

An investigation on photocatalytic activities of mixed TiO₂-rare earth oxides for the oxidation of acetone in air

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Abstract

The photocatalytic activities of the mixtures of TiO₂ (P25) with three rare earth oxides were investigated. The effects of the rare earth oxide contents and calcination temperature on the photocatalytic activities were studied. The results reveal that the mixtures of TiO₂ with La₂O₃ (0.5 wt.%) or Y₂O₃ (0.5 wt.%) calcined at 700°C or 650°C exhibit higher photoactivity than pure TiO₂ (P25) for the oxidation of acetone. On the other hand, the mixtures of TiO₂ with CeO₂ have lower photoactivity than pure TiO₂. Experimental results of polycrystalline X-ray diffraction, photoexcited transient absorption decay and zeta potential measurements show that the presence of these rare earth oxides can inhibit anatase to rutile transformation at elevated temperatures. The lower photocatalytic activity of TiO₂/CeO₂ mixtures can be explained by the fast recombination rate of photogenerated electron-hole pairs and high isoelectric point in terms of pH value. The preparation method of these mixtures is also described. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Over the past 10 years, the semiconductor TiO₂ as a photocatalyst has become the focus of numerous studies owing to its attractive characteristics and applications in the treatment of environmental contaminants [1]. Complete mineralization of a broad variety of organic compounds containing unsaturated bonds by TiO₂ photocatalysis has been reported [2,3]. Despite of its great potential, the fast recombination rate of photogenerated electron-hole pairs on the surface or in the lattice of TiO₂ hinders the commercialization of this technology [2]. There is always a high level of interest in improving the photoactivity of TiO₂ for the degradation of VOCs in water and air. Recently, enhanced photocatalysis over binary metal oxides and transition metal-doped TiO₂ has been reported [4–8]. Choi et al. [7] have done a comprehensive investigation on the photocatalytic reactivity of transition metal-doped TiO₂ for the oxidation and reduction of VOCs in aqueous solutions. There are also reports on the use of binary metal oxides as photocatalysts, such as the TiO₂/ZrO₂, TiO₂/WO₃ and TiO₂/MoO₃ systems [4,5]. Among the impressive number of publications, however, we could

not find any reference on gaseous phase photocatalytic degradation using mixed TiO₂-rare earth oxides.

In this study, the photocatalytic activities of mixtures of Y₂O₃, La₂O₃ or CeO₂ with TiO₂ for the oxidation of acetone in air were determined. We have also characterized these mixtures with polycrystalline X-ray diffraction, transient absorption decays and isoelectric point measurement.

2. Experimental

2.1. Preparation of photocatalysts

YCl₃ (>99%), LaCl₃ (>99%), CeCl₂ (>99%) and TiO₂ (Degussa P25) known as a commonly used photocatalyst were used as starting materials. The TiO₂-rare-earth oxide mixtures were prepared by the following method. TiO₂ was placed in water to form a homogenous suspension. A colloid of the rare earth hydroxide was produced by the hydrolysis of the rare earth chloride in desired ratio in the presence of ammonia, followed by centrifugation and rinsing with distilled water. The procedure of centrifugation and washing was repeated several times until the pH of the washing became neutral and no Cl⁻ ions in the washing were detected by reacting with a AgNO₃ solution. The suspension

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of TiO_2 was mixed with the colloid of rare earth hydroxide. Under vigorous stirring, the mixed suspension was heated on a hot plate to remove water. The resulting precipitates were calcined in air at different temperatures for 3 h.

2.2. Measurements of photocatalytic activity

Photocatalytic activity experiments of these mixtures of TiO_2 with the rare earth oxides for the oxidation of acetone in air were performed at ambient temperature using a 7000 ml reactor. The weight of the catalysts used in each experiment was kept at about 0.26 g. Fresh catalysts pretreated in an oven at 100°C for 2 h were used for each run.

