

Degradation of Acetaldehyde with Doped TiO₂ Photocatalyst Under Visible Light Irradiation

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Abstract

C-, V-doped TiO₂ photocatalysts are prepared by a sol-gel process. These catalysts are highly active for the degradation of acetaldehyde both under visible irradiation (> 420 nm) and in the dark, especially for 2.0% V-containing co-doped TiO₂. Characterization results suggest that vanadium ions are introduced both on the surface and into the bulk of TiO₂. A free electron, induced by the formation of V⁵⁺ in the sublayers of TiO₂, is delocalized and promoted into the conduction band by thermal energy and further transferred to O₂, generating superoxide radical anion (O₂^{•-}) that is responsible for degradation of acetaldehyde in the dark. The doped elemental carbon increases the visible light sensitivity, the surface area, and the dispersion of vanadium.

Keywords: Visible Light; Carbon; Vanadium; TiO₂; Photocatalyst;

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Introduction

Since the discovery of water splitting by Fujishima and Honda in 1972, enormous efforts have been devoted to photocatalysis for its potential in the conversion of light energy into chemical energy.¹ Photocatalytic degradation and complete mineralization of toxic organic compounds in the presence of catalysts have also received much attention during the last two decades.^{2,3,4} TiO₂ is considered the most promising photocatalyst for its high efficiency, chemical stability, nontoxicity, and relative cost. However, the use of TiO₂ is impaired by its wide band gap (3.2 eV), which requires ultraviolet (UV) irradiation for photocatalytic activation ($\lambda < 387$ nm).^{5,6,7} UV light accounts for only about 5% of solar energy while 45% is visible light.⁸ Thus, a lot of effort has been directed towards the development of visible light active photocatalysts.

One approach to synthesize visible light active photocatalysts is the substitution of Ti by V, Cr, Mn, Ni, or Fe.^{7,9,10} Recently, it has been shown that the optical response of TiO₂ could also be shifted from UV to visible light by doping with nonmetal atoms, such as carbon, nitrogen, and sulfur.^{5,11,12,13,14} In addition, the synergetic effect of transition metal and nonmetal atoms on the photocatalytic activity of TiO₂ was studied. Zhao et al.¹⁵ found that the incorporation of boron atoms into TiO₂ extended the spectral response to the visible region and the loaded Ni₂O₃ species facilitated the charge separation. Wei et al.¹⁶ reported that lanthanum and nitrogen led to significant enhancement in degrading of methyl orange under visible light ($350 < \lambda < 450$ nm); the substitution of N for O was responsible for the band gap narrowing of TiO₂ and La³⁺ doping prevented the aggregation of powder in the process of preparation. Sakatani et al.¹⁷ found the doped La³⁺ hindered the

crystal growth and the number of the paramagnetic N species seemed to control the absorption of visible light and the activity under visible light irradiation.

In this research, carbon and vanadium co-doped TiO₂ photocatalysts are prepared by a sol-gel process. The photocatalytic performance of the doped catalysts is investigated and demonstrated.

Experimental

Sample preparation

3.8 g thiourea (99.0-100.5%, Aldrich) and 3.0 g urea (99% Aldrich) are dissolved in 75 ml deionized water. While under vigorous stirring in an ice bath, the desired amount of vanadyl acetylacetonate is added to the solution. Then 0.0375 mole titanium isopropoxide (97%, Aldrich) is added drop-wise. The mixture is stirred for 24 h and aged for 48 h. The water is removed by drying in air at 80 °C. The dried powder is crushed and calcined at 500 °C for 2 h in air. Pure TiO₂ catalyst is obtained using a similar method without urea and thiourea.

Characterization

X-Ray powder diffraction (XRD) patterns are obtained with a Bruker D8 diffractometer, using Cu K α radiation (1.5406Å) at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) data are recorded using a Perkin-Elmer PHI 5400 electron spectrometer. The spectrometer utilizes achromatic Al K α radiation (1486.6 eV). Diffuse reflectance spectra (DRS) are recorded with a Cary 500 Scan UV-vis NIR spectrophotometer with an integrating sphere attachment for their diffuse reflectance in the range of 200-800 nm. N₂

adsorption-desorption isotherms are obtained at -196°C on a NOVA 1000 series instrument (Quantachrome, USA). The specific surface areas are calculated according to the multi-point Brunauer-Emmet-Teller (BET) method.

Degradation of acetaldehyde

Acetaldehyde is chosen as probe molecule for testing the activity of the catalysts.

Experiments are performed in a cylindrical glass reactor (305 ml), which has a quartz window. The light source is a 1000 W high pressure Hg arc lamp (Oriental Corporation).

