

Comparison Study of Photocatalytic Properties of SrTiO₃ and TiO₂ Powders in Decomposition of Methyl Orange

He, H. Y.

College of Material Science and Engineering, Shaanxi University of Science and Technology, China

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ABSTRACT: Nano-SrTiO₃ and TiO₂ powders were synthesized using sol-gel method. The SrTiO₃ and TiO₂ powders were characterized using XRD, SEM, and spectrophotometry. XRD analysis indicated that the TiO₂ powder was uniform anatase crystals of 9.9 nm and the SrTiO₃ powders were cubic nano-crystal of 16.2nm. Photocatalytic experiments revealed that methyl orange in water can be decomposed on the two powders under sunlight irradiation. Benzyl groups in methyl orange can be fast decomposed on the SrTiO₃ powders than on TiO₂ powders although color peak was decreased in the reverse order. After irradiation of 4h, the decrease of the color peak and character peak of benzyl were respectively about 72% and 53% on the TiO₂ powder; however, the decrease of the color peak and character peak of benzyl were respectively about 93% and 88% on the SrTiO₃.

Key words: SrTiO₃, TiO₂, Powder, Photocatalysis, Benzyl degradation, Wastewater treatment

INTRODUCTION

The SrTiO₃ is a semiconductor with a band gap energy (~3.2eV) closed to TiO₂, and has been used for photochemical oxidation and reduction of metal species in water in forms of ceramics and single crystal (Giocondi and Rohrer, 2003). Recently some attempts have been made to investigate photocatalytic activity of SrTiO₃ powders (Han *et al.*, 2008 and Wang *et al.*, 2006) and substituted SrTiO₃ powders (Zhang *et al.*, 2006; Liu, *et al.*, 2006; Wang *et al.*, 2005; Ohno *et al.*, 2005 and Wang *et al.*, 2004) in destruction of organic contaminants.

Nano-TiO₂ materials as a familiar photocatalyst were studied widely for potential application in decontamination of environment. Its catalytic property has been improved by various doping (Scot *et al.*, 1994; Liu and Kamat, 1993; Audreas and Hoffmann, 1994; Lindgren *et al.*, 2003). Nano-TiO₂ materials with large specific surface area can be synthesized using critical point drying and freeze-drying processes. However, the SrTiO₃ powders with specific surface area closed to TiO₂ powders have not been currently

synthesized using wet chemical process. For this reason, it is of interest to investigate potential advantage in the active and selective for catalytic reaction on the SrTiO₃ powders by comparison with the TiO₂ powders.

SrTiO₃ powders have been synthesized with various processes, including sol-gel method (Cui *et al.*, 2007), Combustion process (Ishikawa *et al.*, 2008), hydrothermal reaction method (Wang *et al.*, 2006 and Chen *et al.*, 2001), for application of electric material. In present paper, we describe synthesis of SrTiO₃ and TiO₂ powders with sol-gel method and their photocatalytic features in destruction of methyl orange.

MATERIALS & METHODS

For the preparation of the precursor solution of SrTiO₃, equal molar amounts of the strontium chlorite hexahydrate (SrCl₂·6H₂O) and titanate butoxide (TiC₁₆H₃₆O₄) were stabilized with little acetylacetone to prevent the titanium butoxide from hydrolyzing and dissolved in a solution of acetic acid and water at volume ratio of 1: 1 at room temperature with constant stirring. The citric

*Corresponding author E-mail: hehy@sust.edu.cn

acid (CA) at molar ratio of CA: (Ti⁴⁺+Sr²⁺)= 2.5: 1 was added to this solution with constant stirring. The resultant stable precursor was yellow-colored transparent solution. The concentrations of the solution are 0.005M and 0.005M for Sr²⁺ and Ti⁴⁺ cation respectively, which is calculated on molar amounts of the strontium chlorite hexahydrate (SrCl₂·6H₂O) and titanate propoxide and volume of the solution. The precursor was dried successively at 80°C for 4h and 100°C for 10h and 120°C for 2h and 150°C for 1h. The color of the solution was changed from yellow to deep yellow and black successively. The gel was maintained transparent during the drying. During the initial stage of the drying, higher temperature made the solution muddy. So the slow drying schedule was used for drying the solution. The dried precursor was calcined at 750°C for 0.5h. TiO₂ particles were prepared with sol-gel method. Titanium isopropoxide was dissolved in ethanol and stabilized with little acetylacetonate and adjusted pH=5 with HCl with constant stirring and stable for a period of 3 day. Concentration of Ti⁴⁺ ion in the solution was 0.05M. The solution was then dried for 48h at 60-80°C. The gel was changed from yellowish to yellow. The gel was maintained transparent during the drying. As-dried precursor was calcined for 1h at 400°C in air.

