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Article (Dedicated to Professor Yi Chen on the occasion of his 80th birthday)

Evolution of surface and bulk structures of $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites

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ABSTRACT

A series of $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites were synthesized using a coprecipitation method, and their structures were investigated using X-ray diffraction, N_2 adsorption-desorption isotherms, X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, H_2 temperature-programmed reduction, selective chemisorption of methyl orange, and isoelectric point measurements. The selective chemisorption of methyl orange and isoelectric point measurements successfully characterized the outmost surface structures of the $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites, and the term “equivalent CeO_2 surface coverage” in a monolayer was introduced to describe the outmost surface compositions. $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites with $x \geq 0.7$ form a cubic fluorite phase solid solution, the $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ oxide composite is a pure monoclinic compound, and the other oxide composites have mixed phase structures. The outmost surface structure evolves in a different way from the bulk structure. A cubic fluorite $\text{Ce}_{0.7}\text{Ti}_{0.3}\text{O}_2$ solid solution partially undergoes cubic fluorite solid solution-to-monoclinic $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ phase transition on its outmost surface, and $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ on the outmost surface of $\text{Ce}_{0.7}\text{Ti}_{0.3}\text{O}_2$ grows from the surface to the bulk. Cubic fluorite $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions exhibit good reducibilities at relatively low temperatures, whereas $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ exhibits good reducibility at relatively high temperatures. These results provide comprehensive and in-depth structural information for important $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites.

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1. Introduction

Titania (TiO_2) and ceria (CeO_2) are among the most important oxides in catalysis [1,2]. TiO_2 has important applications as catalysts in photocatalysis [3] and environmental catalysis [2]. CeO_2 is widely used as an excellent catalyst support in various important oxidation reactions [4–9]. Pure metal oxides often suffer from drawbacks arising from their chemical or physical properties, which limit their practical applications. For example, the wide band gap of anatase TiO_2 seriously constrains its applications in solar energy use [10], and CeO_2 is

known to have poor thermal stability and to undergo rapid sintering at high temperatures [11,12]. One of the approaches used to overcome these problems is to prepare oxide composites. Oxide composites consisting of TiO_2 and CeO_2 have been much studied. Preuss et al. [13] successfully synthesized a series of Ce-Ti-O oxides such as Ce_2TiO_5 , $\text{Ce}_2\text{Ti}_2\text{O}_7$, and $\text{Ce}_4\text{Ti}_9\text{O}_{24}$, containing Ce(III) and Ti(IV). Reddy et al. [14,15] investigated the structure of a CeO_2 - TiO_2 mixed oxide (Ce:Ti molar ratio = 1) in detail. López et al. [16] studied the structures and thermal properties of CeO_2 - TiO_2 mixed oxides (10 wt% CeO_2 -90 wt% TiO_2) calcined at different temperatures. Nakagawa and

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coworkers [17] reported that $\text{CeO}_2\text{-TiO}_2$ mixed oxides showed higher oxidation capacities towards I^- than pure CeO_2 did under visible-light irradiation. Yang et al. [18] synthesized $\text{CeO}_2\text{-TiO}_2$ catalysts with different Ce:Ti molar ratios and found that the mixed oxides exhibited better catalytic performance than the individual TiO_2 and CeO_2 components in the catalytic wet-air oxidation of acetic acid. Luo et al. [19] successfully synthesized $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ with a new phase structure via a sol-gel method followed by calcination at $650\text{ }^\circ\text{C}$; the oxide exhibited a high oxygen-storage capacity. Dutta et al. [20] proposed the presence of strongly and weakly bound oxygen atoms in $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions prepared by a solution combustion method; weakly bound oxygen atoms are responsible for the enhanced oxygen-storage capacities of solid solutions compared with that of pure CeO_2 . Li et al. [21] reported that amorphous Ce-Ti mixed oxides are active in catalyzing the selective reduction of NO_x with NH_3 .

Although many studies have been reported, there is still a lack of comprehensive and detailed studies of the structures of $\text{CeO}_2\text{-TiO}_2$ oxide composites, particularly with respect to the surface structures, which are closely related to the catalytic properties. We previously elucidated the surface and interface structures of $\text{CeO}_2\text{-TiO}_2$ oxide composites with different $\text{CeO}_2\text{:TiO}_2$ mass ratios prepared by a sol-gel method [22,23]. However, because of limitations of the sol-gel method used, the Ce:Ti molar ratio of the synthesized $\text{CeO}_2\text{-TiO}_2$ oxide composites could only reach 0.8. In this work, we prepared $\text{CeO}_2\text{-TiO}_2$ oxide composites with a wide range of Ce:Ti molar ratios using a coprecipitation method and investigated their structures in detail. Selective chemisorption of methyl orange (MO) and isoelectric point measurements were developed to characterize the evolution of the outmost surface structures of these oxide composites, and the term “equivalent CeO_2 surface coverage” in a monolayer (ML) was defined to describe their outmost surface compositions.