A small amount of acetone was injected into the reactor. A Photoacoustic IR Multi-gas Monitor (INNOVA Air Tech Instruments Model 1312) was used to monitor the concentrations of acetone, carbon dioxide and water in the reactor. The acetone vapor was allowed to reach adsorption equilibrium with the catalysts in the reactor before an experiment. The acetone concentration remained constant until the reactor was illuminated by a 15 W 365 nm UV lamp (Cole-Parmer Instrument). The initial concentration of acetone after reaching adsorption equilibrium was 400 ppm. The starting humidity in the reactor was controlled at 12 ± 0.2 vol.%, and the initial temperature was maintained at $25 \pm 1^\circ\text{C}$. The degradation rate was the average amount of acetone destroyed per minute during the 60-min period of reaction.

2.3. Characterization of photocatalysts

The polycrystalline X-ray diffraction patterns and crystal size of these mixtures were obtained with a Philips MPD18801 diffractometer using $\text{Cu-K}\alpha$ radiation, and single-crystal silicon was used as the standard to determine instrumental peak broadening.

2.4. Measurement of the isoelectric point

Zeta potential measurements were carried out on a Brookhaven Zeta Plus analyser. The suspension fluid was a 1 mM aqueous solution of potassium nitrate. The concentration of catalyst in this suspension was 1 mg ml^{-1} . The pH value of the suspension was adjusted with the addition of 0.1 M nitric acid and 0.1 M potassium hydroxide solutions.

2.5. Transition absorption experiments

Samples for the laser flash photolysis experiments were prepared by the addition of aqueous suspension of catalysts in a quartz cell ($10 \text{ mm} \times 1 \text{ mm}$). The samples were excited with pulses from a Q-switch frequency-tripled Nd:YAG laser (355 nm, 5 ns FWHM). Excitation pulse energies were $\sim 10 \text{ mJ/pulse}$. Single-wavelength transient absorption kinetics was observed using a CW He-Ne laser as a source probe. All the decay kinetics was monitored by following the trapped charge carrier absorption at 543.5 nm.

3. Results

3.1. Photocatalytic activity for the oxidation of acetone

Fig. 1 shows the measured rate of photocatalytic reaction for the oxidation of acetone as a function of rare earth oxide contents in the mixtures. Fig. 2 displays the effects of calcination temperature on the photoactivity. As shown in Fig. 1, the mixtures of La_2O_3 or Y_2O_3 with TiO_2 have an optimum content at 0.5 wt.%, while the mixtures of CeO_2 with TiO_2 have a lower photocatalytic activity than pure TiO_2 over the content range measured. From Fig. 2, the photocatalytic activity of $\text{TiO}_2/\text{La}_2\text{O}_3$ or Y_2O_3 mixtures increases gradually

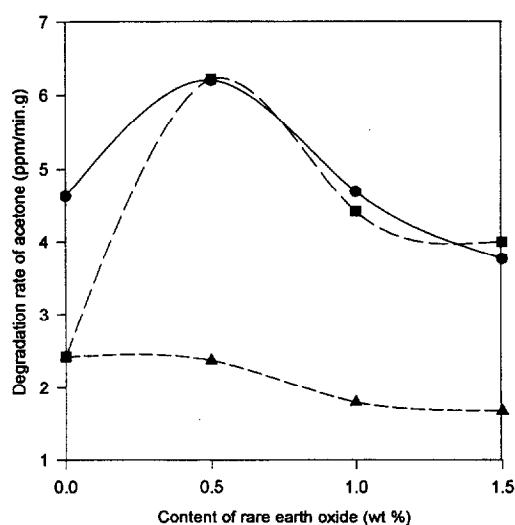


Fig. 1. Degradation rate of acetone as a function of rare earth oxide content in mixture. (●) $\text{TiO}_2/\text{La}_2\text{O}_3$ calcined at 650°C ; (■) $\text{TiO}_2/\text{Y}_2\text{O}_3$ calcined at 700°C and (▲) $\text{TiO}_2/\text{CeO}_2$ calcined at 700°C .

