ISSN 1009 - 3095 *Journal of Zhejiang University* (*SCIENCE*) V.2, No.3, P.271 - 274, July - Sep., 2001
http://www.chinainfo.gov.cn/periodical; http://www.zju.edu.cn;
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PHOTOCATALYTIC ACTIVITY OF LANTHANUM DOPING TiO_2

YUE Lin-hai(岳林海), SHUI Miao(水 淼), ZHU Wang-liang(朱万良), XU Zhu-de(徐铸德)
(*Department of Chemistry, Zhejiang University, Hangzhou 310027, China*)

Received Feb.26, 2000; revision accepted Aug.18, 2000

Abstract: The photocatalytic activity of the mixtures of TiO_2 with the rare earth oxide La was investigated. The study on the effect of the rare earth oxide content, calcinating temperature and calcinating time on the performance of the mixture revealed that sample treated under higher temperature and longer time had higher photoactivity than pure TiO_2. The experimental results of polycrystalline X-ray diffraction showed that the extent of the lattice expansion varied with the variation of calcinating temperature or time. It is suggested that this might be due to the variation of La content diffused into the TiO_2 lattice. The La in the lattice may inhibit the recombinatin of photogenerated electron-hole pairs and thus enhance the photoactivity.

Key words: La doping, lattice expansion, TiO_2, photocatalytic activity
Document code: A **CLC number:** O612.4

INTRODUCTION

Over the past 10 years, the semiconductor TiO_2 as a promising photocatalyst has become the focus of numerous studies owing to its stability in various solvents under photoirradiation, suitable redox potential and many environmental applications, such as solar energy conversion and storage, reduction of carbon dioxide, mineralization and/or detoxification of toxic organic compounds. Researches on (Kakuta et al., 1985; Papp et al., 1994) TiO_2/Al_2O_3, TiO_2/SiO_2, TiO_2/ZrO_2, TiO_2/WO_3, TiO_2/MoO_3 systems showed that these binary metal oxide systems could enhance the photocatalytic degradation rates of some volatile organic compounds in the environment. Choi et al. (1994) conducted systematic studies on transition-metal ions doping in quantum sized TiO_2 colloids. There are many articles reporting the correlation of photocatalytic activity with TiO_2 powders' physical properties, such as crystal structure (anatase, rutile, amorphous or brookite), surface area, particle size, surface hydroxyls (Keiichi et al., 1991), etc. and further extension of photoresponse into the visible region and enhancement of photocatalytic efficiency by surface modifications (Yue et al., 1998). But, the authors have not seen reports of researches on the effect of rare earth doping on photocatalytic activity, especially that of titanium dioxide dispersions from the lattice expansion point of view.

In this paper, the effects of Lanthanum doping on photocatalytic activity of TiO_2 dispersion was investigated and preliminary explatations were also given.

EXPERIMENTAL DETAILS

1. Sample preparation

Titanium dioxide containing 0.2, 0.5, 0.8, 1.2 (wt)% rare earth oxide La_2O_3, respectively, was diffused into 200 ml water to form suspension. The water was vaporized under 80℃ and stirring. The residue was dried at 110℃ to steady weight and sieved through # 120 mesh as starting powder. Starting powder containing 0.5 (wt)% La was calcinated at 300℃, 500℃, 700℃ for 3 hours, respectively, and referred to as series1; containing 0, 0.2, 0.5, 0.8, 1.2 (wt)% La was calcinated at 700℃ for 3 hours, respectively, and referred to as series 2; containing 0.5 (wt)% La was calcinated at 700℃ for 1, 3, 5 hours, respectively, and referred to as series 3. To prevent possible agglomeration of particles under higher temperature treatment, the powder after heat treatment was crushed and sieved through 120 mesh.

2. The characterization of sample

X-ray powder diffraction patterns were obtained at room temperature by a Philips diffractometer model X Pert MPD using CuK_α radiation at step size 0.02°and step rate 1°/min. PC-APD 4.0 software was used to separate $K_{\alpha 2}$ from $K_{\alpha 1}$ and Philips Profile Fit was used to obtain 2w and β. The standard instrumental broadening curve $g(x)$ was obtained by using calibration sample supplied by NIST. Diffraction line profile from 20° to 160° was collected under the same operating conditions as the sample testing procedure.