2. Experimental

2.1. Sample preparation

All chemicals reagents (AR grade) were purchased from Sinopharm and used without further purification unless stated otherwise. $\text{CeO}_2\text{-TiO}_2$ oxide composites, denoted by $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ (x from 1 to 0), were prepared using a coprecipitation method. Calculated amounts of $\text{Ti}(\text{SO}_4)_2$ and $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ were dissolved in a solution of HCl ($\text{pH} = 2$). The solution was adequately stirred at $60\text{ }^\circ\text{C}$ for 5 min, and then $\text{NH}_3\cdot\text{H}_2\text{O}$ was added to adjust the pH of the solution to 10. The resulting suspension was adequately stirred at $60\text{ }^\circ\text{C}$ for 6 h, and then aged for 2 h at room temperature. The precipitate was filtered off and washed five times with distilled water, dried at $70\text{ }^\circ\text{C}$ for 2 h, and finally calcined in air at $800\text{ }^\circ\text{C}$ for 2 h.

2.2. Sample characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Philips X'Pert PROS diffractometer using a Ni-filtered $\text{Cu } K_\alpha$

(0.15418 nm) radiation source, with an operating voltage and current of 40 kV and 50 mA, respectively. N_2 adsorption-desorption isotherms were measured on a Micromeritics ASAP 2020 M+C system. The sample was degassed at $200\text{ }^\circ\text{C}$ in N_2 for 4 h prior to the measurements. The pore size distribution of mesopores in the samples was analyzed using the BJH method. X-ray photoelectron spectroscopy (XPS) measurements were performed with an ESCALAB 250 high-performance electron spectrometer, using monochromated $\text{Al } K_\alpha$ ($h\nu = 1486.7\text{ eV}$) as the excitation source. The possible charging of samples was corrected by setting the binding energy of adventitious carbon ($\text{C } 1s$) at 284.5 eV. H_2 temperature-programmed ($\text{H}_2\text{-TPR}$) experiments were carried out with a laboratory-made apparatus, using a GC-1650 (Hangzhou KeXiao Instrument Co., Ltd. China) gas chromatograph equipped with a thermal conductivity couple to detect H_2 consumption. During $\text{H}_2\text{-TPR}$, a 20 mg-sample was heated at a rate of $5\text{ }^\circ\text{C/min}$, and 5 vol% H_2 in Ar was fed at a flow rate of 20 mL/min. Isoelectric point measurements were conducted using the dynamic light-scattering and non-invasive back-scattering modes on a zeta potential meter (Zetasizer Nano ZS, UK); the light source was a highly stable He-Ne laser with a wavelength of 633 nm and a power of 4.0 mW.

X-ray absorption spectroscopy (XAS) measurements of the Ti K-edge (4815–5612 eV) and the Ce L_{III} -edge (5573–6151 eV) were performed in transmission mode at room temperature at the X-ray absorption fine structure (XAFS) station of the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (Shanghai, China). The O K-edge X-ray absorption near-edge spectra (XANES) of various samples were measured at the soft X-ray magnetic circular dichroism beamline (U19) at the National Synchrotron Radiation Laboratory (Hefei, China). Extended XAFS (EXAFS) spectra were analyzed using the ATHENA 0.8.056 package, in which the $k^3\text{-}\chi(k)$ -weighted EXAFS oscillation was Fourier transformed to the R space in the range $2.0\text{--}11\text{ \AA}^{-1}$ for Ti and $2.1\text{--}10\text{ \AA}^{-1}$ for Ce, after the removal and normalization of atomic absorptions.

2.3. Chemisorption of MO

A sample (0.12 g) was added to 40 mL of a solution of MO (20 mg/L) at room temperature. The suspension was adequately stirred. Suspension samples (ca. 4 mL) were collected every 30 min and centrifuged, and the concentration of MO in the centrifuged aqueous solution was determined by measuring the absorption of MO at 464 nm, using a Shimadzu UV-2450 ultraviolet-visible spectrophotometer. All experiments were carried out in the absence of light. HCl or NaOH aqueous solutions were used to perform chemisorption experiments at different pH values.

