

## Visible Light Absorption Characteristics of TiO<sub>2</sub>-CeO<sub>2</sub> Compound Oxides Prepared by Co-Precipitation Method

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**Abstract** A series of TiO<sub>2</sub>-CeO<sub>2</sub> prepared by co-precipitation method was characterized by XRD, UV-Vis DRS, SEM, EDX and N<sub>2</sub> gas adsorption. XRD results showed that the phase of TiO<sub>2</sub>-CeO<sub>2</sub> began to convert from anatase to cerianite at Ce 23.1% and average crystallite size of samples calculated by Scherrer's equation from anatase (101) and cerianite (111) was about 20nm and crystallinity of TiO<sub>2</sub>-CeO<sub>2</sub> compound oxide was the lowest at Ce 23.1%. UV-Vis DRS results showed that the light absorption onset of Ce 23.1% sample was shifted most by 475nm (*E<sub>g</sub>* 2.61eV). There are good relations between XRD intensity, specific surface area and band gap of samples. The maximum visible light absorption is presented in TiO<sub>2</sub>-CeO<sub>2</sub> compound oxide containing Ce 23.1%.

**Key words** TiO<sub>2</sub>-CeO<sub>2</sub> compound oxide, visible light absorption, band gap, N<sub>2</sub> gas adsorption

### Introduction

Titania is the most widely investigated as the photo-catalyst due to low cost, low toxicity and good chemical-thermal stability [1]. Ceria has oxygen storage capacity and ability to form a redox couple of Ce<sup>4+</sup> and Ce<sup>3+</sup>, but is not stable at high temperature [2–5]. Therefore, ceria and ceria-based materials are widely used in catalysis, fuel cells and other fields [5].

Because the radius of Ti<sup>4+</sup> (0.068nm) is smaller than that of Ce<sup>4+</sup> (0.094nm), Ti<sup>4+</sup> can be substituted for Ce<sup>4+</sup> to form Ce<sub>1-x</sub>Ti<sub>x</sub>O<sub>2</sub>, in which both Ce<sup>4+</sup> and Ti<sup>4+</sup> can be reduced to +3 states [3, 5–7]. The complication of TiO<sub>2</sub> and CeO<sub>2</sub> was found to facilitate the formation of small initial oxide crystallites and to improve thermal stability [2].

The compound oxides may significantly enhance the photo-catalytic efficiency by decreasing the recombination rate of the photo-generated electron-hole pairs and present potential applications in water splitting, organic decomposition, and photovoltaic devices [1].

Ce<sub>1-x</sub>Ti<sub>x</sub>O<sub>2</sub> (x 0~0.4) prepared by a single step solution combustion method was reduced by hydrogen to a larger extent as compared to CeO<sub>2</sub> or TiO<sub>2</sub> [6]. There was always plenty of cerium on surface of titania-ceria prepared by sol-gel method [8]. TiO<sub>2</sub>-CeO<sub>2</sub> compound oxides have been used in many catalytic reactions for partial oxidation of methane [2, 7], water-gas-shift(WGS) reaction [4], photo-oxidation reaction of high-strength liquid pollutants [9], selective hydrogenation of aldehyde [8], catalytic decomposition of methanol [10], CO oxidation [11] and so on, as catalyst or supports.

There is not a report on the visible light absorption characteristics of TiO<sub>2</sub>-CeO<sub>2</sub> compound oxides prepared by co-precipitation method up to the present.

In this paper, we investigated on the visible light absorption characteristics of TiO<sub>2</sub>-CeO<sub>2</sub> compound oxide prepared by co-precipitation method.

## 1. Experiment

### 1.1. TiO<sub>2</sub>-CeO<sub>2</sub> compound oxide preparation

Compound oxides were prepared by co-precipitation method. After heating the aqueous solution of TiCl<sub>4</sub> (A.R.) dissolved in 100mL of deionized ice water up to 70°C, certain amount of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (A.R.) was added in this solution. The solution was adjusted with aqueous ammonia solution (A.R., 25~28%) by pH 10 prior to maintaining at 70°C for 3h. In all processes, this system was kept stirring.

The precipitates washed enough with deionized water were dried at 110°C overnight and calcined in air at 500°C for 3h after heating up to 500°C with a heating rate of 10°C/min. In prepared samples, the Ce contents, indicating amount fractions of metal atoms (Ce/(Ti+Ce)), were 5.7, 10.7, 23.1, 28.6, 37.5 and 44.4%, respectively.

