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Enhanced photocatalytic activity of $Ti_{1-x}V_xO_2$ solid solution on the degradation of acetone

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Abstract

Solid solutions of $Ti_{1-x}V_xO_2$ ($0.00<x\leq0.025$) exhibit higher photocatalytic activity than pure TiO_2 for the oxidation of acetone. Results from X-ray photoelectron spectrometry, X-ray diffractometry and photoionization detection reveal that the photocatalytic activity of the solid solution increases with increasing V substitution, but decreases with a decrease in the anatase to rutile ratio. The optimum composition in terms of activity is $x=0.015$, with an anatase to rutile ratio of 9 : 1. Zeta potential measurements indicate that the isoelectric point (in terms of the pH value) is affected by the amount of V substitution. The catalyst with $x=0.015$ has the lowest isoelectric point (at pH 5.5). All these results suggest that V substitution may enhance the adsorption of hydroxide ions onto the surface of the catalyst. More hydroxyl radicals can be generated, resulting in a higher photocatalytic activity. The synthesis of the catalyst and the effect of the crystalline form of the catalyst on its activity are also presented. © 1997 Elsevier Science S.A.

Keywords: Acetone degradation; Isoelectric point; Photocatalytic oxidation; Titanium dioxide; Vanadium

1. Introduction

Since Carey et al. [1] first reported the photocatalytic degradation of biphenyl and chlorobiphenyls over the surface of titanium dioxide irradiated by near-UV light, the application of semiconducting TiO_2 as a photocatalyst has received increasing attention due to its potential application to the purification of groundwater, soils and air polluted by volatile organic compounds (VOCs). In the past two decades, most of the heterogeneous photocatalysis studies have focused on the degradation mechanisms of VOCs in water and air over TiO_2 [2,3], the effects of the photoreaction conditions [4] and the design of the photoreactor [5]. All of these studies have made a considerable contribution to the improvement and application of photocatalytic TiO_2 in environmental protection.

So far, this technology has not been successfully commercialized, in part because of the low photocatalytic degradation rate of VOCs on the surface of TiO_2 particles. One solution to this problem is to dope metal oxides or elements into the photocatalyst. Recently, Do et al. [6], Papp et al. [7] and Fu et al. [8] have published results on TiO_2/WO_3, TiO_2/MO_3, TiO_2/SiO_2 and TiO_2/ZrO_2 systems. They found that the degradation rates of VOCs over these binary metal oxides were enhanced. They also found a correlation between the enhanced photoreactivity and a higher surface acidity resulting from the addition of metal oxides. The surface acidity is thought to take the form of stronger surface hydroxyl groups. These groups accept holes generated by illumination and oxidize adsorbed molecules.

In this paper, the synthesis of a solid solution of $Ti_{1-x}V_xO_2$ as photocatalyst is described, and the enhanced photocatalytic performance of $Ti_{1-x}V_xO_2$ is demonstrated. Finally, a discussion is given about the relationship between the photocatalytic activity, crystalline form, chemical composition and surface hydroxide ions based on the results of polycrystalline X-ray diffraction (XRD), X-ray photoelectron spectrometry (XPS) and zeta potential measurements.

2. Experimental details

2.1. Synthesis of $Ti_{1-x}V_xO_2$

The starting materials were V_2O_5 (99.9%, AnalaR), $TiCl_4$ (99.5%, Riedel-deHaen), 10% HCl and citric acid (99.7%, AnalaR). The $Ti_{1-x}V_xO_2$ photocatalysts ($x=0.00$, 0.005, 0.01, 0.015, 0.02 and 0.025) were prepared by the citric acid complexing method by the addition of citric acid to an aque-

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ous HCl solution of the chlorides of the corresponding metal ions in the required stoichiometry with constant stirring. After sonication for 5 min, this solution was heated on a hot plate to remove HCl and H_2O thoroughly. The resulting precipitates were calcined in air at 400 °C for 3 h. This method can yield highly dispersed solid solutions [9]. Pure TiO_2 catalysts with different anatase to rutile ratios were obtained using a similar method, but at different calcination temperatures.