3. Results and discussion

Figure 1 shows XRD patterns of various $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites. Pure TiO_2 and CeO_2 display the pure anatase phase structure (JCPDS 83-2243) and cubic fluorite phase structure (JCPDS 43-1002), respectively. $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites with $x \geq 0.7$ all exhibit the pure cubic fluorite phase structure,

Fig. 1. XRD patterns of $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites. (1) CeO_2 ; (2) $\text{Ce}_{0.99}\text{Ti}_{0.01}\text{O}_2$; (3) $\text{Ce}_{0.98}\text{Ti}_{0.02}\text{O}_2$; (4) $\text{Ce}_{0.95}\text{Ti}_{0.05}\text{O}_2$; (5) $\text{Ce}_{0.9}\text{Ti}_{0.1}\text{O}_2$; (6) $\text{Ce}_{0.8}\text{Ti}_{0.2}\text{O}_2$; (7) $\text{Ce}_{0.7}\text{Ti}_{0.3}\text{O}_2$; (8) $\text{Ce}_{0.6}\text{Ti}_{0.4}\text{O}_2$; (9) $\text{Ce}_{0.5}\text{Ti}_{0.5}\text{O}_2$; (10) $\text{Ce}_{0.4}\text{Ti}_{0.6}\text{O}_2$; (11) $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$; (12) $\text{Ce}_{0.2}\text{Ti}_{0.8}\text{O}_2$; (13) $\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$; (14) TiO_2 .

indicating the formation of CeO_2 -like solid solutions. Interestingly, the XRD pattern of $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ could not be matched with any of the currently available JCPDF card files, either pure or mixed phase. The XRD pattern is identical to that of a new phase structure of $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$, prepared via a sol-gel method followed by calcination at 650°C , previously reported by Luo et al. [19]. It is a monoclinic phase belonging to the $C2/m$ space group, with lattice parameters of $a = 0.9811(8)$ nm, $b = 0.3726(3)$ nm, $c = 0.6831(6)$ nm, and $\beta = 118.84^\circ$. The other $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites exhibited mixed phase structures. The phase structure evolution of the $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites prepared using a coprecipitation method can therefore be described as follows. Pure TiO_2 is anatase phase; on addition of Ce, monoclinic $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ gradually develops, and $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$

Table 1

Macrostructural parameters of $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites with pure phase structures.

Sample	Crystallite size(d_{XRD} , nm)	BET surface area (m^2/g)	Pore volume (cm^3/g)	Average pore size (nm)
TiO_2	29.6	13	0.054	9.4
$\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$	16.4	26	0.138	22.2
$\text{Ce}_{0.7}\text{Ti}_{0.3}\text{O}_2$	13.1	25	0.198	28.4
$\text{Ce}_{0.8}\text{Ti}_{0.2}\text{O}_2$	18.4	14	0.103	27.5
$\text{Ce}_{0.9}\text{Ti}_{0.1}\text{O}_2$	18.3	13	0.122	37.8
$\text{Ce}_{0.95}\text{Ti}_{0.05}\text{O}_2$	17.5	19	0.169	30.7
CeO_2	15.1	38	0.151	12.7

oxide composites ($0 < x < 0.3$) are mixtures of anatase TiO_2 and monoclinic $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ until the formation of the pure $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ phase. With further increases in x ($0.3 < x < 0.7$), the $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites formed are solid solutions of mixtures of monoclinic $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ and cubic fluorite. The $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites with $x \geq 0.7$ are all pure cubic fluorite solid solutions. In our previous work, we did not observe the formation of either TiO_2 -like solid solutions or $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ in CeO_2 - TiO_2 oxide composites with Ce:Ti molar ratios up to 0.8 prepared using a sol-gel method [22,23]. The preparation method therefore strongly affects the structures of the synthesized CeO_2 - TiO_2 oxide composites.

Figure 2 shows the N_2 adsorption-desorption isotherms and corresponding pore size distributions of $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites with a pure phase structure. All the isotherms were type IV with a type H3 hysteresis loop at high relative pressures, indicating the presence of slit-like mesopores, associated with aggregates of plate-like particles [24]. Table 1 summarizes the macrostructural parameters obtained from XRD data and N_2 adsorption-desorption isotherms. It is worth noting that the average pore sizes of $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ and cubic fluorite $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$

Fig. 2. (A) N_2 adsorption-desorption isotherms and (B) pore size distributions of $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites with pure phase structures.

solid solutions are larger than those of both TiO_2 and CeO_2 .