### 1.2. Characterization

The powder X-ray diffraction patterns (XRD) were recorded on the powder diffractometer ("Rigaku D/Max-rC") using CuK $\alpha$  radiation(40kV and 100mA) in the 2 $\theta$  range of 10~80° with a 2 $\theta$  step size of 0.01° and a step time of 10s.

The UV-visible diffuse reflectance spectra (UV-Vis DRS) of samples were measured on UV-Vis spectrometer ("Shimadzu UV-2201"). The band gaps of samples were calculated by the method of the previous research [12] using the wavelength of absorption onset.

The specific surface areas were determined by N<sub>2</sub> gas adsorption on the automated gas sorption analyzer ("Quantachrome autosorb-iQ-c") after pretreatment of about 100mg samples in vacuum at 250°C, 3h.

The SEM image and EDX spectrum of Ce 23.1% sample was observed using scanning electron microscope ("JSM-6610A") working at 60kV together equipped with electron dispersive X-ray spectrum analyzer.

## 2. Results and Discussion

### 2.1. X-Ray diffraction

XRD patterns of the samples were shown in Fig. 1.

As shown in Fig. 1, CeO<sub>2</sub> and TiO<sub>2</sub> had the crystalline structures of cerianite [11] and anatase [9, 11], respectively. The samples with Ce up to 23.1% had crystalline structure of anatase but not diffraction peak of cerianite and the diffraction intensities decreased with Ce content increase.

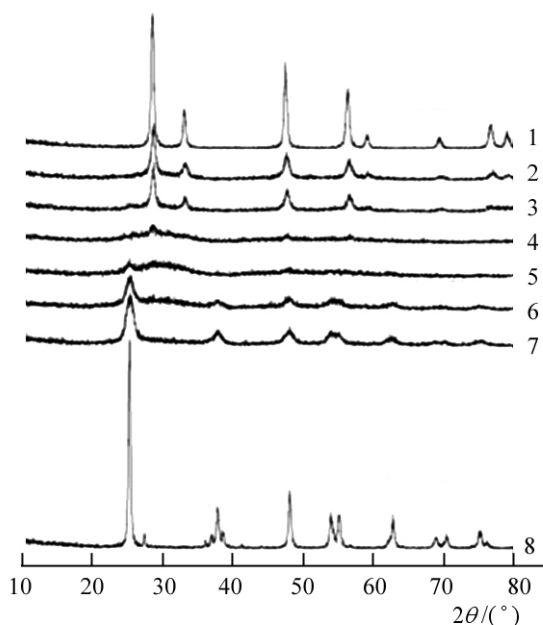


Fig. 1. XRD profiles of  $\text{TiO}_2\text{-CeO}_2$  compound oxides

1— $\text{CeO}_2$ , 2—Ce 44.4%, 3—Ce 37.5%, 4—Ce 28.6%,  
5—Ce 23.1%, 6—Ce 10.7%, 7—Ce 5.7%, 8— $\text{TiO}_2$

Considering the previous researches [9, 11] and the small Ce contents in these samples, it is estimated that  $\text{CeO}_2$  either is presented as an amorphous structure or has the crystalline size smaller than 3nm to disperse finely on  $\text{TiO}_2$ .

Conversely, the samples with Ce above 28.6% had crystalline structure of cerianite but not diffraction peak of anatase and the diffraction intensities increase with Ce content increase.

The particle sizes of the samples, calculated by Scherrer's equation from anatase (101) and cerianite (111), were in 12.2~27.4nm and the smallest particle size was 12.2nm presented in Ce 23.1% sample. Considering the previous researches [12, 13], it is estimated that in these samples, the crystallinity may increase and surface area, due to particle size increaser than

Ce 23.1% sample, may decrease according as Ce content increases.

From XRD results, it is estimated that due to the synergistic interaction, the complication of  $\text{TiO}_2$  and  $\text{CeO}_2$  leads to change of the crystal structures of  $\text{CeO}_2$  and  $\text{TiO}_2$ , and to improvement of dispersibility, that the formation mechanism of  $\text{TiO}_2\text{-CeO}_2$  compound oxides in samples up to Ce 23.1% differs from that in samples above Ce 28.6%.

Further, it is suggested that the Ce 23.1% sample, in which diffraction intensity and particle size are the smallest, is capable to show the best light absorption characteristic and the largest specific surface area.