2.2. Measurements of photocatalytic activity

Photocatalytic oxidation experiments of all catalysts were performed at ambient temperature using a 5000 ml reactor. The weight of the photocatalyst used in the experiment was kept constant at 0.2 g. A small amount of acetone was injected into the reactor. The photocatalysts were allowed to come to adsorption equilibrium with the reactant gas in the reactor before they were illuminated by UV light. The concentrations of acetone were determined by a photoionization detector (MiniRAE Plus Professional PID), and the initial concentration after adsorption equilibrium had been reached was 1200 ppm. The starting relative humidity was controlled at 38.0%–40.0% and the initial temperature was 22 °C, as measured with a Testo 610 humidity/temperature meter. The catalyst was illuminated by a 15 W 365 nm UV lamp (Cole-Parmer Instrument Company).

2.3. Characterization of photocatalysts

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

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 using 0.1 M nitric acid and 0.1 M potassium hydroxide solutions.

3. Results and discussion

3.1. Effects of crystalline form and composition of the photocatalyst on its activity

XRD analysis indicates that the main phase present in the photocatalyst $Ti_{1-x}V_xO_2$ calcined at 400 °C is anatase. Table 1 shows the phase composition of $Ti_{1-x}V_xO_2$. According to the literature [9], the anatase phase of TiO_2 is the stable crystallographic form in pure TiO_2 at temperatures below 700 °C. However, we found a small amount of rutile phase in the samples calcined at 400 °C. We believe that this is partly due to the presence of citric acid in our preparation method. The calcination temperature is sufficient for the pyrolysis of citric acid. The heat generated from this pyrolysis promotes the anatase–rutile transformation [10]. The amount of citric acid used in the synthesis of each solid solution is the same; the larger amount of rutile phase in $Ti_{1-x}V_xO_2$ ($x \geq 0.02$) than in $Ti_{1-x}V_xO_2$ ($x \leq 0.015$) may result from the different amount of V_2O_5 used in the synthesis of these catalysts.

Table 1
Phase composition of $Ti_{1-x}V_xO_2$

Nominal value of x	Anatase	Rutile (%)	Amorphous TiO_2 (%)
0.00	Main phase	~ 10	< 1
0.005	Main phase	10–11	< 1
0.01	Main phase	10–11	< 1
0.015	Main phase	10–11	< 1
0.02	Main phase	15–16	< 1
0.025	Main phase	25–26	< 1

Fig. 1 shows the initial degradation rate of acetone over pure TiO_2 catalyst as a function of the rutile content, calculated by comparing the area of the most intense rutile peak in the XRD pattern with that of 100% rutile. The initial degradation rate of acetone decreases gradually with increasing rutile content in the TiO_2 photocatalyst. Therefore the crystalline form of TiO_2 is an important factor determining its photocatalytic activity. The greater the anatase content in the catalyst, the higher its photocatalytic activity. These results are in agreement with those reported previously [11].

The initial degradation rate of acetone over solid solutions of $Ti_{1-x}V_xO_2$ is shown in Fig. 2. With increasing amounts of V substitution for Ti in the structure of TiO_2, the initial degradation rate increases gradually up to $x = 0.015$, and then begins to decrease. To explain these observations, the curve in Fig. 2 is divided into two regions. In region 1 ($x \leq 0.015$),

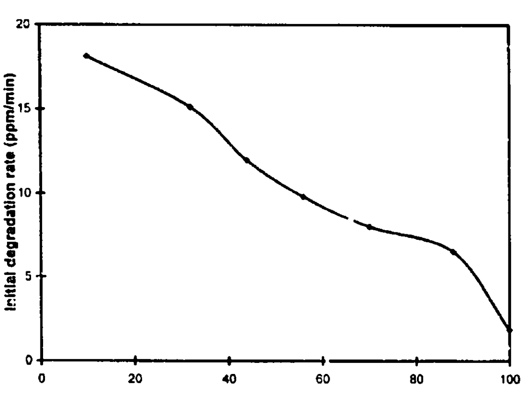

Fig. 1. Initial degradation rate of acetone over pure TiO_2 as a function of rutile content.