The local structures of the $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites were investigated in detail using XAS. Figure 3 shows the Ti K-edge XANES, and Figure 4 presents the corresponding Fourier-transform (FT)-EXAFS spectra. The Ti K-edge XANES and FT-EXAFS spectra of $\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$ are similar to those of anatase TiO_2 , demonstrating that the electronic configuration and local structure of Ti in $\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$ are similar to those in anatase TiO_2 . This agrees with the XRD results, which showed that $\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$ is dominated by anatase TiO_2 . The Ti K-edge XANES of $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ and cubic fluorite $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions are essentially similar to that of anatase TiO_2 , indicating similar electronic configurations of Ti. However, the peaks attenuate and broaden somewhat, and obvious changes occur in the pre-edge region. These changes are strongly modulated by the surrounding atomic environments and provide rich structural and electronic information. A total of four features, labeled A_1 (4969.0 eV), A_2 (4971.0 eV), A_3 (4972.1 eV), and B (4974.5 eV), appear in the pre-edge region of the Ti K-edge XANES of anatase TiO_2 . The A_2 feature was observed for anatase TiO_2 but not for rutile TiO_2 [25–29]. Wu et al. [29] performed multiple scattering calculations and assigned the A_1 , A_2 , and A_3 features to transitions to $3d-4p$ hybridized states, and the B feature to an orbital with a mainly p character. They further proposed that four Ti atoms 3.039 Å from the central Ti atom in anatase TiO_2 contribute to features A_1 and A_2 , and four Ti atoms 3.784 Å from the central Ti atom contribute to features A_1 and A_3 . However, Luca et al. [26] assigned the A_2 feature to five-coordinated Ti species on the surface of anatase TiO_2 particles. With increasing Ce content of the $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites, the A_2 feature grows at the expense of the A_3 feature and becomes dominant in the case of the $\text{Ce}_{0.9}\text{Ti}_{0.1}\text{O}_2$ oxide solution. These observations demonstrate the different coordination environments of Ti atoms in anatase TiO_2 , $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$, and cubic fluorite $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions. For example, the Ti atoms in anatase TiO_2 are six coordinated, whereas those in cubic

Fig. 4. Ti-K edge FT-EXAFS spectra of $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites.

fluorite $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions adopt the coordination environment of Ce, and thus are eight coordinated. The Ti K-edge FT-EXAFS spectra also reflect the different local coordination environments of Ti in anatase TiO_2 , $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$, and cubic fluorite $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions. Peaks corresponding to the first Ti–O shell, second Ti–Ti shell, and third Ti–O shell can be well resolved in the Ti K-edge FT-EXAFS spectra of anatase TiO_2 and the $\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$ oxide composite. The first Ti–O shell peaks of $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ and cubic fluorite $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions are similar to that of anatase TiO_2 , indicating that their Ti–O bond lengths are similar; however, their second Ti–Ti shell peaks differ very much. Compared with anatase TiO_2 , the Ti–Ti second shell peaks of $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ and cubic fluorite $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions are greatly attenuated, and their peak maxima shift

Fig. 3. (A) Ti K-edge XANES spectra and (B) expanded pre-edge region of Ti K-edge XANES spectra of $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites.

Fig. 5. (A) Ce L_{III}-edge XANES spectra and (B) Ce L_{III}-edge FT-EXAFS spectra of Ce_xTi_{1-x}O₂ oxide composites.

downwards. This suggests that the Ti–Ti second shells in Ce_{0.3}Ti_{0.7}O₂ and cubic fluorite Ce_xTi_{1-x}O₂ solid solutions exhibit a smaller coordination number and a shorter distance than that in anatase TiO₂. These experimental results strongly support the model proposed by Wu et al. [29] to explain the pre-edge peaks of the Ti *K*-edge XANES, in which, within the Ti–Ti second shell of anatase TiO₂, four Ti atoms 3.039 Å from the central Ti atom contribute to features A₁ and A₂, whereas four Ti atoms 3.784 Å from the central Ti atom contribute to features A₁ and A₃. Ce_{0.3}Ti_{0.7}O₂ and cubic fluorite Ce_xTi_{1-x}O₂ solid solutions, which mainly have Ti–Ti second shells at shorter distances in the Ti *K*-edge FT-EXAFS spectra, exhibit strong A₂ features and weak A₃ features.

Figure 5 shows Ce L_{III}-edge XANES of Ce_xTi_{1-x}O₂ oxide composites and the corresponding FT-EXAFS spectra. Pure CeO₂ exhibits two peaks, labeled A and B, in its Ce L_{III}-edge XANES. Peaks A and B correspond to two final-state configurations [30]: A has a 2p4f⁰5d* final-state configuration, where 2p denotes a hole in the 2p shell and 5d* refers to an excited electron in the 5d state, and B has a 2p4f⁰5d*L final-state configuration, where L stands for a hole in the anionic ligand orbital. Cubic fluorite Ce_xTi_{1-x}O₂ solid solutions exhibit Ce L_{III}-edge XANES very similar to that of CeO₂. Besides features A and B, a new shoulder feature, C, is clearly resolved in the low-energy region in the spectrum of Ce_{0.3}Ti_{0.7}O₂, and is assigned to Ce(III) [31]. This suggests that the Ce(III) concentration is higher in Ce_{0.3}Ti_{0.7}O₂ than in cubic fluorite Ce_xTi_{1-x}O₂ solid solutions and CeO₂. Cubic fluorite Ce_xTi_{1-x}O₂ solid solutions and pure CeO₂ also exhibit very similar Ce L_{III}-edge FT-EXAFS spectra, in which the first Ce–O shell, the second Ce–Ce shell, and the third Ce–O shell can be well resolved. The first Ce–O shell peak of Ce_{0.3}Ti_{0.7}O₂ is similar to that of CeO₂, indicating that the Ce–O bond length in Ce_{0.3}Ti_{0.7}O₂ is similar to that in CeO₂; however, no second coordination peak can be resolved in the Ce L_{III}-edge FT-EXAFS spectrum of Ce_{0.3}Ti_{0.7}O₂; this might be related to its monoclinic crystal structure with large lattice parameters.