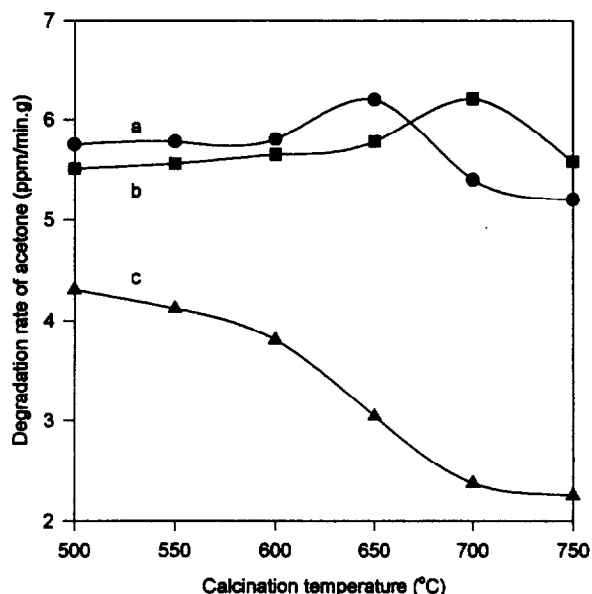


Fig. 2. The effect of calcination temperature on the photocatalytic activity. (a) $\text{TiO}_2/\text{La}_2\text{O}_3$ (0.5 wt.%); (b) $\text{TiO}_2/\text{Y}_2\text{O}_3$ (0.5 wt.%); and (c) $\text{TiO}_2/\text{CeO}_2$ (0.5 wt.%).

with increasing calcination temperature until $T=650^{\circ}\text{C}$ or 700°C , and then begins to drop; the photoactivity of $\text{TiO}_2/\text{CeO}_2$ mixtures decreases with an increase of the calcination temperature. For comparison, the degradation rate of acetone on the surface of TiO_2 (P25 Degussa) without heat treatment was found to be 5.31 ppm/min g.

3.2. Results of XRD

The polycrystalline X-ray diffraction results of TiO_2 /rare earth oxide mixtures reveal that the presence of these rare earth oxides can inhibit the anatase to rutile phase transformation during calcination even for the mixtures calcined at moderately high temperatures ($\leq 650^{\circ}\text{C}$ for $\text{TiO}_2/\text{La}_2\text{O}_3$; $\leq 700^{\circ}\text{C}$ for $\text{TiO}_2/\text{Y}_2\text{O}_3$ or CeO_2), they have the same phase constitutions as their precursor TiO_2 (P25 Degussa). The percent rutile in these mixtures (rare earth oxide content = 0.5 wt.%) calcined at different temperatures are shown in Table 1. The crystal size was determined from the diffraction peak broadening with the following equation:

$$D = K\lambda / (\beta_c - \beta_s) \cos \theta$$

where D is the crystal size of the catalyst; λ is the X-ray wavelength; β_c and β_s are the FWHM of the catalyst and the standard (single-crystal silicon), respectively; the number $K=0.89$ is a coefficient; θ is the diffraction angle. On the other hand, the X-ray diffraction peaks of crystal plane (101) and (200) in anatase are selected to determine the lattice parameter of TiO_2 in mixture. The lattice parameters are obtained by using the following equations:

Bragg's law:

$$d_{(hkl)} = \lambda / 2 \sin \theta, \text{ and } d_{(hkl)}^{-2} = h^2 a^{-2} + k^2 b^{-2} + l^2 c^{-2}$$

Table 1
Percent rutile of TiO_2 in the mixtures at different temperatures

Mixture	500°C	650°C	700°C	750°C
$\text{TiO}_2/\text{La}_2\text{O}_3$	14%	14%	28%	32%
$\text{TiO}_2/\text{Y}_2\text{O}_3$	14%	14%	14%	28%
$\text{TiO}_2/\text{CeO}_2$	14%	14%	14%	29%

Each mixture contains 0.5 wt.% of rare earth oxide.