## 2.2. Scanning electron microscope and electron dispersive X-ray spectrum

SEM image of the Ce 23.1% sample, shown in Fig. 2, indicated that the irregular particles with size above  $1\mu\text{m}$  were obtained via the preparation of  $\text{TiO}_2\text{-CeO}_2$  compound oxide using co-precipitation method. Comparing with the particle size calculated by Scherrer's equation, it is reasonable that particles of the sample are preferred to aggregate to form larger secondary particles.

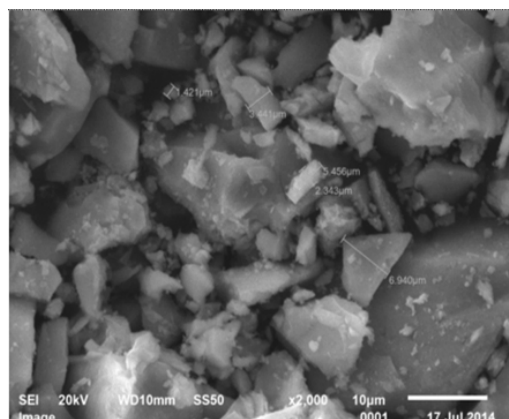


Fig. 2. SEM image of Ce 23.1% sample

EDX spectrum of the Ce 23.1% sample, shown in Fig. 3, indicated that the product was made up of Ti, O and Ce.

The Ce content was calculated to be 25.0%, which was somewhat larger than the Ce content in preparation process. Considering XRD results and the previous research[8], it is estimated that most of Ce are covered on  $\text{TiO}_2$  surface and formed compound oxide.

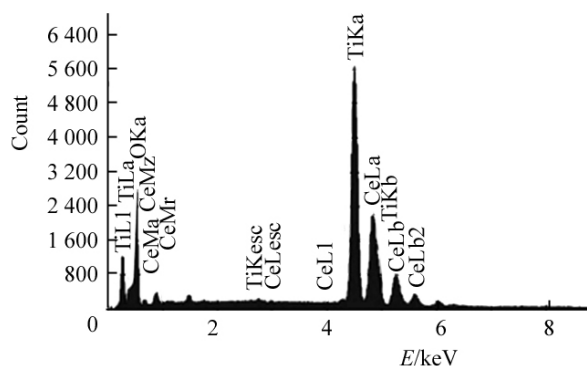


Fig. 3. EDX spectrum of Ce 23.1% sample

### 2.3. UV-Visible diffuse reflectance spectroscopy

UV-VIS DRS spectra of the samples, shown in Fig. 4, indicated that the absorption onset in all compound samples were shifted more toward visible light region than that in pure  $\text{TiO}_2$  and  $\text{CeO}_2$ , maintaining UV absorption intensities.

On the other hand, the absorption regions in samples up to Ce 23.1% were broaden visible light region with increase in Ce content but in samples above Ce 28.6%, there was no remarkable change.

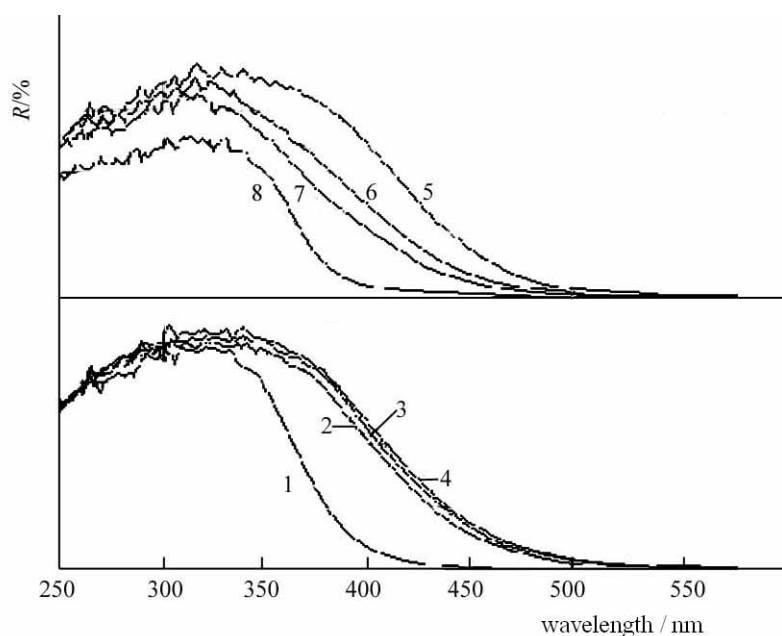


Fig. 4. UV-Vis DRS of  $\text{TiO}_2\text{-CeO}_2$  compound oxides  
1— $\text{CeO}_2$ , 2—Ce 44.4%, 3—Ce 37.5%, 4—Ce 28.6%, 5—Ce 23.1%,  
6—Ce 10.7%, 7—Ce 5.7%, 8— $\text{TiO}_2$