The O *K*-edge XANES features of O atoms in transition-metal oxides are sensitive to their chemical environments. We therefore measured the O *K*-edge XANES of Ce_xTi_{1-x}O₂ oxide composites (Fig. 6). The O *K*-edge XANES of anatase TiO₂ displays the density of unoccupied electronic states of O 2*p*-type orbitals that are hybridized with Ti 3*d* and 4*sp* orbitals. Two energy regions can be distinguished, as follows [32]. (1) The 530–535 eV region, which is associated with transitions to the O (2*p*)–Ti (3*d*) band. Two peaks, labeled a and b, appear because the crystal field splits the Ti 3*d* levels into *t*_{2g} and *e*_g. (2) The 540–550 eV region, which is associated with transitions to the O 2*p* antibonding state (peak c) and O(2*p*)–Ti(4*sp*) band (peak d). Three features, labeled A, B, and C, appear in the O *K*-edge XANES of CeO₂, and correspond to transitions from the O 1*s* core levels to the empty O 2*p*-hole states located in the Ce-dominated 4*f*, 5*d*-*e*_g, and 5*d*-*t*_{2g} levels, respectively [33]. The O

Fig. 6. O *K*-edge XANES spectra of Ce_xTi_{1-x}O₂ oxide composites.

Fig. 7. (A) Normalized Ti 2p XPS spectra, (B) normalized Ce 3d XPS spectra of $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites, and (C) the surface and bulk Ce:Ti atomic ratio of $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites. (a) $\text{Ce}_{0.2}\text{Ti}_{0.8}\text{O}_2$; (b) $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$; (c) $\text{Ce}_{0.4}\text{Ti}_{0.6}\text{O}_2$; (d) $\text{Ce}_{0.5}\text{Ti}_{0.5}\text{O}_2$; (e) $\text{Ce}_{0.6}\text{Ti}_{0.4}\text{O}_2$; (f) $\text{Ce}_{0.7}\text{Ti}_{0.3}\text{O}_2$; (g) $\text{Ce}_{0.8}\text{Ti}_{0.2}\text{O}_2$; (h) $\text{Ce}_{0.9}\text{Ti}_{0.1}\text{O}_2$; (i) $\text{Ce}_{0.95}\text{Ti}_{0.05}\text{O}_2$.

K-edge XANES of cubic fluorite $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions are very similar to that of CeO_2 . This is reasonable because Ti and Ce in cubic fluorite $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions have the same crystal field and exhibit the same *d*-orbital splitting mode. $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ exhibits an O *K*-edge XANES significantly different from those of cubic fluorite $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions. Both CeO_2 -like and TiO_2 -like features are observed in the spectrum, but the spectrum cannot be considered as a simple sum of CeO_2 -like and TiO_2 -like features. This could be attributed to the unique monoclinic phase structure of $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$.

The above XRD and XAS results demonstrate the evolution of the phase and local structures of $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites. XPS was then used to study their surface composition evolution (Fig. 7). All samples exhibit the same Ti 2p_{3/2} binding energy at 458.3 eV (Fig. 7A), a characteristic value for Ti(IV) [34]. The Ti 2p XPS peak attenuates with the decreasing amount of Ti in the $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composite. Figure 7B shows the Ce 3d XPS spectra of the $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites. The Ce 3d XPS spectrum shows multiple states arising from different Ce 4f level occupancies in the final state. It is worth noting that a feature at 885.6 eV, arising from the 3d_{5/2} component of Ce(III), is more obvious in oxide composites containing $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ than it is in cubic fluorite $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions and CeO_2 . This agrees with the above Ce L_{III}-edge XANES results, demonstrating that the Ce(III) concentration is higher in $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ than in cubic fluorite $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions and CeO_2 . Figure 7C compares the Ce:Ti atomic ratios derived from the XPS results and the calculated values. No obvious surface enrichment within the XPS depth was observed, indicating that the compositions of $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites are quite homogeneous.

