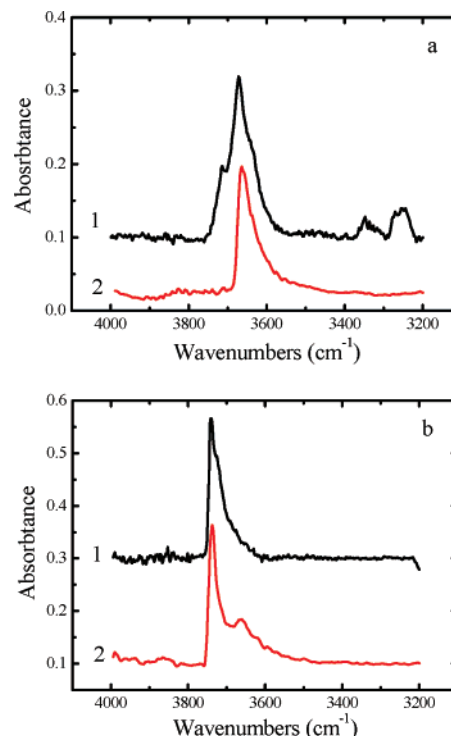
The quantity of CA7 chemically reacted onto the particle surface can be estimated from the weights of the pre- and postmodified samples at 600 °C by the method described by Wang et al.,<sup>8</sup>

$$W_{CA7} = (W_0 - W_2)/(W_2 - W_1) \times 100\% \quad (1)$$

$$D_{CA7} = (N_A \times W_{CA7})/(MW_{CA7} \times SSA \times 10^{18}) \quad (2)$$

where  $W_{CA7}$  is the quantity of CA7 chemically reacted on the particle surface, %;  $W_0$  is the weight of premodified particle at 600 °C, %;  $W_1$  is the weight of CA7 at 600 °C, %, i.e., 21.33%; and  $W_2$  is the weight of postmodified particles at 600 °C, %.  $D_{CA7}$  is the density of CA7 chemically reacted, molecule nm<sup>-2</sup>;  $N_A$  is the Avogadro constant, MW<sub>CA7</sub> is the molecular weight of CA7 (1311 g·mol<sup>-1</sup>), and SSA is the specific surface area of particles, m<sup>2</sup>·g<sup>-1</sup>. The TG analysis results and the quantities of chemical modification for anatase TiO<sub>2</sub>, γ-Al<sub>2</sub>O<sub>3</sub>, and monoclinic ZrO<sub>2</sub> are listed in Table 3, from which the quantities of CA7 reacted on different particle surfaces were 1.66, 1.79, and 4.29 molecule nm<sup>-2</sup>, respectively.

**3.3. Reactive Hydroxyls on TiO<sub>2</sub>.** In order to investigate the effects of hydroxyl from different crystal structure of TiO<sub>2</sub> on the modification reaction, experiments were designed to determine which specific hydroxyl groups reacted with CA7. The pre- and postmodified anatase and rutile TiO<sub>2</sub> were dehydrated at 170 °C under a vacuum of 10<sup>-3</sup> Pa for 3 h and analyzed by FTIR. The results are shown in Figure 5. Figure 5a shows that the premodified anatase sample had hydroxyl adsorption bands at 3714 and 3672 cm<sup>-1</sup>. The ~3360 and ~3260 cm<sup>-1</sup> bands were assigned to the hydrogen bonds of



**Figure 5.** FTIR spectra of hydroxyls on the TiO<sub>2</sub> particle surface under vacuum: (a) anatase TiO<sub>2</sub> and (b) rutile TiO<sub>2</sub>; (1) premodified and (2) postmodified.