The cell parameters were obtained using the following two equations and numerical optimization.

$$2d\sin\theta = \lambda \qquad (1)$$

$$l/d^2 = (h^2 + k^2)/a^2 + l^2/c^2 \qquad (2)$$

3. Measurement of photoactivity

The photocatalytic reaction was confined in a glass tube（ø30 mm × 150 mm）containing X-3B pigment（chemical purity，Ling An Chemical Corp.，80 $mg \cdot L^{-1}$）solution mixed with TiO_2 catalyst（2 $g \cdot L^{-1}$）. The stirred dispersion was irradiated by a 300W Hg high-pressure lamp（Ya Ming Electric Lamp Corp.，Shanghai），after which suspended TiO_2 was separated from solution by centrifugation. The absorbance of the separated solution at wavelength of 540 nm was measured by a Beckman DU-50 UV spectro scope . Fig . 1 shows the A - λ scanning curve of the above dispersion under 0，5，10，20，30 minutes of irradiation. From the figure，the alignment of the position of absorption peaks showed that the component of the degenerated mixture varied little with irradiation time. The strongest absorption peak was at about 540 nm，which justifies the use of percentage of degraded pigment at 540 nm to characterize the photocatalytic activities of suspended TiO_2 in the following experiments.

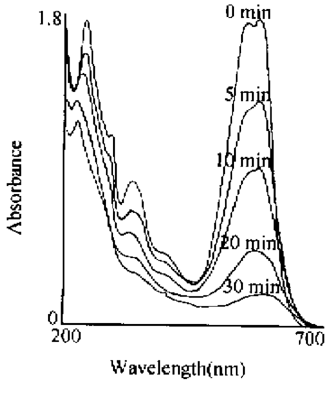

Fig.1 UV absorption spectra of sample under 0，5，10，20，30 min illumination

RESULTS AND DISCUSSION

Fig.2 shows the percentage of degraded pigment of series 1 and pure TiO_2 under 10 min illumination vs. calcinating temperature（calcination for 3 hours）. It can be seen from the figure that the photoactivity of pure TiO_2 has decreasing tendency with increase of calcinating temperature to at about 240℃ and then increases rapidly and maximizes at 700℃. The reason for this was discussed elsewhere（Yue et al.，1999）The photocatalytic activities of series 1 exhibit the similar tendency with increase of calcinating temperature. The photoactivities of rare earth doping TiO_2 is lower than pure TiO_2 when calcinating temperature is below 700℃ while above 700℃，the photoactivities of the former is higher than that of the latter. Fig.3 shows the XRD patterns of（101）plane for sample series 1. It can be seen from the figure that the braggle angle of（101）plane shifts toward lower value，that is，the crystal lattice of TiO_2 expands with the increase of calcinating temperature. We suggest that a large quantity of La_2O_3 can not diffuse into the TiO_2 lattice，but deposit on the surface of TiO_2 particles at low calcinating temperature. Their existence on the particle surface lessen the specific area of TiO_2，impede the absorption of reactant and thus inhibit the photocatalytic activity. The tendency of La^{3+} diffusing into the crystal lattice becomes stronger with increase of calcinating temperature. Accordingly，the cell parameters of TiO_2 grains are larger examined by XRD measurements（see Table 1）. The interaction between the doping ion and TiO_2 crystal lattice possibly causes the enhancement of photocatalytic activity.

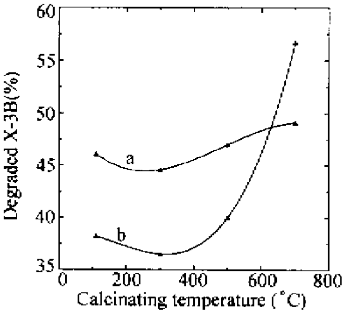

Fig.2 The percentage of degradid pigment vs. calcinating temperature in
a: pure TiO_2; b: 0.5 (wt)% La content TiO_2 suspension

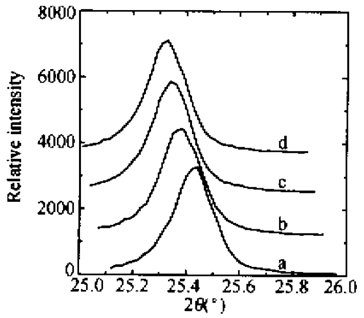

Fig.3 The XRD pattern of (110) plane for 0.5 (wt)% La content TiO_2 treated at
(a) 110℃; (b) 300℃; (c) 500℃; (d) 700℃ for 3 hours

Table 1 Cell parameters of sample series 1 at calcinating temperature

Series 1	110℃	300℃	500℃	700℃
a(Å)	3.758	3.766	3.770	3.775
c(Å)	9.484	9.505	9.512	9.515

Many authors suggested that the surface absorbed O_2^- species and surface hydroxyls are important intermediates in the process of organic compounds oxidation(Khalil et al. 1998; Jun et al. 1998). We suggest that relatively large lattice strain may exist in crystal containing larger amount of doping ion. To offset this strain, lattice oxygen, especially surface oxygen atom can escape from the lattice and exist as a hole trap. Thus, compared to usual ways photogenerated hole-electron pairs recombine (Jimmy et al. 1998).