Selective chemisorption is an effective technique for probing the outmost surface compositions of solids. We previously found that MO chemisorbs substantially on CeO_2 but barely on TiO_2 , and is thus a suitable molecule for probing the outmost surface compositions of $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites [23]. Fig-

ure 8 shows the specific chemisorption capacities normalized to the specific surface areas of various samples toward MO. CeO_2 exhibits a specific chemisorption capacity, but TiO_2 and $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ do not chemisorb MO. $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites ($0 < x < 0.3$) consisting of TiO_2 and $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ therefore do not chemisorb MO either. Interestingly, although they have the same phase structures, cubic fluorite $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions ($0.7 \leq x \leq 1$) exhibit decreasing specific chemisorption capacities with a decreasing Ce amount. This suggests that the outmost surface compositions of cubic fluorite $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions are different. For $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites ($0.3 \leq x \leq 0.7$) consisting of cubic fluorite $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions and $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$, the specific chemisorption capacities do not vary much for oxide composites with $0.5 \leq x \leq 0.7$, and then decrease to zero as the *x* value decreases from 0.5 to 0.3. Electrostatic interactions often play an important role in the chemisorption

Fig. 8. (Red) The isoelectric point for various composites. (Blue) the chemisorption capacity of various samples toward MO normalized to the BET specific surface area.

of organic molecules on oxide surfaces, so we measured the isoelectric points of $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites to understand their chemisorption behavior towards MO. The results are shown in Fig. 8. The isoelectric point of CeO_2 is 6.25, very close to the pH value of MO aqueous solution (6.39), but the isoelectric points of TiO_2 (4.2) and $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ (4.5) are much lower. In MO aqueous solution, therefore, the surfaces of TiO_2 and $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ are strongly negatively charged. MO is an anionic dye. This could be why TiO_2 and $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ do not chemisorb MO. Interestingly, the trend in the changes in the measured isoelectric points of $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites is similar to the trend in their specific chemisorption capacities towards MO. It is therefore the formation of Ti–O bonds on the outmost surfaces of the $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites that changes the local outmost surface charge and thus affects the chemisorption capacity towards MO. These results clearly demonstrate that the isoelectric point, a characteristic of metal oxides, is a promising parameter for sensitively probing the outmost surface compositions of oxide composites, and isoelectric point measurement is a more convenient technique than selective chemisorption.

We introduce the term “equivalent CeO_2 surface coverage” in an ML, defined as the specific chemisorption capacity towards MO of a $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composite normalized to that of CeO_2 , to describe the outmost surface composition of $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites. Figure 9 compares the equivalent CeO_2 surface coverages, the Ce:Ti atomic ratios (XPS results), and the bulk phase structures (XRD results) of $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites. The equivalent CeO_2 surface coverages of cubic fluorite $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions ($x \geq 0.8$) coincide with the Ce molar percentages and the Ce:(Ce+Ti) molar ratios quite well, indicating homogeneous distributions of Ti and Ce on the outmost surface. However, the equivalent CeO_2 surface coverage of a cubic fluorite $\text{Ce}_{0.7}\text{Ti}_{0.3}\text{O}_2$ solid solution is far less than the Ce:(Ce+Ti) molar ratio. This implies that the outmost surface of $\text{Ce}_{0.7}\text{Ti}_{0.3}\text{O}_2$ might partially undergo a cubic fluorite solid solution-to-monoclinic $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ phase transition. The presence of the monoclinic $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ phase on the outmost surface of

Fig. 9. Equivalent CeO_2 surface coverage determined by selective chemisorption of methyl orange results, Ce:(Ce+Ti) atomic ratio determined by XPS results, and bulk phase structure determined by XRD results of $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites.

$\text{Ce}_{0.7}\text{Ti}_{0.3}\text{O}_2$ is beyond the detection limit of XRD; therefore, the XRD results show that $\text{Ce}_{0.7}\text{Ti}_{0.3}\text{O}_2$ is still a pure cubic fluorite solid solution. The equivalent CeO_2 surface coverage does not vary much when the x value decreases from 0.7 to 0.5, but the fraction of $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ grows continuously. This suggests that the formed $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ is located in the bulk of the $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites ($0.5 \leq x < 0.7$). The $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ on the outmost surface of $\text{Ce}_{0.7}\text{Ti}_{0.3}\text{O}_2$ should therefore grow from the surface to the bulk. The equivalent CeO_2 surface coverage decreases with the further decreases in x and becomes zero with the formation of pure $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$. Therefore, via combinations of XRD and XAS results, and selective chemisorption and isoelectric point measurement results, we have successfully clarified the evolution of both the outmost surfaces and bulk structures of $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites.