The phase identification of the calcined powders was conducted at room temperature using X-Ray diffractometer (XRD, CuK_{α1}, λ=0.15406nm, Model No. D/Max-2200PC, Rigaku, Japan). The phase and the particle sizes of powders and films were determined with the Jade5 analysis software that was provided with X-Ray diffractometer. Scanning electron microscopy (SEM, Model No: JXM-6700F, Japan) was used to analysis the particles morphology and the agglomeration of the powders.

In this study, methyl orange was used as a photocatalytic substrate to study photo degradation on the SrTiO₃ powders. Photodecomposition experiments were performed in glass beaker. In each experiment, 100ml methyl orange solutions at concentration of 6×10⁻⁶M were added to the glass beakers containing 100mg SrTiO₃ and 100mg TiO₂ powders respectively, and then dispersed for 5min with ultrasonic generator (UG, 40kHz, Modal No: KQ-5200DE, China) at 100W. Sunlight was used as the light sources. The absorbance is of

methyl orange solutions before and after irradiations for times of 2h and 4h were measured on WFZ-900D4 spectrophotometer.

RESULTS & DISCUSSION

The TiO₂ and SrTiO₃ powders prepared by sol-gel method were soft powders and white in color respectively. Fresh surface of the powders should possess higher catalytic activity. The XRD patterns of TiO₂ and SrTiO₃ powders are shown in (Fig.1). which indicate that TiO₂ powder had anatase and little rutile phase and was of a particle size of 9.9nm determined with strong peak (101) at 2θ=25.3° and SrTiO₃ powders had cubic phase and was of particle size of 16.2nm determined with strong peak (001) at 2θ=15.04°. Specific surface area of powders (S_{BET}) were approximately calculated using this particle size (s, nm) and bulk density (d), 4.1g/cm³ for TiO₂ and 5.13 g/cm³ for SrTiO₃, according to:

$$S_{BET} = \frac{6}{s \cdot d}$$

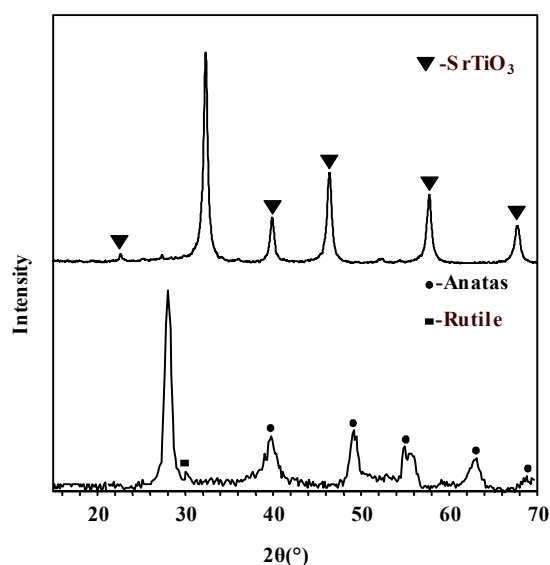
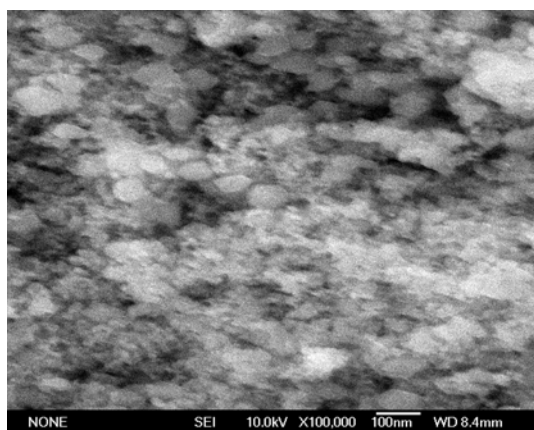
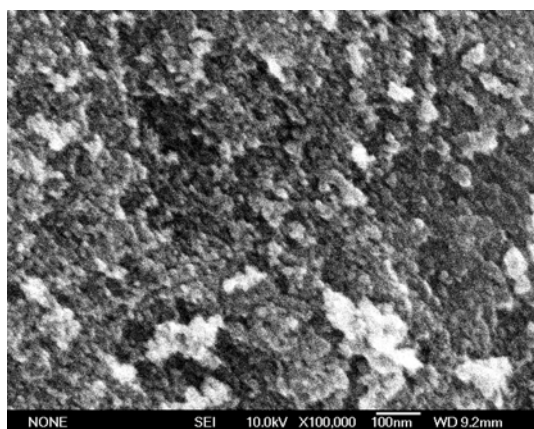