It is found that  $\text{TiO}_2\text{-CeO}_2$  compound oxides have visible light absorption characteristics due to the structure formed by strong synergistic interaction of  $\text{TiO}_2$  with  $\text{CeO}_2$  and that the interaction

intensity gets stronger as Ce content increases up to 23.1% and has the maximum visible light absorption (absorption onset 475nm) in Ce content 23.1% and in samples above Ce 28.6%, have no sufficient changes.

Considering XRD results and the previous research [1], it is estimated that visible light absorption characteristic appeared in not cerianite but anatase crystalline type and the lower the crystallinity is, the more the light absorption is broaden toward visible light region and that these  $\text{TiO}_2\text{-CeO}_2$  compound oxides may decrease the recombination rate of the photo-generated electron-hole pairs.

#### 2.4. $\text{N}_2$ gas adsorption isotherms

$\text{N}_2$  gas adsorption isotherms of samples up to Ce 23.1%, shown in Fig. 5, revealed that these samples took typical IV-type isotherms indicating the presence of mesopores in the  $\text{TiO}_2\text{-CeO}_2$  compound oxides.

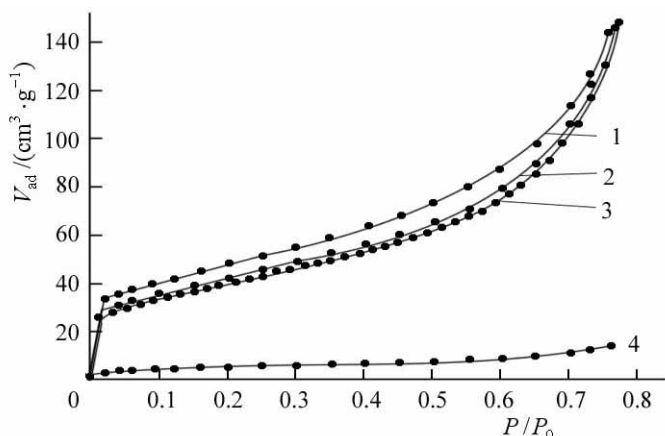


Fig. 5.  $\text{N}_2$  gas adsorption isotherms of  $\text{TiO}_2\text{-CeO}_2$  compound oxides  
1—Ce 23.1%, 2—Ce 10.7%, 3—Ce 5.7%, 4— $\text{TiO}_2$

The average poros size of samples was about 7nm and scarcely changed with Ce content.

It is estimated that during preparation, the porosity is scarcely changed and the size of particles gets smaller with increasing Ce content. The result is in agreement with XRD results.

#### 2.5. The relation between XRD intensity, band gap and specific surface area

Fig. 6, 7 are presented the relations of band gap ( $E_g$ ), XRD relative intensity (intensity of anatase (101) was 100) and specific surface area determined by BET method with Ce content.

Fig. 8 is presented the relations of  $E_g$  and specific surface area with XRD relative intensity.

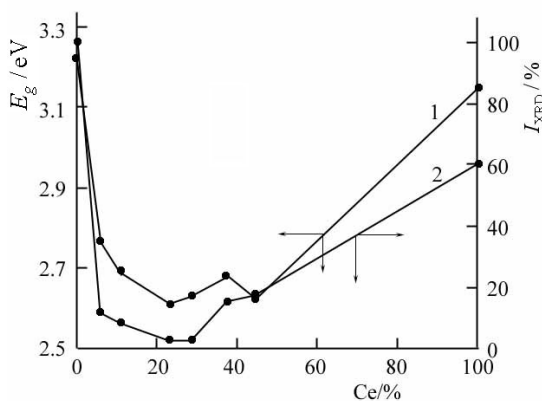


Fig. 6. The relations between  $E_g$  (1), XRD relative intensity(2) and Ce content