Filters are used to eliminate UV radiation during visible light experiments ($>420\text{ nm}$). 100 mg catalyst and 100 μl of liquid acetaldehyde are introduced into the reactor. The gaseous mixture of acetaldehyde and air inside the reactor is magnetically stirred constantly. Prior to analysis, the catalyst and acetaldehyde are kept in the reactor for about 30 min to obtain desorption-adsorption equilibrium. The reactor is cooled by water circulation and experiments are performed at 25°C . Gaseous samples are periodically extracted from the reactor and analyzed by GCMS (QP5000 from Shimadzu).

Results and discussion

The evolution of CO_2 during acetaldehyde degradation is used to estimate the activity of the catalysts. Figure 1 shows the CO_2 evolution on different catalysts. It can be seen that the photo-catalytic activity of co-doped TiO_2 is greatly enhanced. Most important, the co-doped TiO_2 has high activity in the dark: the higher values at zero time are due to reaction in the dark which occurs during the 30 min period prior to sampling. In order to enable quantitative comparison, the initial rates for the initial 40 min are calculated to represent

the activities. These values are shown in Table 1. In the dark, P25 TiO₂ shows no activity. However, the co-doped TiO₂ catalysts are highly active for the degradation of acetaldehyde, especially when the vanadium loading is 2%. Under visible light irradiation, co-doped TiO₂ for a 2.0% loading has 6.6 times higher activity than P25 TiO₂. Moreover, for co-doped TiO₂ with 2% vanadium content, the activity is comparable in the dark and under visible irradiation. The different activities among these catalysts likely result from different physical properties and reaction mechanisms, as discussed later.

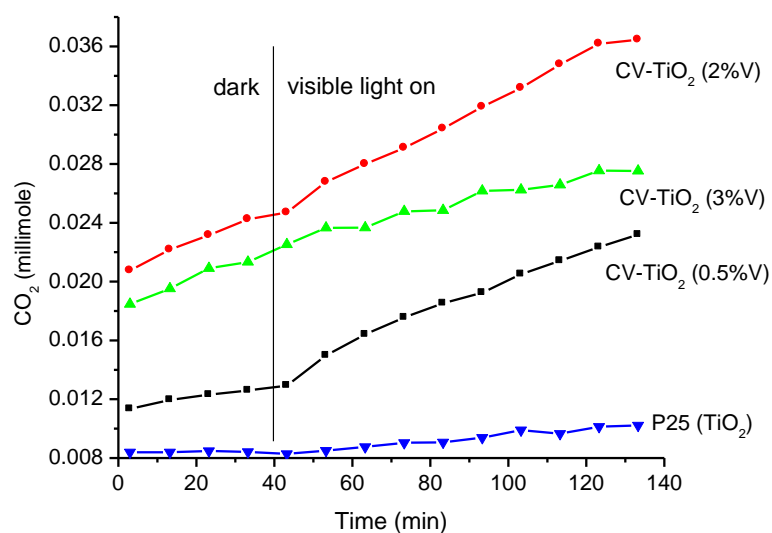


Figure 1 CO₂ evolution during CH₃CHO degradation on P25 TiO₂ and doped TiO₂

Table 1 Kinetic data and physical properties

Sample	Rate in the dark (mmol/min)	Rate under visible light (mmol/min)	Surface area (m ² /g)	Particle size (nm)
P25 TiO ₂	0	2.13×10 ⁻⁵	57	-
C, V-TiO ₂ (0.5% V)	3.81×10 ⁻⁵	1.38×10 ⁻⁴	96	8.9
C, V-TiO ₂ (2.0% V)	1.26×10 ⁻⁴	1.37×10 ⁻⁴	94	9.2
C, V-TiO ₂ (3.0% V)	6.9×10 ⁻⁵	5.57×10 ⁻⁴	59	10.3

Figure 2 shows the XRD patterns of catalysts. The peak at $2\theta = 25.3^\circ$ is representative of (101) anatase phase reflections. No other crystal phase (rutile or brookite) is detected. Compared with pure TiO₂, the peak position of the (101) plane of doped TiO₂ shifts slightly and the peak is broader, which suggests that the crystal lattice is distorted. The structures are distorted further with higher content of vanadium, indicating vanadium (V⁴⁺) is incorporated into the lattice and substitutes for Ti⁴⁺ as suggested by the XPS spectra (see later discussion). From the full width at half maximum (FWHM) of the diffraction pattern, the particle sizes are calculated using Scherrer's equation: pure TiO₂ has the particle size of 14 nm and the values for doped TiO₂ are about 9 nm (shown in Table 1). No diffraction lines due to TiC, TiN, and TiS are found. Furthermore, no separate VO_x phases are observed possibly due to the high dispersion or the very small crystallite size of vanadia species that may be present.