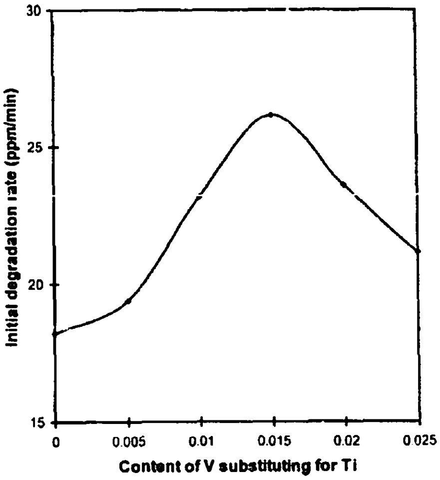

Fig. 2. Initial degradation rate of acetone over $Ti_{1-x}V_xO_2$ as a function of V content.

the degradation rate increases to a maximum value at $x=0.015$. As shown in Table 1, the phase compositions of the four $Ti_{1-x}V_xO_2$ catalysts ($x=0.00$, 0.005, 0.01 and 0.015) are virtually the same. Therefore the increase in degradation rate is not due to the change in the anatase to rutile ratio; it must be related to changes on the surface of $Ti_{1-x}V_xO_2$ resulting from V substitution. Possible changes on the surface of the catalyst will be discussed in the following sections based on the results of XPS and isoelectric point measurements on $Ti_{1-x}V_xO_2$. The reason for the decrease in the initial degradation rate in region 2 is quite obvious. As shown in Table 1, the two photocatalysts with high vanadium contents have a much higher percentage of rutile phase. Such a high rutile content causes a decrease in the photocatalytic activity. The crystal structure of the photocatalyst plays a dominant role in this region.

3.2. Relationship between the photocatalytic activity, chemical composition and surface hydroxyl ions of $Ti_{1-x}V_xO_2$

From XPS measurements, it is clear that the peak position and peak shape of the binding energy for $V_{2p_{3/2}}$ in $Ti_{1-x}V_xO_2$ are different from those for $V_{2p_{3/2}}$ in pure V_2O_5, due to the different coordination in the two crystal structures. After further analysis, it was found that the peak of $V_{2p_{3/2}}$ in the solid solution consists of two signals at binding energies of 517.93 eV and 517.20 eV. The comparison of the two values with the binding energy of V_{2p} in pure V_2O_5 (Fig. 5) and with the values reported in the literature for a number of vanadium oxides [12] shows that the binding energy of 517.93 eV corresponds to V in the form of pure V_2O_5 and the binding energy of 517.20 eV can be attributed to V in $Ti_{1-x}V_xO_2$. The presence of a signal with a binding energy at 517.93 eV in the X-ray photoelectron spectrum of the $Ti_{1-x}V_xO_2$ sample reveals that some V atoms fail to enter the lattice of TiO_2 to substitute for Ti and exist in the form of pure V_2O_5. From the X-ray photoelectron spectrum, the actual values of x in $Ti_{1-x}V_xO_2$ determined for the nominal compositions $x=0.01$, $x=0.015$, $x=0.02$ and $x=0.025$ are 0.007, 0.011, 0.010 and 0.010 respectively. The x values determined are lower than expected because some of the vanadium from V_2O_5 does not enter into the lattice of the catalyst. More than 50% of vanadium exists as pure V_2O_5 in the catalysts with $x=0.02$ and $x=0.025$. Since it has been reported that pure V_2O_5 does not show any photocatalytic activity [13], the greater amounts of pure V_2O_5 present in these two catalysts contribute to their lower photocatalytic activity. The presence of a higher V_2O_5 content, together with TiO_2, can cause a high exothermic reaction, leading to locally very high temperatures and enhancing the anatase–rutile transformation [14–18]. Therefore the content of the rutile phase is greater in $Ti_{1-x}V_xO_2$ with $x=0.02$ and $x=0.025$ than in $Ti_{1-x}V_xO_2$ with $x=0.00$, $x=0.005$, $x=0.01$ and $x=0.015$, as shown in Table 1. The signal of $V_{2p_{3/2}}$ in $Ti_{1-x}V_xO_2$ (nominal $x=0.005$) in the X-ray photoelectron spectrum is too weak to be detected. The X-ray photoelectron spectra of $V_{2p_{3/2}}$ in $Ti_{1-x}V_xO_2$ ($x=0.01$ and $x=0.015$) and in pure V_2O_5 are shown in Figs. 3, respectively.

