

Ti_{1-x}Zr_xO₂ Solid Solutions for the Photocatalytic Degradation of Acetone in Air

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Solid solutions of Ti_{1-x}Zr_xO₂ (0.00 < x ≤ 0.10) exhibit higher photocatalytic activity than pure anatase TiO₂ for the degradation of acetone in air. The activity increases with increase of zirconium substitution in the TiO₂ lattice until nominal x = 0.075. The results of polycrystalline X-ray diffraction analysis, BET surface area, XPS, and zeta potential measurements show that the increase in activity is related to changes in the lattice parameters and cell volume. A mechanism is proposed suggesting that lattice O²⁻ and O⁻ species ionosorbed on surface are responsible for the increased activity. The synthesis of the solid solutions and the effects of zirconium addition on phase constitution, lattice parameters, BET surface area, and surface hydroxyl groups are also discussed.

Introduction

Semiconductor photocatalysis has received a lot of attention as a promising technique for the degradation of inorganic and organic pollutants in air and water.¹ Titanium dioxide in the anatase form appears to be the most practical photocatalyst among the semiconductors for widespread environmental application. To enhance the quantum efficiency of TiO₂, modifications have been introduced to the crystalline matrix by selective doping of foreign metal ions.²

The use of binary metal oxides as photocatalysts for photo-oxidation of volatile organic compounds is not entirely new. As early as 1985, Kakuta et al. reported that the photocatalytic activity of a ZnS·CdS/SiO₂ mixture was higher than those of its individual components.³ Recently, Anderson et al., Fu et al., Do et al., and Papp et al. have investigated the TiO₂/Al₂O₃, TiO₂/SiO₂, TiO₂/ZrO₂, TiO₂/WO₃, and TiO₂/MoO₃ systems.⁴⁻⁷ They found that these binary metal oxide systems could enhance the photocatalytic degradation rates of some volatile organic compounds in the environment, such as salicylic acid in water and ethylene in air. They proposed that the increase in photocatalytic activity of these binary mixtures was caused by increased surface acidity.

Besides the binary metal oxides, size-quantized transition-metal-doped TiO₂ as photocatalyst also attracts a greater deal of attention. The use of size-quantized semiconductors to increase photoefficiencies was first reported over a decade ago.⁸ Subsequent studies also revealed the positive influence of size quantization and doped transition metal upon photocatalytic properties.⁹⁻¹¹ More recently, Choi et al. have conducted systematic studies on transition-metal ions doping in quantum-sized TiO₂ colloids by measuring their photoreactivities and transition charge carrier recombination dynamics.¹² Their results suggest that the activity of doped TiO₂ photocatalysts appears to be a complex function of the dopant concentration, the energy level of dopants within TiO₂ lattice, their d electronic configurations, the distribution of dopants, the electron donor concentration, and the light intensity. A review paper by Hoffmann et

al. indicates that the mechanisms of doped quantum-sized TiO₂ are not well understood.² One of the unanswered questions is whether the transition-metal ions are located primarily on the surface or in the lattice.

We have recently discovered that solid solutions with the composition of Ti_{1-x}V_xO₂ are effective photocatalysts for the degradation of acetone.¹³ When the +5 vanadium ions replace the +4 titanium in the lattice, a positive charge imbalance is created. This attracts hydroxide ions onto the photocatalyst's surface, generating highly reactive hydroxyl radicals for the oxidation of acetone. It would be interesting to study other Ti_{1-x}M_xO₂ (M represents a transition metal) solid solutions, particularly those with a +4 metal ion substitution.

In this study, some of the Ti⁴⁺ ions in an anatase lattice were substituted with Zr⁴⁺ to form Ti_{1-x}Zr_xO₂ solid solutions. The photocatalytic activities of these solid solutions for the oxidation of acetone were determined. We have also characterized the solid solutions with X-ray diffractometry (XRD), X-ray photoelectron spectrometry (XPS), BET surface area, and zeta potential measurements. In addition, a photocatalytic mechanism of this new system has been proposed based on the experimental results and theoretical considerations.