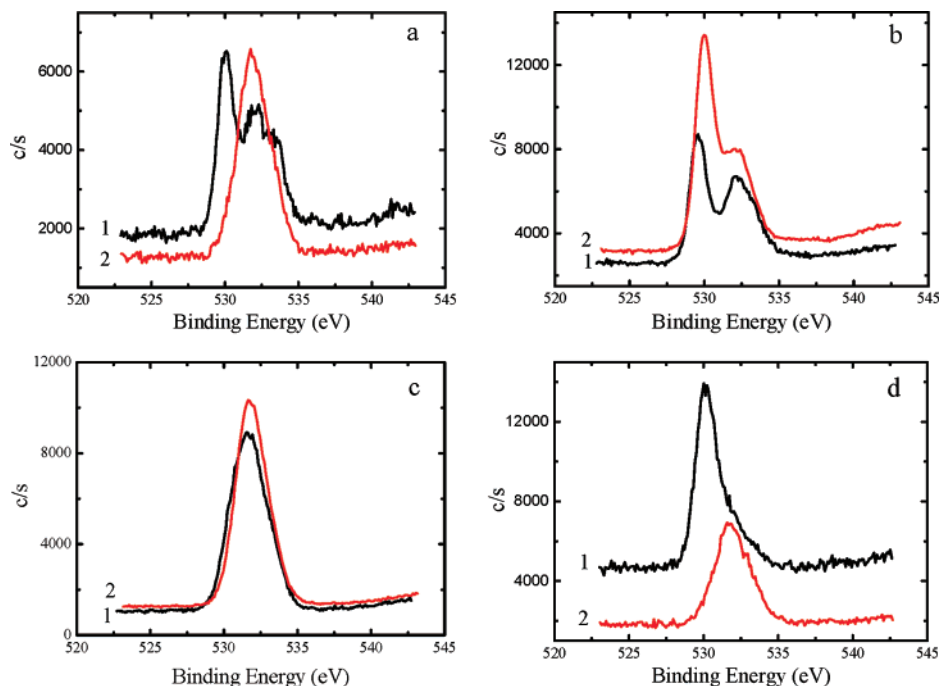
water on the surface and water complexes.<sup>6</sup> However, the postmodified anatase sample had no adsorption bands at 3714 cm<sup>-1</sup>. It is inferred that the hydroxyls with the adsorption bands at 3714 cm<sup>-1</sup> had reacted with CA7. Figure 5b shows that the premodified rutile sample had a hydroxyl adsorption band at 3739 cm<sup>-1</sup>, and the postmodified rutile sample showed nearly the same spectrum. It is inferred that the hydroxyls on rutile TiO<sub>2</sub> did not react with CA7.

Therefore, the surface hydroxyl with the vibration frequency of 3714 cm<sup>-1</sup> on anatase TiO<sub>2</sub> reacted with CA7, whereas the hydroxyl groups with the frequency of 3672 cm<sup>-1</sup> on anatase TiO<sub>2</sub> particle and all the surface hydroxyl groups of rutile TiO<sub>2</sub> did not react with CA7.

**3.4. Chemical States of Surface Oxygen and Metal.** **3.4.1. Chemical States of Surface Oxygen.** The XPS binding energies of O on the surface of pre- and postmodified particles were measured. The spectra are shown in Figure 6, from which it can be seen that the surface O atoms had two bands at 529.9 and 532.0 eV. The 529.9 eV peak can be assigned to the O atom of Me—O:, and the 532.0 eV peak can be assigned to the O atom of Me—OH on the surface and Me—O—Me on the surface or in the bulk of the particles, with the reference to McCafferty and Wightman's work.<sup>9</sup>

For the anatase TiO<sub>2</sub> particles, the premodified sample had both 529.9 and 532.0 eV bands, but the postmodified sample had only the 532.0 eV band, which is shown in Figure 6a. The increase of the binding energy indicated that the Ti—O: on anatase TiO<sub>2</sub> reacted with CA7, forming a chemical bond to give Ti—O—Ti. Taking into account the results in Section 3.3, it can be inferred that the surface hydroxyl with the frequency of 3714 cm<sup>-1</sup> had lost a proton and the Ti—O: formed reacted with CA7.

The binding energy spectrum of surface O on rutile TiO<sub>2</sub> showed that both the pre- and postmodified samples had the 529.9 and 532.0 eV bands, and the spectrum was hardly changed after modification, as shown in Figure 6b. This indicates that



**Figure 6.** XPS spectra of O 1s on the surface of pre- and postmodified oxides: (a) anatase TiO<sub>2</sub>, (b) rutile TiO<sub>2</sub>, (c)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and (d) monoclinic ZrO<sub>2</sub>; (1) premodified and (2) postmodified.

**Table 4. Binding Energies and Chemical Shifts of the Metal Atoms on the Particle Surface**

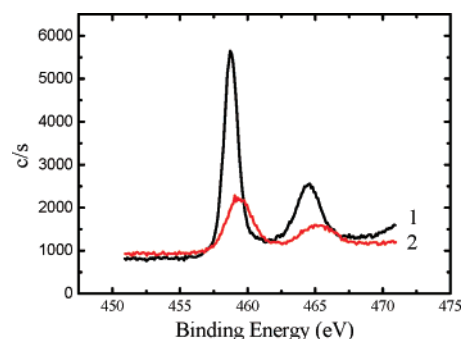
oxide particles	Ti 2p (anatase)	Ti 2p (rutile)	Al 2p	Zr 3d
binding energy (premodified), eV	458.7	458.4	74.3	182.1
binding energy (postmodified), eV	459.3	458.6	74.6	182.6
chemical shift, eV	0.6	0.2	0.3	0.5

the Ti–O: on the surface of rutile TiO<sub>2</sub> particle did not react with CA7.