The system $Ti_{1-x}V_xO_2$ with $x \leq 0.015$ exhibits an increase in activity with increasing V substitution for Ti, as shown in Fig. 2. The increase is not likely to be related to the formation of new compounds, because there is no thermodynamically stable vanadium–titanium phase at these compositions under the calcination conditions used [19]. Our XRD spectra also suggest that no new vanadium–titanium compound is present. The V_2O_5 which fails to enter the structure of the solid solution exhibits no photoactivity. Therefore the increase in photocatalytic activity must be due to a change in the surface of the catalyst resulting from V substitution. Because of the high calcination temperature used in the preparation, and from the binding energy value of V_{2p} in $Ti_{1-x}V_xO_2$, we believe that

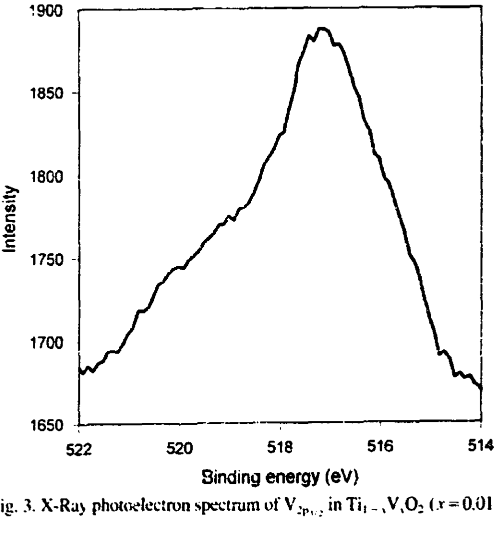

Fig. 3. X-Ray photoelectron spectrum of $V_{2p_{3/2}}$ in $Ti_{1-x}V_xO_2$ ($x=0.01$).

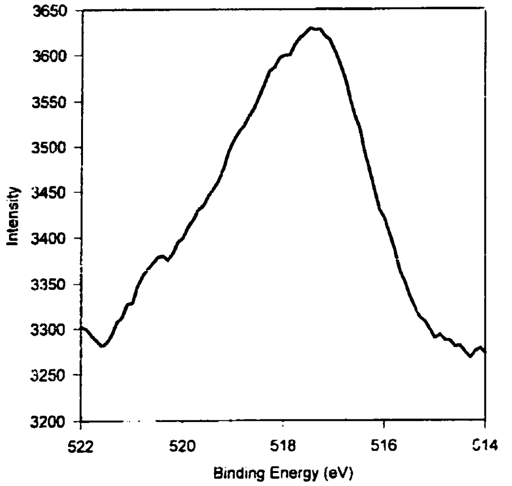

Fig. 4. X-Ray photoelectron spectrum of $V_{2p_{3/2}}$ in $Ti_{1-x}V_xO_2$ ($x=0.015$).

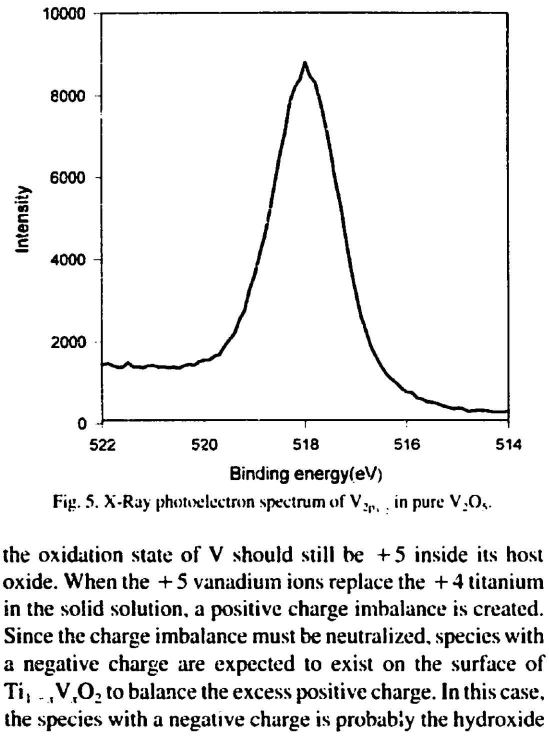

Fig. 5. X-Ray photoelectron spectrum of $V_{2p_{3/2}}$ in pure V_2O_5.