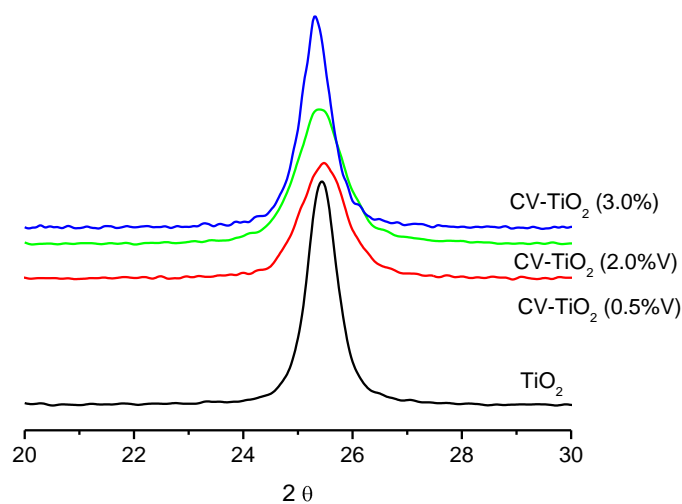


Figure 2 X-Ray diffraction patterns

XPS was used to investigate the chemical states of dopants incorporated into TiO_2 . The results are shown in Figure 3. The C 1s XPS spectrum shows one peak at 284.8 eV and a shoulder around 288.6 eV. The feature at 284.8 eV is assigned to elemental carbon and the shoulder around 288.6 eV suggests the existence of carbonate species. After sputtering, the shoulder around 288.6 eV disappears and the peak at 284.8 eV still exists. These results strongly imply that carbonate species only exist on the surface and elemental carbon deposits not only on the surface but also in the bulk of the TiO_2 powder. A peak around 281 eV, which was reported to result from the Ti-C bond,¹⁸ is not observed for our sample. It is obvious that the O 1s satellite interferes with the V 2p_{3/2} XPS peak. The magnitude of the V 2p_{3/2} peak is small. The shoulder at binding energy of 516.9 eV suggests V^{5+} species, while the shoulder at 516.3 eV is assigned to V^{4+} . These values are consistent with binding energy of V 2p_{3/2} measured for $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst.^{19,20} We know that vanadium ions are incorporated into the crystal lattice of TiO_2 and no vanadium-titanium phase is

present from the previous XRD discussion, so V^{4+} ions substitute for Ti^{4+} ions and form Ti-O-V bond. Obviously, some V^{4+} ions are oxidized into V^{5+} in the preparation process since vanadium only exists as V^{4+} in the precursor; the formation of V^{5+} possibly occurs during the annealing. The both disappearance of S 2p and N 1s peaks in XPS spectra (not shown here) indicated that sulfur and nitrogen species only existed on the surface.

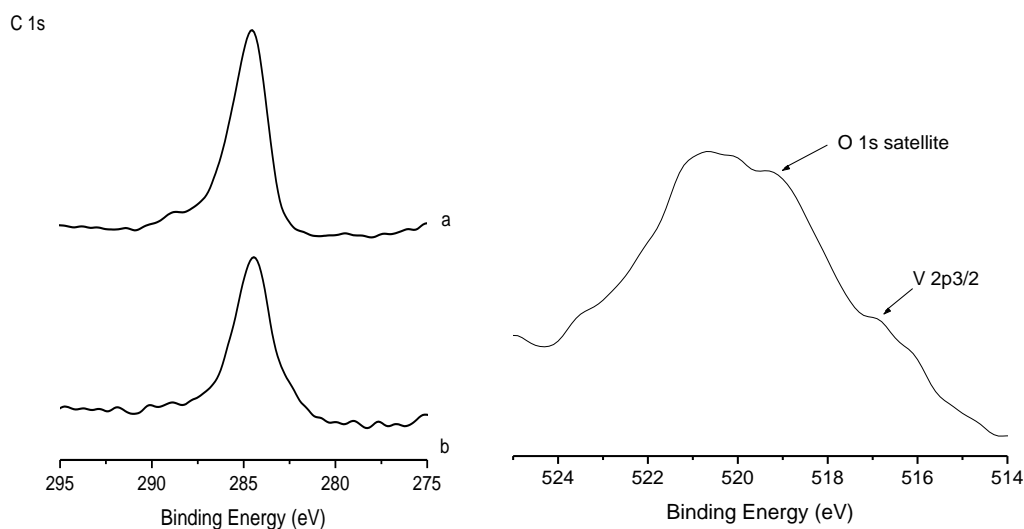


Figure 3 XPS spectra of C 1s (a: before sputtering; b: after sputtering) and V 2p3/2