Experimental Methods

Synthesis of Ti_{1-x}Zr_xO₂ Solid Solutions. ZrCl₄, TiCl₄ (99.5%, Riedel-dehaen), citric acid (99.7%, AnalaR), and 5% HCl were used as starting materials. Ti_{1-x}Zr_xO₂ solid solutions (x = 0.00, 0.025, 0.05, 0.075, and 0.10) were prepared by the citric acid complexing method. TiCl₄ and ZrCl₄ in the required stoichiometry were added to a HCl aqueous solution under vigorous stirring, and then citric acid was added to this solution. After sonication for 10 min and aging for 24 h, this solution was heated on a hot plate to remove HCl and H₂O thoroughly under constant stirring. The resultant precipitates were calcined in air at 400 °C for 5 h.

Characterization of Ti_{1-x}Zr_xO₂ Solid Solutions. The BET surface areas of the solid solutions were determined by using nitrogen adsorption data at 77 K obtained with a Micromeritics ASAP2000 accelerated surface area and porosimetry system. Polycrystalline X-ray diffraction patterns were recorded with a

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Philips MPD18801 diffractometer using Cu-K α radiation. XPS measurements were performed in a Kratos AXIS-HS system with a monochromatic Al-K α source and a charge neutralizer; all the binding energies were referenced to the C_{1s} peak at 285.0 eV of the surface adventitious carbon.

Measurement of Isoelectric Points. Zeta potential measurements were carried out on a Brookhaven Zeta Plus analyzer. The suspension fluid was a 1 mM aqueous solution of potassium nitrate. The concentration of catalyst in the suspension was 1 mg mL⁻¹. The pH value of the suspension was adjusted using solutions of 0.05 M nitric acid and 0.05 M potassium hydroxide.

Measurements of Photocatalytic Activity. Photocatalytic activity experiments of Ti_{1-x}Zr_xO₂ solid solutions for the oxidation of acetone in air were performed at ambient temperature using a 50 L reactor. The catalysts were prepared by coating an aqueous slurry of the solid solutions onto two pieces of glass plates, each measured 50 mm \times 100 mm. The weight of the photocatalyst used in each experiment was kept at about 0.2 g. The solid solutions were pretreated in an oven at 100 °C for 2 h and then cooled to room temperature before use.

A small amount of acetone was injected into the reactor. A photoionization detector (MiniRAE Plus Professional PID) monitored the concentration of acetone in the reactor. The acetone vapor was allowed to reach adsorption equilibrium with the photocatalyst in reactor prior to an experiment. The initial concentration of acetone after reaching adsorption equilibrium was 800 ppm. The acetone concentration remained constant until the reactor was illuminated by a 15 W 365 nm UV lamp (Cole-Parmer Instrument Co.).

The concentration of carbon dioxide in reactor was determined by a nondispersive infrared (NDIR) monitor (Metrosonics aq511). The starting relative humidity in the reactor was controlled at $57 \pm 1\%$, and the initial temperature was maintained at 25 ± 1 °C as measured with a Testo 610 humidity/temperature meter. During the experiment, the concentration of carbon dioxide increased with decreasing concentration of acetone in the reactor, and a near 3:1 ratio of carbon dioxide formation to acetone degradation was observed. Each reaction was followed for 30 min. The degradation rate, expressed as mol min⁻¹ m⁻², was the average amount of acetone degraded per minute during the 30 min period per unit BET surface area of the catalyst.

Results

Analysis of Phase Constitution by XRD. The polycrystalline X-ray diffraction patterns of the solid solutions are shown in Figure 1. XRD results show that anatase is the main phase of the Ti_{1-x}Zr_xO₂ solid solutions calcined at 400 °C. The rutile phase is present in only two samples, namely the pure TiO₂ and Ti_{1-x}Zr_xO₂ ($x = 0.025$). These samples contain 13% and 10% of rutile phase, respectively. The content of rutile phase decreases with increase of zirconium in the solid solution. The samples Ti_{1-x}Zr_xO₂ ($x = 0.05$, $x = 0.075$, and $x = 0.1$) consist practically of pure anatase. This is probably due to the presence of some zirconium as ZrO₂ in the samples. ZrO₂ inhibits the formation and crystallite growth of rutile phase by providing dissimilar boundaries.⁴

Determination of Lattice Parameters by XRD. The X-ray diffraction peaks of crystal plane (101) and (200) in anatase are selected to determine the lattice parameter of Ti_{1-x}Zr_xO₂ solid solutions. The lattice parameters are obtained by using the following equations:

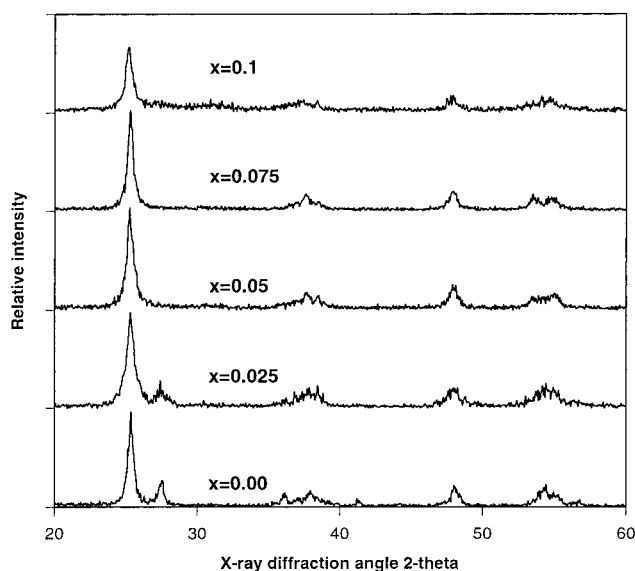


Figure 1. X-ray diffraction patterns of photocatalysts Ti_{1-x}Zr_xO₂.

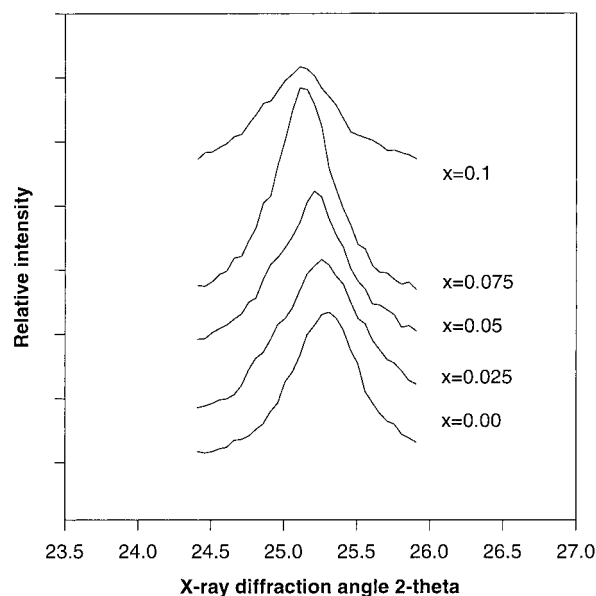


Figure 2. X-ray diffraction peaks of crystal plane (101).

TABLE 1: Lattice Parameter and Cell Volume of Ti_{1-x}Zr_xO₂

Ti _{1-x} Zr _x O ₂	<i>a</i> = <i>b</i> (Å)	<i>c</i> (Å)	cell vol (Å ³)
<i>x</i> = 0.00	3.7833	9.5279	136.37
<i>x</i> = 0.025	3.7982	9.4890	136.89
<i>x</i> = 0.05	3.7982	9.5631	137.96
<i>x</i> = 0.075	3.8019	9.6420	139.37
<i>x</i> = 0.1	3.8057	9.5807	138.76

$$\text{Bragg's law: } d_{(hkl)} = \lambda / 2 \sin \theta$$

$$d_{(hkl)}^{-2} = h^2 a^{-2} + k^2 b^{-2} + l^2 c^{-2}$$

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, and a , b , and c are lattice parameters (in anatase form, $a = b \neq c$).

The lattice parameters and cell volumes of Ti_{1-x}Zr_xO₂ solid solutions are summarized in Table 1. Figure 2 shows the enlarged X-ray diffraction peaks of crystal plane (101). From Figure 2, it is clear that the X-ray diffraction peaks of crystal plane (101) shift to lower diffraction angle with increasing