Fig. 1. XRD patterns of SrTiO₃ and TiO₂ powders

As-calculated S_{BET} were 148m²/g and 72m²/g for TiO₂ and SrTiO₃ respectively. SEM micrographs of TiO₂ and SrTiO₃ powders were shown in (Fig. 2). It is obvious that the SrTiO₃ powders were of average particle size of 10-50nm and the TiO₂ powders was of average particle size of 5-15nm and was aggregated to some content.



(a)



(b)

Fig. 2. SEM micrographs of (a) SrTiO₃ and (b) TiO₃ powders

Photo degradation of methyl orange solutions on TiO₂ and SrTiO₃ powders were studied in the experiments. In the absorption profile of methyl orange solution at a range of ultraviolet – visible light, there are two primary peaks, one is color peak at ~465nm, and another is characteristic peak of benzyl at ~192nm. Fig. 3.(a) show absorbance variations of methyl orange solutions at ~462nm with irradiation time. It is obvious that photo degradation on two powders were respectively increased with increasing irradiation time. Photo degradation was faster on the TiO₂ powders than on the SrTiO₃ powders, which may be due to difference in specific surface area of two powders.

Fig.3. (b) showed the absorbance variation of methyl orange solution at ~192nm with irradiation time. Benzyl in methyl orange were also photo degraded on two powders with

irradiation time but fast photo degraded on the SrTiO₃ powders than on the TiO₂ powders which is a reversal order of degradation at ~465nm. This can be explained as follow. Sr cation in SrTiO₃ is strong alkaline site playing a role of reducing catalysis. In aquatic environment, benzene and benzyl is more easily decomposed in condition of reducing catalysis than in oxide catalysis by hydrogen reaction. In general, product of preliminary photodecomposition of many organic contaminants containing benzyl on the photocatalyst, concluding TiO₂ powders, is benzene and various substituted benzene that are also detrimental to human health and the environment. The SrTiO₃ powders can faster photo degraded benzyl in comparison with the TiO₂ powders, which make them potential advantage in decontaminant of aquatic environment.

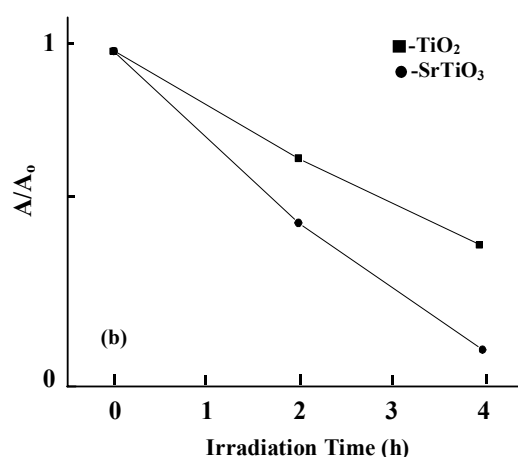
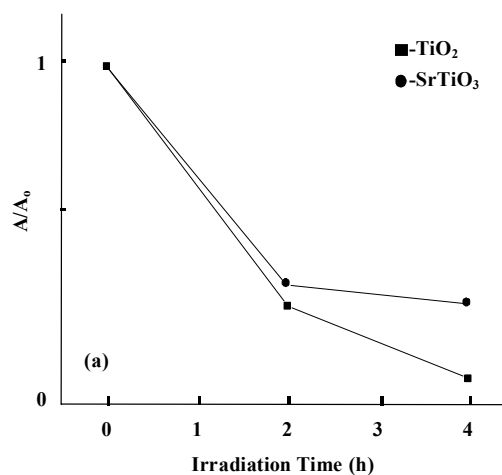


Fig. 3. Absorbance variations of methyl orange (a) at 462nm and (b) at ~192nm with irradiation time

CONCLUSION

The SrTiO₃ and TiO₂ powders were efficiently synthesized using sol-gel methods. Two powders have a large surface area and a good photo degradation property. The activity and selective of catalytic degradation of methyl orange on two powders were compared. SrTiO₃ powder has potential advantage in photodecomposition of benzyl. This, together with narrow band gap energy of SrTiO₃, makes the SrTiO₃ powders able for many applications of heterogeneous catalyses and environment decontamination.

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