Table 2
Lattice parameters, cell volume and crystal size of TiO_2 in the mixture

Mixture	$a=b$ (Å)	c (Å)	Cell volume (Å ³)	Crystal size (nm)
TiO_2 (P25)	3.780	9.332	133.35	25.4
$\text{TiO}_2/\text{La}_2\text{O}_3$	3.783	9.279	132.79	25.0
$\text{TiO}_2/\text{Y}_2\text{O}_3$	3.777	9.387	133.91	24.6
$\text{TiO}_2/\text{CeO}_2$	3.783	9.279	132.79	25.8

The content of rare earth oxide in all above mixtures is 0.5 wt.%, and the calcination temperatures are 650°C for $\text{TiO}_2/\text{La}_2\text{O}_3$ and 700°C for $\text{TiO}_2/\text{Y}_2\text{O}_3$ and $\text{TiO}_2/\text{CeO}_2$.

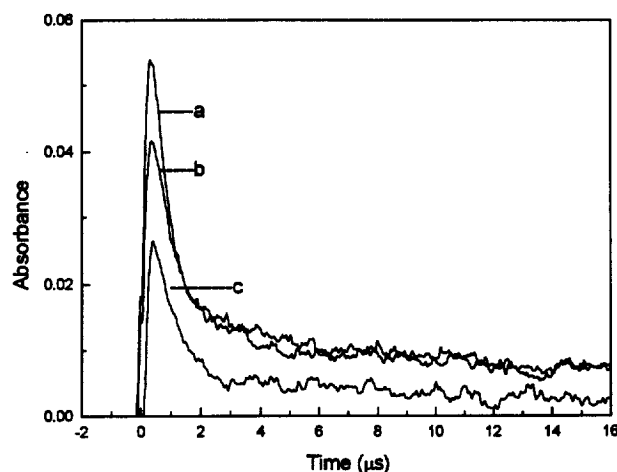


Fig. 3. Transient absorption decays observed at 543.5 nm in the microsecond time scale for (a) $\text{TiO}_2/\text{La}_2\text{O}_3$ (0.5 wt.%) calcined at 650°C ; (b) $\text{TiO}_2/\text{Y}_2\text{O}_3$ (0.5 wt.%) calcined at 700°C and (c) $\text{TiO}_2/\text{CeO}_2$ (0.5 wt.%) calcined at 700°C .

where $d(hkl)$ is the distance between crystal planes of (hkl) ; λ is the X-ray wavelength; θ is the diffraction angle of crystal plane (hkl) ; hkl is the crystal plane index; a , b and c are lattice parameters (in anatase form, $a = b \neq c$).

The results of lattice parameter and crystal size determined for these mixtures were shown in Table 2.

3.3. Results of isoelectric point and transient absorption decay measurements

The zeta potentials of $\text{TiO}_2/\text{La}_2\text{O}_3$ (0.5 wt.%) calcined at 650°C , $\text{TiO}_2/\text{Y}_2\text{O}_3$ (0.5 wt.%) calcined at 700°C and $\text{TiO}_2/\text{CeO}_2$ (0.5 wt.%) calcined at 700°C at different pH values were determined. According to the results of the zeta potential determined, the three mixtures have isoelectric points at pH = 5.08, 5.08 and 5.92, respectively.

Fig. 3 shows the transient absorption decay spectrum of the three mixtures. It shows that the lifetime of electron-holes photogenerated by UV illumination is longer in the mixtures of $\text{TiO}_2/\text{La}_2\text{O}_3$ (0.5 wt.%) calcined at 650°C and $\text{TiO}_2/\text{Y}_2\text{O}_3$ (0.5 wt.%) calcined at 700°C than in the mixture of $\text{TiO}_2/\text{CeO}_2$ (0.5 wt.%) calcined at 700°C .