the oxidation state of V should still be +5 inside its host oxide. When the +5 vanadium ions replace the +4 titanium in the solid solution, a positive charge imbalance is created. Since the charge imbalance must be neutralized, species with a negative charge are expected to exist on the surface of $Ti_{1-x}V_xO_2$ to balance the excess positive charge. In this case, the species with a negative charge is probably the hydroxide ion, since the Cl^- ion and other organic anions react completely during synthesis and calcination. The presence of hydroxide ions on the surface may enhance the photocatalytic activity of TiO_2. According to the photocatalytic mechanism of TiO_2 [20–22], when the anatase phase of the TiO_2 particle is illuminated by UV light at wavelengths of less than 370 nm, the valence band electrons of TiO_2 can be promoted to the conduction band, creating highly reactive electron and hole pairs. The electrons and holes migrate to the solid surface

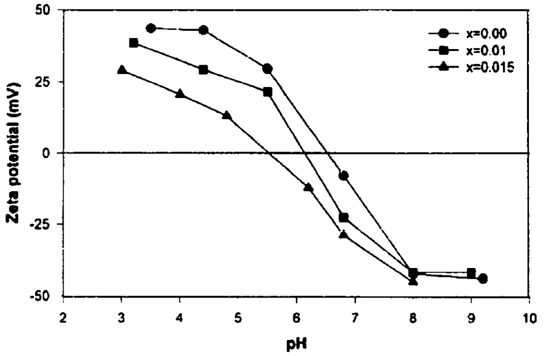

Fig. 6. Zeta potential of $Ti_{1-x}V_xO_2$ as a function of pH value.

of TiO_2 and are trapped at different sites. For gas–solid homogeneous photocatalysis, the O_2 in air can scavenge the trapped electrons and, in this case, the photogenerated holes may be trapped by the hydroxide ions adsorbed on the surface of the catalyst to form hydroxyl radicals, which can oxidize adsorbed organic molecules. Thus these hydroxide ions used as hole traps prevent electron–hole recombination and increase the quantum yield. The initial photoreaction steps may be summarized as follows

$$Ti_{1-x}V_xO_2+h\nu\leftrightarrow h^++e^-$$

$$h^++OH^-\rightarrow OH^\bullet$$

$$e^-+O_2\rightarrow O_2^{\bullet -}$$

$$OH^\bullet+CH_3COCH_3\rightarrow {}^\bullet CH_2COCH_3+H_2O$$

The oxidative reaction of acetone is believed to be initiated by OH radicals. A larger number of hydroxide ions may be expected to yield a higher photocatalytic reaction rate.

Zeta potential studies of three $Ti_{1-x}V_xO_2$ catalysts ($x=0.00$, 0.01 and 0.015) were performed on a Brookhaven Zeta Plus analyser. Since the zeta potential of the catalyst particles suspended in solution is changed by adjusting the pH of the solution, the hydroxide groups on the surface of the catalyst are assumed to lose and gain protons accordingly. Fig. 6 shows the zeta potential data for the three catalysts. The results show a clear difference in isoelectric point between the three catalysts. The isoelectric points of $Ti_{1-x}V_xO_2$ ($x=0.00$, 0.01 and 0.015) are 6.5, 6.1 and 5.5 pH units respectively. The lower isoelectric point in terms of the pH value means a higher concentration of hydroxide ions on the surface of the catalyst. Thus it can be concluded that the number of hydroxide ions on the surface of the $Ti_{1-x}V_xO_2$ catalyst increases with increasing V^{5+} substitution. Therefore at a higher value of x, the catalyst $Ti_{1-x}V_xO_2$ ($x\leq 0.015$) has a larger number of hydroxide ions on its surface, and exhibits a higher photocatalytic reaction rate.

4. Conclusions

The crystalline form of TiO_2 is an important factor in determining the photocatalytic activity for the oxidation of acetone. Doping vanadium into TiO_2 to form a solid solution of $Ti_{1-x}V_xO_2$ ($x \leq 0.015$) can enhance the photocatalytic activity of acetone degradation. The increase in activity is probably due to the higher concentration of surface hydroxide ions resulting from the replacement of Ti^{4+} with V^{5+}.

Acknowledgements

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