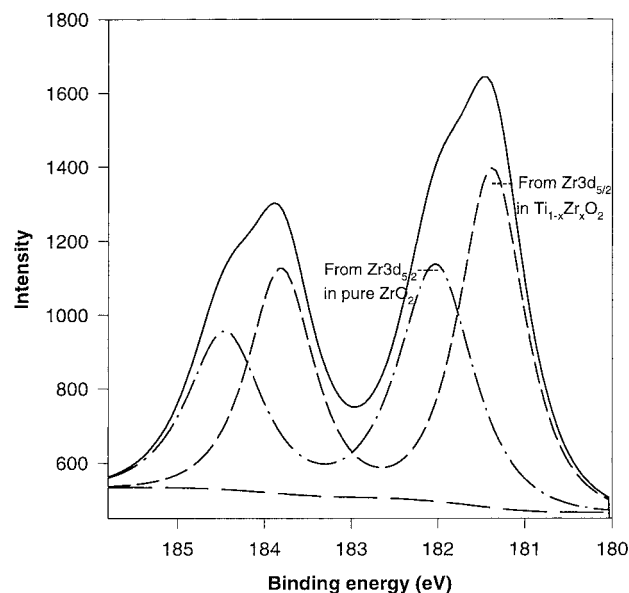


Figure 3. X-ray photoelectron spectrum of $Zr3d_{5/2}$ in photocatalyst $Ti_{1-x}Zr_xO_2$ (nominal $x = 0.075$).

TABLE 2: BET Surface Area (m^2/g) of $Ti_{1-x}Zr_xO_2$

$Ti_{1-x}Zr_xO_2$	BET surf. area	$Ti_{1-x}Zr_xO_2$	BET surf. area
$x = 0.00$	44.876	$x = 0.075$	96.908
$x = 0.025$	90.816	$x = 0.1$	104.504
$x = 0.05$	97.225		

zirconium content. According to Table 1, the cell volume and lattice parameter (a , b , and c) generally increase with increase of zirconium substitution in the solid solutions. It is because the ionic radius of zirconium is larger than that of titanium. In the sample with the highest zirconium content ($x = 0.1$), the extra zirconium may not enter the TiO_2 lattice, and it may be present as ZrO_2 . Therefore, the cell volume of $Ti_{1-x}Zr_xO_2$ ($x = 0.1$) is not larger than that of $Ti_{1-x}Zr_xO_2$ ($x = 0.075$).

Results of XPS Measurements. According to XPS measurements on $Ti_{1-x}Zr_xO_2$ solid solution, it can be found that the peak of binding energy for $Zr3d_{5/2}$ in each sample is composed of two signals at binding energies of 182.03 and 181.38 eV. When these values are compared with the binding energy value of $Zr3d_{5/2}$ in pure ZrO_2 , it shows that the binding energy at 182.03 eV is attributed to $Zr3d_{5/2}$ in pure ZrO_2 , and the other at 181.38 eV should be ascribed to $Zr3d_{5/2}$ in the $Ti_{1-x}Zr_xO_2$ solid solution. Based on the peak area ratio of the two signals, the XPS measured values of x in $Ti_{1-x}Zr_xO_2$ ($x = 0.025, 0.05, 0.075$, and 0.1) are 0.016, 0.03, 0.045, and 0.042, respectively. These results reveal that, in samples $Ti_{1-x}Zr_xO_2$ (nominal $x = 0.025, 0.05$, and 0.075), some zirconium atoms fail to enter into the TiO_2 lattice and are present as ZrO_2 . The results also show that once a maximum amount of zirconium is incorporated into the lattice (nominal $x = 0.075$), extra zirconium can only exist in the form of ZrO_2 . This is consistent with the results by XRD. XPS of $Zr3d_{5/2}$ in $Ti_{1-x}Zr_xO_2$ (nominal $x = 0.075$) is shown in Figure 3. In addition, the XPS spectra indicate that both Ti and Zr of Ti exhibit oxidation state of $4+$.

BET Surface Areas. Table 2 shows the results of BET surface area measurements. The $Ti_{1-x}Zr_xO_2$ solid solutions display much higher BET surface areas than pure TiO_2 . However, with increase of zirconium, there are only small changes in the BET surface areas. The higher BET surface areas of solid solutions are due to the presence of zirconium as ZrO_2 , which inhibits crystallite growth of a solid solution.