$$OH^-(ads) + h^+ \rightarrow OH. \qquad (3)$$

$$O_2(ads) + e^- \rightarrow O_2^-(ads) \qquad (4)$$

Sample containing larger amount of doping ion may take part in other trapping process, such as

$$O_L^{2-} + h^+ \rightarrow O^- \qquad (5)$$

$$O^- + h^+ \rightarrow O. \qquad (6)$$

$$O^-(ads) + h^+ \rightarrow O. \qquad (7)$$

$$O^-(\text{or } O^-(ads)) + H_2O(ads) \rightarrow OH\bullet(ads) + OH^-(ads) \qquad (8)$$

It is well known that the dissociated atomic oxygen species formed in reaction (6) and (7) can attack the chemical bonds of surface adsorbed organic compounds, and that the OH radicals are powerful oxidizing agents capable of mineralizing most organic pollutants (Ollis et al., 1993; Ohtani et al., 1997).

These are additional ways to inhibit the recombination rate of photo-generated electron-hole pairs and enhance the photoactivity.

Fig.4 shows the percentage of degraded pigment under 10 min illumination for sample series 2 at 110℃ and 700℃, respectively. It is seen from the figure that the photoactivity of TiO_2 suspension decreases all the time with the increasing of doping ion at calcinating temperature 110℃ while the photoactivity of the one treated under 700℃ increase, and maximize at La content 0.8 (wt)% and decrease with further increase of doping ion. The photocatalytic activities of samples treated under 110℃ were much lower than those of the samples treated under 700℃.

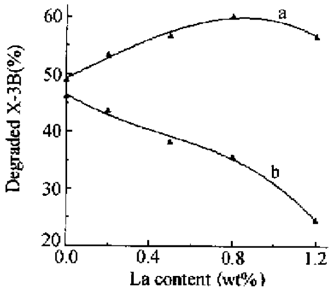

Fig.4 The percentage of degraded pigment vs. La content at calcinating temperature
a: 700℃; b: 110℃

Fig.5 shows the X-ray diffraction patterns of (101) plane for sample series 2 at calcinating temperature of 700℃. It seems that the way the variation of extent of lattice expansion is similar to, and can explained by the way the photoactivity of the system varies. We suggest that doping ion is saturated in the TiO_2 lattice treated at 700℃ for 3 hours. Accordingly, such sample exhibits the highest photoactivity. Further increase of doping ion inhibits the activity of the system as the excess doping ion deposit on the surface of the TiO_2 particles.

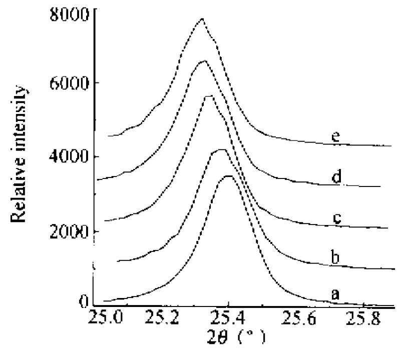

Fig.5 The XRD patterns of (110) plane for TiO_2 containing (a) 0; (b) 0.2; (c) 0.5; (d) 0.8; (e) 1.2 (wt)% La calcinated at 700℃ for 3 hours

Fig.6 shows the percentage of degraded pigment of sample series 3 under 10 min illumination. It is seen from the figure that the longer the calcinating time, the higher is the photocatalytic activity. The variation of doping La with the calcinating time may explain this tendency.

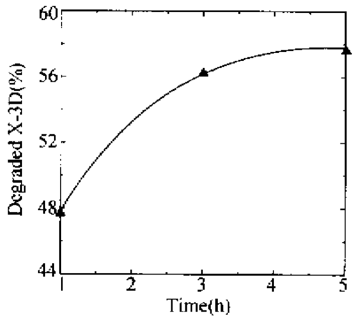

Fig.6 The percentage of degraded pigment *vs*. calcinating time for TiO_2 containing 0.5 (wt)% La treated at 700℃

CONCLUSIONS

The experimental results showed that the photoactivity of rare earth doping TiO_2 suspension is lower than that of pure TiO_2, but higher when treated under higher temperature and longer time. The X-ray diffraction results showed that the lattice expansion or the amount of doping oxide diffused into the crystal lattice is larger under higher temperature, longer time and larger amount of doping oxide when the amount of doping oxide is lower than 0.8 (wt)%. Accordingly, those samples exhibit higher photocatalytic activity because the suggested inhibiting effect on the recombination of photogenerated electron-hole pairs results in the extra hole trapping pathways.

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