The reducibility is one of the most important properties of CeO_2 -based materials. Figure 10 shows the H_2 -TPR profiles of $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites. Anatase TiO_2 does not exhibit an evident H_2 -reduction peak below 800 °C. Pure CeO_2 exhibits two broad reduction peaks at 452 and 528 °C, which correspond to the surface reduction features [19,35]. The formation of cubic fluorite $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions enhances the reducibility, and $\text{Ce}_{0.8}\text{Ti}_{0.2}\text{O}_2$ exhibits the best reducibility. The much poorer reducibility of cubic fluorite $\text{Ce}_{0.7}\text{Ti}_{0.3}\text{O}_2$ solid solution than of cubic fluorite $\text{Ce}_{0.8}\text{Ti}_{0.2}\text{O}_2$ solid solution can be associated with the formation of $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ on the outmost surface of $\text{Ce}_{0.7}\text{Ti}_{0.3}\text{O}_2$. However, with further decreases in x and growth of the $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ phase, the $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites exhibit much greater reducibilities, and the reduction temperatures increase. This implies that bulk $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ is more easily reduced than a $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ thin film supported on cubic fluorite $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions. When x is below 0.3, the reducibilities of the $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites become very poor; this can be attributed to the growth of anatase TiO_2 . The H_2 -TPR results show that the addition of Ti to CeO_2 can greatly promote its reducibility; cubic fluorite $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions and

Fig. 10. H_2 -TPR profiles of $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites.

$\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ exhibit good reducibilities at relatively low and high temperatures, respectively.

4. Conclusions

We have successfully elucidated the evolution of surface and bulk structures of $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites synthesized by coprecipitation methods. Selective chemisorption of MO and isoelectric point measurements were shown to be capable of characterizing the outmost surface structures of $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites, and the term “equivalent CeO_2 surface coverage” in an ML was introduced to describe their outmost surface compositions. The compositions of $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites are quite homogeneous between the bulk and the surface within the probe depth of XPS. In terms of the bulk phase structure, $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites with $x \geq 0.7$ form pure cubic fluorite solid solution phases, $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites with $0.3 < x < 0.7$ are mixtures of monoclinic $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ and a cubic fluorite solid solution, $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ forms a pure monoclinic phase, and $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites with $0 < x < 0.3$ are mixtures of anatase TiO_2 and monoclinic $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$. In terms of the outmost surface structures, the outmost surfaces of composites with $x \geq 0.8$ have homogeneously distributed Ti and Ce, but that of a cubic fluorite $\text{Ce}_{0.7}\text{Ti}_{0.3}\text{O}_2$ solid solution partially undergoes a cubic fluorite solid solution-to-monoclinic $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ phase transition; $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ on the outmost surface of $\text{Ce}_{0.7}\text{Ti}_{0.3}\text{O}_2$ grows from the surface to the bulk, and eventually pure $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ is formed. Cubic fluorite $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions exhibit good reducibilities at relatively low temperatures, whereas $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ exhibits good reducibility at relatively high temperatures. These results provide comprehensive and in-depth structural information on important $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites.

References

- [1] Trovarelli A, de Leitenburg C, Boaro M, Dolcetti G. *Catal Today*, 1999, 50: 353
- [2] Hadjiivanov K I, Klissurski D G. *Chem Soc Rev*, 1996, 25: 61
- [3] Fujishima A, Zhang X T, Tryk D A. *Surf Sci Rep*, 2008, 63: 515
- [4] Kakuta N, Ikawa S, Eguchi T, Murakami K, Ohkita H, Mizushima T. *J Alloys Compd*, 2006, 408: 1078
- [5] Zhu H Q, Qin Z F, Shan W J, Shen W J, Wang J G. *J Catal*, 2004, 225: 267
- [6] Qian K, Lü S S, Xiao X Y, Sun H X, Lu J Q, Luo M F, Huang W X. *J Mol Catal A*, 2009, 306: 40
- [7] Lin S S, Chen C L, Chang D J, Chen C C. *Water Res*, 2002, 36: 3009
- [8] Imamura S, Shono M, Okamoto N, Hamada A, Ishida S. *Appl Catal A*, 1996, 142: 279
- [9] Damyanova S, Pawelec B, Arishtirova K, Huerta M V M, Fierro J L G. *Appl Catal A*, 2008, 337: 86
- [10] Asahi R, Morikawa T, Ohwaki T, Aoki K, Taga Y. *Science*, 2001, 293: 269
- [11] Káspár J, Fornasiero P. *Catalysis by Ceria and Related Materials*. London: Imperial College Press, 2002
- [12] Trovarelli A. *Catal Rev-Sci Eng*, 1996, 38: 439
- [13] Preuss A, Gruehn R. *J Solid State Chem*, 1994, 110: 363
- [14] Reddy B M, Lakshmanan P, Khan A. *J Phys Chem B*, 2004, 108: 16855
- [15] Reddy B M, Khan A, Lakshmanan P, Aouine M, Lorient S, Volta J C. *J Phys Chem B*, 2005, 109: 3355
- [16] López T, Rojas F, Alexander-Katz R, Galindo F, Balankin A, Buljan A. *J Solid State Chem*, 2004, 177: 1873
- [17] Nakagawa K, Murata Y, Kishida M, Adachi M, Hiro M, Susa K. *Mater Chem Phys*, 2007, 104: 30
- [18] Yang S X, Zhu W P, Jiang Z P, Chen Z X, Wang J B. *Appl Surf Sci*, 2006, 252: 8499
- [19] Luo M F, Chen J, Chen L S, Lu J Q, Feng Z C, Li C. *Chem Mater*, 2001, 13: 197
- [20] Dutta G, Waghmare U V, Baidya T, Hegde M S, Priolkar K R, Sarode P R. *Chem Mater*, 2006, 18: 3249
- [21] Li Y, Xin Y, Li Q, Wang Z P, Zhang Z L, Zheng L R. *Environ Sci Technol*, 2012, 46: 9600
- [22] Fang J, Bi X Z, Si D J, Jiang Z Q, Huang W X. *Appl Surf Sci*, 2007, 253: 8952
- [23] Fang J, Bao H Z, He B, Wang F, Si D J, Jiang Z Q, Pan Z Y, Wei S Q, Huang W X. *J Phys Chem C*, 2007, 111: 19078
- [24] Sing K S W, Everett D H, Haul R A W, Moscou L, Pierotti R A, Rouquerol J, Siemieniowska T. *Pure Appl Chem*, 1985, 57: 603