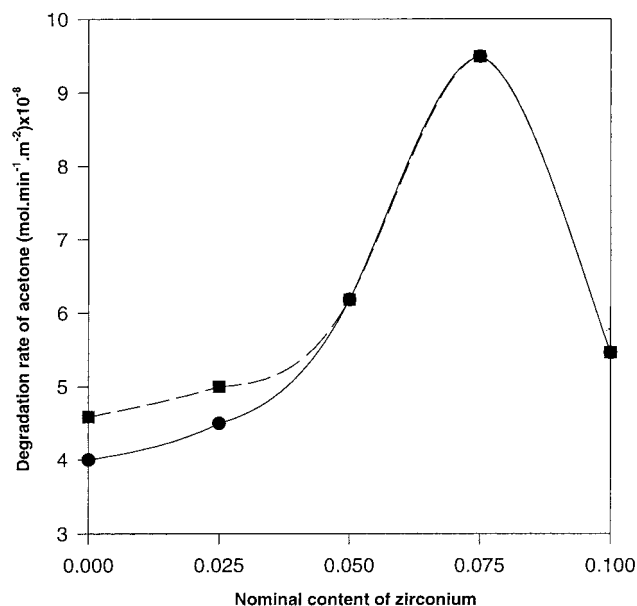


Figure 4. Degradation rate of acetone as a function of Zr content in $Ti_{1-x}Zr_xO_2$. The segmented line represents the theoretical rate after correction of the rutile phase.

TABLE 3: Isoelectric Point (pH unit) of $Ti_{1-x}Zr_xO_2$

$Ti_{1-x}Zr_xO_2$	isoelectric point	$Ti_{1-x}Zr_xO_2$	isoelectric point
$x = 0.00$	5.25	$x = 0.075$	4.05
$x = 0.025$	4.75	$x = 0.1$	4.10
$x = 0.05$	4.40		

Results of Zeta Potential Measurement. The isoelectric points of the samples are shown in Table 3. In general, the isoelectric point (in terms of pH) decreases with an increase in Zr^{4+} substitution in the TiO_2 lattice.

Photocatalytic Activity for Oxidation of Acetone in Air. Degradation rates of acetone over the solid solutions irradiated by UV light are shown in Figure 4. The solid solutions $Ti_{1-x}Zr_xO_2$ have significantly higher activities than the pure TiO_2 for the oxidation of acetone, and their activities increase with increase of zirconium content. Interestingly, the solid solution with the highest nominal zirconium content ($x = 0.1$) does not have the highest photocatalytic activity.

Discussion

Factors Affecting the Photocatalytic Activity of a $Ti_{1-x}Zr_xO_2$ Solid Solution. All of the solid solutions show higher photocatalytic activities than the pure TiO_2 for the oxidation of acetone in air. As the foreign atom zirconium is introduced to substitute for titanium in the TiO_2 lattice, the solid solution formed may be different from TiO_2 in both physical and chemical characteristics such as the phase constitution, surface area, surface hydroxyl groups, and chemical compositions. We will discuss the effects of these physical and chemical changes on the photocatalytic activities of the solid solutions.

It can be found in Table 2 that the presence of a small amount of ZrO_2 increases the surface area of a $Ti_{1-x}Zr_xO_2$ solid solution. To ensure a fair evaluation of the photocatalysts' activities, the degradation rates shown in Figure 4 are normalized in terms of surface area.

Pure TiO_2 and $Ti_{1-x}Zr_xO_2$ ($x = 0.025$) contain 13% and 10% rutile phase, respectively. It has been shown that rutile is less effective than anatase as a photocatalyst for the oxidation of most volatile organic compounds.^{1,14,15} However, the photocatalytic activities of solid solutions are still higher than that of

the pure TiO₂ even after correcting for the rutile phase (shown as the segmented line in Figure 4). Furthermore, the other three samples are all free of rutile phase, yet they exhibit very different photoactivities. It can be concluded that the rutile content in a Ti_{1-x}Zr_xO₂ solid solution does not play a significant role in determining its photocatalytic activity.

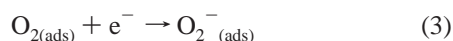
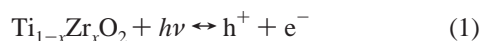
Based on the results of XPS measurements, some zirconium atoms are not incorporated into the lattice to form Ti_{1-x}Zr_xO₂ solid solutions. They exist as ZrO₂ particles mixed evenly with Ti_{1-x}Zr_xO₂. It is known that the band gap energy of ZrO₂ (~5 eV) is higher than that of anatase TiO₂ (3.2 eV).¹⁶ Therefore, the presence of ZrO₂ in a solid solution can only decrease its quantum yield. This may explain why the sample with nominal $x = 0.1$ has a relatively poor photoactivity. However, it cannot account for the fact that all solid solutions are more photoactive than the pure TiO₂.