Figure 4 shows the UV-Vis absorption spectra. As expected, commercial Degussa P-25 TiO_2 has absorption only in the UV region. However, the absorption curve of the co-doped TiO_2 extends to 800 nm. It was reported that V^{5+} shows an absorption at lower than 570 nm and that V^{4+} has an absorption band centered at 770 nm.²¹ Therefore, the spectra suggest the co-existence of V^{5+} and V^{4+} , consistent with XPS spectra. The extended visible absorption obviously suggests modified electronic properties by incorporation of vanadium, forming impurity energy levels between the valence band and conduction band of TiO_2 .⁷

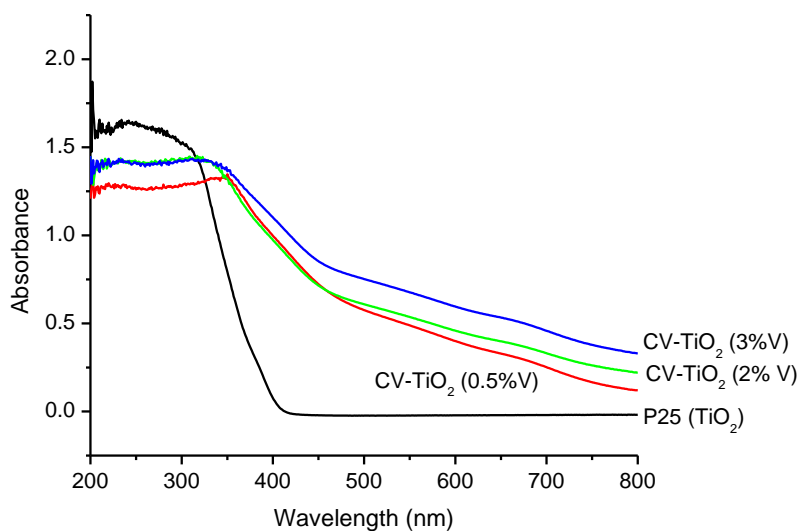


Figure 4 Diffuse reflectance spectra of P25 TiO₂ and C, V-doped TiO₂

Mechanistic studies

Figure 1 illustrates that P25 TiO₂ is inactive in the dark for the degradation of acetaldehyde. After the modification, catalysts show high activity in the dark. Based on the characterization results, one explanation could be considered for the high activity in the dark: it is possible that incorporated V⁴⁺ in the sublayers of TiO₂ is oxidized to V⁵⁺ during preparation, such as water-removal or annealing. If pentavalent V⁵⁺ ions are present at tetravalent sites, the substitution could induce a free electron.²² V⁵⁺ ion only shares four valence electrons with four O²⁻ neighbor ions. The fifth electron cannot be shared and is delocalized around the V⁵⁺ positive center. Only a small amount of thermal energy is needed to delocalize this electron and promote it into the conduction band.²² Therefore, the promoted electron can be transferred to surface adsorbed oxygen molecule to generate the superoxide radical anion O₂^{•-}, which was known to degrade organic compounds.^{14,23} When the loading of vanadium increases from 0.5 to 2.0%, more V⁴⁺ ions in the sublayer of TiO₂

are possibly oxidized into V^{5+} , enhancing the activity. However, further increased the vanadium content could deteriorate the dispersion and lead to the aggregation of vanadium, proven by the smaller surface area. That is why the activity decreases in Figure 1 when the vanadium loading increases from 2.0 to 3.0%.

Under visible light irradiation, two major reaction pathways could be considered: (1) the elemental carbon acts as a photosensitizer. In the presence of visible light, the excited photosensitizer injects an electron into the conduction band of titanium dioxide.

Subsequently, the electron is transferred to oxygen adsorbed on the TiO_2 surface producing $O_2^{\cdot-}$.¹⁴ After a series of reactions, acetaldehyde molecules are finally degraded into CO_2 and H_2O . (2) The incorporation of vanadium into the crystal lattice of TiO_2 modifies the electronic properties of TiO_2 . Because the oxidation V^{4+} to V^{5+} occurs 2.1 eV below the TiO_2 conduction band, a 3d electron from a V^{4+} center is easily photoexcited into the TiO_2 conduction band under visible light irradiation, generating $O_2^{\cdot-}$ similarly as mentioned in pathway 1.

Conclusions

C-, V-doped TiO_2 catalysts are successfully synthesized by a sol-gel process. The doped elemental carbon acts as photosensitizer and increases the surface area, resulting in the high dispersion of vanadium for the co-doped TiO_2 catalysts which have high activity both in the dark and under visible light irradiation. For the first time, we report here that the activities are comparable in the dark and under visible light irradiation for the co-doped TiO_2 , especially when the vanadium content is 2.0%.

Acknowledgment

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