Graphical Abstract

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Evolution of surface and bulk structures of $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ oxide composites

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The cubic fluorite solid solution-to-monoclinic $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ phase transition initially occurs on the outmost surface of a cubic fluorite $\text{Ce}_{0.7}\text{Ti}_{0.3}\text{O}_2$ solid solution and then grows from the surface to the bulk.

- [25] Chen L X, Rajh T, Wang Z, Thurnauer M C. *J Phys Chem B*, 1997, 101: 10688
- [26] Luca V, Djajanti S, Howe R F. *J Phys Chem B*, 1998, 102: 10650
- [27] Luca V, Hanley T L, Roberts N K, Howe R F. *Chem Mater*, 1999, 11: 2089
- [28] Parlebas J C, Khan M A, Uozumi T, Okada K, Kotani A. *J Electron Spectrosc, Relat Phenom*, 1995, 71: 117
- [29] Wu Z Y, Ouvrard G, Gressier P, Natoli C R. *Phys Rev B*, 1997, 55: 10382
- [30] Hu Z, Bertram S, Kaindl G. *Phys Rev B*, 1994, 49: 39
- [31] Wolczyr M, Kepinski L. *J Solid State Chem*, 1992, 99: 409
- [32] Stewart S J, Fernández-García M, Belver C, Mun B S, Requejo F G. *J Phys Chem B*, 2006, 110: 16482
- [33] Rodriguez J A, Hanson J C, Kim J Y, Liu G, Iglesias-Juez A, Fernández-García M. *J Phys Chem B*, 2003, 107: 3535
- [34] Moulder J F, Stickle W F, Sobol P E, Bomben K D. *Handbook of X-Ray Photoelectron Spectroscopy*. Eden Prairie, MN: Perkin-Elmer Corporation, 1992
- [35] Gennequin C, Lamallem M, Cousin R, Siffert S, Aïssi F, Aboukaïs A. *Catal Today*, 2007, 122: 301

Ce_xTi_{1-x}O₂复合氧化物表面结构和体相结构的演变

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摘要: 利用X射线衍射、N₂吸附等温线、X射线光电子能谱、X射线吸收谱、H₂-程序升温还原、甲基橙选择化学吸附和等电点测定等方法研究了共沉淀方法制备的一系列Ce_xTi_{1-x}O₂复合氧化物的结构。成功发展了甲基橙选择化学吸附和等电点方法研究Ce_xTi_{1-x}O₂复合氧化物的最外层表面结构,并定义了“等价CeO₂表面覆盖度”来描述Ce_xTi_{1-x}O₂复合氧化物的最外层表面结构。Ce_xTi_{1-x}O₂复合氧化物($x \geq 0.7$)形成立方萤石相固溶体,Ce_{0.3}Ti_{0.7}O₂表现出纯的单斜相,而其它复合氧化物表现出混合相。Ce_xTi_{1-x}O₂复合氧化物最外层表面结构的演变行为不同于其体相结构。Ce_{0.7}Ti_{0.3}O₂立方萤石相固溶体最外层表面已经部分形成了单斜相Ce_{0.3}Ti_{0.7}O₂,随Ce含量的降低,单斜相Ce_{0.3}Ti_{0.7}O₂从最外层表面向体相生长。Ce_xTi_{1-x}O₂复合氧化物立方萤石相固溶体和单斜相Ce_{0.3}Ti_{0.7}O₂分别在相对较低和较高的温度表现出好的还原性能。上述结果提供了全面和深层次的Ce_xTi_{1-x}O₂复合氧化物结构信息。

关键词: 二氧化钛; 氧化铈; 复合氧化物; 相结构; 表面结构; X射线吸收谱; 选择化学吸附; 等电点

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