4. Discussion

4.1. Effects of calcination temperature and rare earth oxide contents on the photocatalytic activity

When pure TiO_2 is heated to 650°C , the thermodynamically favoured rutile content begins to increase (as shown in Fig. 4). Although the presence of rare earth oxides may inhibit the anatase to rutile phase transformation, rutile formation is inevitable at calcination temperatures much higher

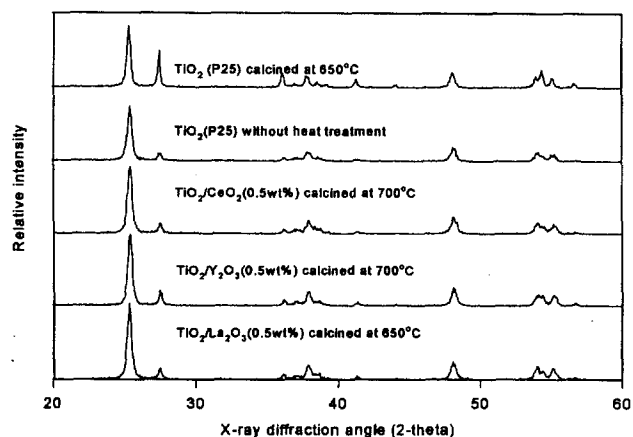


Fig. 4. Polycrystalline X-ray diffraction patterns of the three mixtures and pure TiO_2 (P25).

than 650°C or 700°C (see Table 1). It is well known that rutile phase is less effective than anatase as a photocatalyst for the oxidation of volatile organic compounds [1,9–11]. Therefore, it is not surprising that $\text{TiO}_2/\text{La}_2\text{O}_3$ calcined at 700°C and $\text{TiO}_2/\text{Y}_2\text{O}_3$ calcined at 800°C have lower photoactivity than those calcined at lower temperatures.

A major requirement of a good semiconductor photocatalysts for organic compound degradation is that the redox potential of the $\text{H}_2\text{O}/\bullet\text{OH}$ couple ($\text{OH}^- \leftrightarrow \bullet\text{OH} + e^-$; $E^\circ = -2.8 \text{ V}$) must lie within the bandgap domain of the material [12]. The band-gap energies of the rare earth oxides used in the experiment are not sufficient for initiating photocatalytic reaction after UV illumination [13]. Excess amounts of rare earth oxide covering the surface of TiO_2 would result in low photoactivity. Therefore it is not a surprise that the mixed TiO_2 -rare earth oxides with more than 0.5 wt.% rare earth content show poor photocatalytic activity. The decrease in the photoactivity of $\text{TiO}_2/\text{CeO}_2$ contents and calcination is discussed in Section 4.2.

4.2. Effects of interaction between TiO_2 and the rare earth oxides on photocatalytic activity

As shown in Fig. 1, both $\text{TiO}_2/\text{La}_2\text{O}_3$ and $\text{TiO}_2/\text{Y}_2\text{O}_3$ mixtures exhibit optimum photocatalytic activity at 0.5 wt.% rare earth content. On the other hand, the mixtures containing CeO_2 show much lower activity over the concentration range studied. Knowing that pure rare earth oxides do not possess photocatalytic oxidation properties, such variation in activity must be due to the differences in interactions between rare earth oxides and TiO_2 . Lattice parameters were measured to determine whether the rare earth elements could enter the TiO_2 lattice resulting in the formation of solid solutions. Table 2 shows that the lattice parameters of TiO_2 in these mixtures are virtually the same as that of pure TiO_2 , meaning that those rare earth atoms could not enter the TiO_2 lattice. This is not a surprise considering the relatively large difference in the

ion radii of rare earth elements and Ti^{4+} . The ionic radius of Ti^{4+} is only 0.68 Å but Y^{3+} , La^{3+} and Ce^{4+} are 0.93 Å, 1.15 Å and 1.02 Å, respectively [14]. The bulky rare earth ions cannot substitute Ti^{4+} to form stable solid solutions.