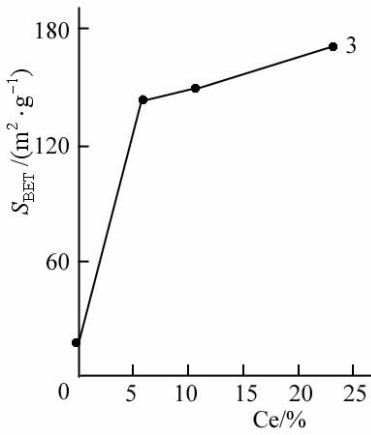


Fig. 7. The relation between specific surface area and Ce content

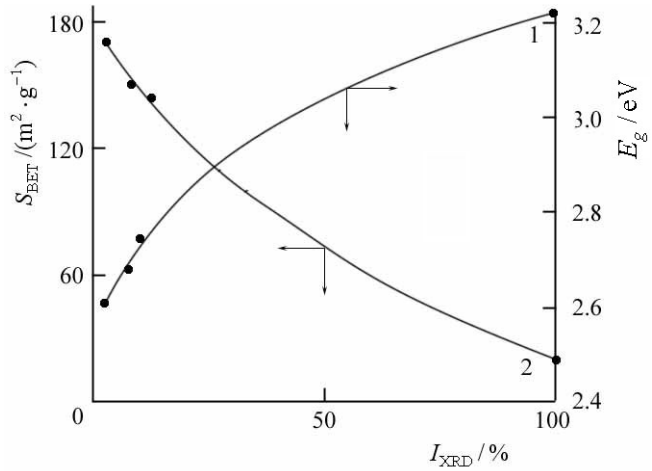


Fig. 8. The relations between  $E_g$  (1), specific surface area(2) and XRD relative intensity in samples below Ce 23.1%

As shown in Fig. 6, 7, with increase in Ce content up to 23.1%,  $E_g$  and XRD relative intensity decreased regularly but specific surface area increased regularly. Conversely, in above Ce 28.6%,  $E_g$  and XRD intensity increased irregularly. It is expected that specific surface area in samples above Ce 28.6% may be smaller than in sample with Ce 23.1%. Considering XRD intensity, UV-VIS DRS result and the previous research [13, 14], lower crystallinity and stronger synergistic interaction are followed by narrower band gap and larger specific surface area.

As shown in Fig. 8, both relations of  $E_g$  and specific surface area with XRD intensity in samples up to Ce 23.1% were well fitted by function  $y=a+b\ln(x+c)$ .

The estimated results were listed in table.

Table. Function fitting results

$y$	$x$	$a$	$b$	$c$	$r_2$
$E_g/\text{eV}$	$I_{\text{XRD}}/\%$	1.74eV	0.313eV	13.3%	0.995 8
$S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$	$I_{\text{XRD}}/\%$	$584.0\text{m}^2 \cdot \text{g}^{-1}$	$-115.5\text{m}^2 \cdot \text{g}^{-1}$	33.5%	0.998 4

Table shows that the visible light absorption of the samples is closely related to synergistic interaction of TiO<sub>2</sub> and CeO<sub>2</sub> and the crystallinity of compound oxides.

## Conclusion

In the preparation process of TiO<sub>2</sub>-CeO<sub>2</sub> compound oxides, due to the strong synergistic interaction of TiO<sub>2</sub> and CeO<sub>2</sub>, the crystalline structures of the samples are changed and light absorption region is broaden toward visible light region. The sample with Ce 23.1% has the best visible light absorption characteristic.

## References

- [1] M. Pelaez et al.; Applied Catalysis, B 125, 331, 2012.
- [2] C. B. Karin et al.; Catalysis Communications, 18, 121, 2012.
- [3] M. F. Luo et al.; Chemical Materials, 13, 197, 2001.
- [4] G. Zhou et al.; Applied Catalysis, A 335, 153, 2008.
- [5] Q. Yuan et al.; Journal of Colloid and Interface Science, 335, 151, 2009.
- [6] G. Dutta et al.; Chemical Materials, 18, 3249, 2006.
- [7] Y. Zhang et al.; Chemical Engineering Journal, 121, 115, 2006.
- [8] J. Rynkowski et al.; Applied Catalysis, A 203, 335, 2000.
- [9] D. Wilson et al.; Applied Catalysis, B 123–124, 273, 2012.
- [10] A. S. Karakoti et al.; Applied Catalysis, A 388, 262, 2010.
- [11] H. Q. Zhu et al.; Journal of Catalysis, 225, 267, 2004.
- [12] J. C. Sin et al.; Journal of Colloid and Interface Science, 401, 40, 2013.
- [13] X. Y. Wang et al.; Applied Catalysis, B 86, 166, 2009.
- [14] K. K. Akurati et al.; Solid State Sciences, 9, 247, 2007.