Some investigators attributed the high activities of TiO₂ photocatalysts to a large number of hydroxyl groups on its surface.^{17,18} They proposed that these hydroxyl groups might trap the holes in the valence band and thus enhance the quantum yield. Fu et al. and Do et al. have also indicated that the increase in activities of TiO₂/ZrO₂ and TiO₂/WO₃ systems could be due to high surface acidity.^{4,5} As shown in Table 3, the isoelectric points of the photocatalysts ($x = 0.00, 0.025, 0.05, 0.075$, and 0.1) are 5.25, 4.75, 4.40, 4.05, and 4.10 (in terms of pH unit), respectively. This means that there is an increase of hydroxyl groups on the surface with increasing Zr content, except for the sample ($x = 0.1$). Although the sample ($x = 0.1$) has an isoelectric point comparable to that of the sample ($x = 0.075$), its photoactivity is significantly lower. The excess amounts of ZrO₂ in the sample ($x = 0.1$) may shield the photocatalyst from UV light resulting in a poor activity.

We believe that a probable explanation for the enhanced photoactivity of the Ti_{1-x}Zr_xO₂ solid solutions is the structural defects induced by the introduction of zirconium into the TiO₂ lattice. The cause and consequence of the defects as well as the mechanisms are discussed in the next section.

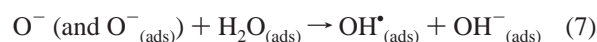
The Lattice Defects and Photocatalytic Mechanisms. From Table 1 and Figure 4, it is quite clear that the photocatalytic activity of a Ti_{1-x}Zr_xO₂ solid solution increases with increase of its lattice parameters and cell volume. The increase in lattice parameters and cell volume of solid solution is caused by the size difference between titanium and zirconium. When Zr⁴⁺ (with an ionic radius of 0.72 Å)¹⁹ substitutes for Ti⁴⁺ (with an ionic radius of 0.605 Å)¹⁹ in the TiO₂ lattice to form Ti_{1-x}Zr_xO₂, the solid solution exists in a strained form with high lattice energy. The Ti_{1-x}Zr_xO₂ solid might have some structural defects such as vacancies in its lattice, particularly on the surface to partially offset the lattice strain. Therefore, it is suggested that some oxygen might be escaped from the surface of the lattice to trap the photogenerated holes. In addition, Sclafani and Herrmann have found recently that metal oxides with more structure defects on surface could ionosorb oxygen as O⁻ species, which were photoactive in mild oxidation reactions.¹⁵

On the basis of our experimental results, we propose that the photocatalytic reactions of Ti_{1-x}Zr_xO₂ solid solution in the presence of water and O₂ in air take place via the following mechanism:



where the symbol (ads) denotes a species adsorbed on the surface of a catalyst, and O²⁻_L represents the oxygen species that escape from the surface of the lattice.

The O⁻ species formed in reaction 4 and the O⁻_(ads) ionosorbed on surface may also oxidize water molecules adsorbed on the photocatalyst:



It is well-known that the dissociated atomic oxygen species formed in reactions 5 and 6 are able to attack the chemical bonds of surface adsorbed organic compounds, and the OH[•] radicals are a powerful oxidizing agent capable of mineralizing the majority of organic pollutants.¹

For a pure TiO₂ anatase photocatalyst with fewer defects than Ti_{1-x}Zr_xO₂, it is unlikely that its photocatalytic mechanisms would include reactions 4–7. We believe that the enhanced photocatalytic activities of Ti_{1-x}Zr_xO₂ solid solutions can be explained by the presence of this additional pathway for the generation of hydroxyl radicals and the highly reactive atomic oxygen species. Results of isoelectric point measurement are consistent with the proposed mechanism.

Conclusion

Ti_{1-x}Zr_xO₂ solid solutions in anatase form can be successfully prepared by the citric acid complexing method. These solid solutions exhibit higher photocatalytic activities than pure TiO₂ for the oxidation of acetone in air. The increase in activity is related to the changes in the lattice parameters caused by zirconium substitution. It is proposed that the lattice O²⁻ and O⁻ ionosorbed on surface are responsible for the increased photoactivity.

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