The interactions between TiO_2 and the rare earth oxides may be better explained by the crystallization behavior of TiO_2 in these mixtures. As shown in the X-ray diffraction patterns in Fig. 4, TiO_2 calcined at 650°C is composed of a significant amount of rutile phase. However, this anatase-to-rutile transformation is somehow inhibited in the mixtures. This may be due to the stabilization of the anatase phase by the surrounding rare earth oxides through the formation of Ti–O–rare earth element bonds. At the interface, titanium atoms substitute for the rare earth elements in the lattice of rare earth oxides to form tetrahedral Ti sites (in La_2O_3 and Y_2O_3) and octahedral Ti sites (in CeO_2). The interaction between the different tetrahedral Ti atoms or between the tetrahedral Ti and octahedral Ti inhibits the phase transformation to rutile. A similar explanation was offered for the $\text{TiO}_2/\text{SiO}_2$ mixture [6].

For the $\text{TiO}_2/\text{La}_2\text{O}_3$ and $\text{TiO}_2/\text{Y}_2\text{O}_3$ mixtures, Ti^{4+} replaces a rare earth metal ion with a +3 oxidation state and creates a charge imbalance. The charge imbalance must be satiated, therefore more hydroxide ions would be adsorbed on the surface for charge balance. These hydroxide ions on the surface can accept holes generated by UV illumination to form hydroxyl radicals which oxidize adsorbed molecules. Thus, the photogenerated electron-hole recombination can be prevented.

On the other hand, the mixture of $\text{TiO}_2/\text{CeO}_2$ does not have such a charge imbalance and therefore has less hydroxyl groups on its surface. Although it has been reported that the photogenerated electrons trapped on TiO_2 surface may result in the formation of Ti^{3+} centers [15,16], we believe that the formation of Ti^{3+} on the surface of $\text{TiO}_2/\text{CeO}_2$ mixtures is unlikely. This is because the Ti^{4+} at the interface enters the CeO_2 lattice to substitute for Ce^{4+} , and the oxidation state of Ti is locked by the 8 coordinated oxygen atoms. We think that the lack of electron scavengers (surface Ti^{4+}) and hole traps (surface hydroxyl groups) is responsible for its more rapid recombination rate of electron-hole, which leads to lower photocatalytic activity for the oxidation of acetone. With the increasing calcination temperature, such effect is enhanced since the interaction between TiO_2 and CeO_2 becomes stronger at high calcination temperature.

The results of zeta potential measurements on the three mixtures show the mixtures of $\text{TiO}_2/\text{La}_2\text{O}_3$ and $\text{TiO}_2/\text{Y}_2\text{O}_3$ have lower isoelectric points in terms of pH value than the mixture of $\text{TiO}_2/\text{CeO}_2$. The lower isoelectric point means there are more hydroxide ions on the surface of catalyst. Hydroxide ions act as hole traps that prevent electron-hole recombination and thus create a higher quantum yield. The results of transient absorption decay experiments on the three mixtures are in good agreement with that of isoelectric point measurements.

5. Conclusions

The mixtures of TiO_2 with La_2O_3 or Y_2O_3 after calcination at high temperature were shown to have higher photocatalytic activities than pure TiO_2 (P25) for the oxidation of acetone, while the mixture of TiO_2 with CeO_2 had lower activity. The presence of these rare earth oxides inhibits anatase to rutile phase transformation in TiO_2 . The activity differences are due to the change in the amount of surface hydroxyl groups resulting from the interaction between the rare earth oxides and TiO_2 . This explanation is consistent with the results of X-ray diffraction, zeta potential and transient absorption decay measurements.

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