Pre- and postmodified  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> had nearly the same spectrum of oxygen binding energy of 532.0 eV, as shown in Figure 6c. This is because the O on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface is very active and forms hydroxyls or hydrogen bonds with water, so the hydroxyls existed in Al–O–H form instead of the Al–O: form. Since the O atoms in Al–O–H and Al–O–Ti had nearly the same binding energy, it is inferred that, in the modification process, the Al–O–H form had lost a proton, and the Al–O: formed reacted with CA7, forming a Al–O–Ti bond.

The oxygen binding energy band of premodified monoclinic ZrO<sub>2</sub> showed an asymmetrical shape, as shown in Figure 6d. This is due to a strong band at 530.0 eV and a weak band at 532.0 eV, which indicated that most of the O atoms on premodified monoclinic ZrO<sub>2</sub> were in the Zr–O: form. After modification, these had all reacted with CA7, that is, the Zr–O: form had converted to Zr–O–Ti, and the asymmetrical 529.9 eV band changed to a symmetrical 532.0 eV band.

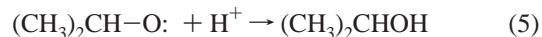
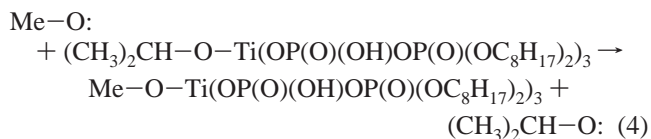
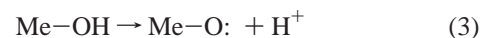
**3.4.2. Chemical States of the Surface Metal.** The binding energies of the metal on the particle surfaces and their chemical shifts are listed in Table 4. It can be seen that the binding energies of the metal increased after modification, which indicated that the outer-shell electron densities had decreased. This is because of the decreased electron density of the adjacent oxygen and the induction effect. The chemical shifts of Ti 2p in anatase TiO<sub>2</sub> and Zr 3d in monoclinic ZrO<sub>2</sub> were higher because their oxygen binding energies changed more, as shown in Figure 6. The 0.2 eV chemical shift of Ti 2p in rutile TiO<sub>2</sub> in Table 4 can be considered negligible and within the error of



**Figure 7.** XPS spectra of Ti 2p on the surface of pre- and postmodified anatase TiO<sub>2</sub>: (1) premodified and (2) postmodified.

the XPS instrument. A typical spectrum of the Ti 2p binding energies of anatase TiO<sub>2</sub> is shown in Figure 7.

**3.5. Mechanism of Surface Modification.** From the above analysis, the mechanism of surface modification can be inferred as



First, the surface hydroxyl groups lose protons to give the Me–O: species. Second, the Me–O: species react with CA7 through replacing their isopropoxys. The isopropoxys combine with the protons and form isopropanol. Me–O: that existed on the particle surface also can react with CA7.

#### 4. Conclusions

Four kinds of nanosized oxide particles, anatase TiO<sub>2</sub>, rutile TiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and monoclinic ZrO<sub>2</sub>, were modified in isopro-

panol by the titanate coupling reagent CA7. Anatase TiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and monoclinic ZrO<sub>2</sub> were chemically modified with CA7, and the quantities of CA7 reacted on the particle surfaces were 1.66, 1.79, and 4.29 molecule nm<sup>-2</sup>, respectively. However, the rutile TiO<sub>2</sub> was not chemically modified.

The surface hydroxyl with the frequency of 3714 cm<sup>-1</sup> on anatase TiO<sub>2</sub> reacted with CA7, whereas the hydroxyls with the frequency of 3672 cm<sup>-1</sup> on anatase TiO<sub>2</sub> particle and all the surface hydroxyls of rutile TiO<sub>2</sub> particle were not reactive toward CA7.

The O atoms existed on the surface of anatase and rutile TiO<sub>2</sub> in Ti—O—H and Ti—O: forms, on monoclinic ZrO<sub>2</sub> mainly in Zr—O: form, and on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in Al—O—H form. The Me—O—H form lost a proton and reacted with the Ti in CA7 by replacing the isopropoxy group. Me—O: that existed on the particle surface can also react with CA7.

### Acknowledgment

The authors wish to express their appreciation of the financial support of this study by the National Natural Science Foundation of China (NSFC No. 20476051) and the Specialized Research Fund for the Doctoral Program of Higher Education (SRFDP No. 20060003089).

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*Received for review August 8, 2007*

*Revised manuscript received December 25, 2007*

*Accepted January 1, 2008*

IE0710824