

Preparation of $\text{TiO}_2\text{-MoO}_3$ nano-composite photo-catalyst by supercritical fluid dry method

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Abstract: A series of $\text{TiO}_2\text{-MoO}_3$ nano-composite photocatalysts were prepared by supercritical fluid dry method (SCFD) and an impregnation technique with TiCl_4 and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ as the starting materials. The catalysts were characterized by the means of XRD, TEM and UV-Vis. Methyl orange was used as model compound for the evaluation of their catalytic activities. The results indicated that the photo-catalyst prepared by SCFD had the advantages of small size (12.84 nm), narrow distribution and good dispersivity. The presence of small amount of Mo in composite catalyst gives rise to the red shift of its absorbance wavelength, decrease of its energy gap and increase of the utility of visible light. Furthermore, higher surface acidity of the photo-catalyst was obtained as the result of the addition of MoO_3 . Compared with pure TiO_2 , the catalytic activity of the $\text{TiO}_2\text{-MoO}_3$ nano-composite photo-catalyst was improved significantly. As the doping concentration of the composite catalysts was controlled at 0.6% (molar percentage), 100% degradation of methyl orange was achieved with in 1.2 h irradiation time.

Keywords: TiO_2 ; MoO_3 ; photocatalytic; supercritical fluid dry method

Introduction

TiO_2 is widely used in multiphase photo-catalytic reactions, and is also one of the most effective catalysts in the degradation of environmental contaminants (Hoffmann, 1995; Fujishima, 2000). However, as a semiconductor of wide bandgap, it could only be activated by ultraviolet. While the fraction of ultraviolet in the sunlight that reaches the earth surface is only 4%—6%. In the recent years, doping of transition metal ions or surface modifications have been applied to extend the range of photo activation and thus to overcome the limitation of low utility of sun energy. The nano TiO_2 has demonstrated distinct surface effect and quantum size effect, its stronger oxidation-reduction ability in the radiation of light makes it a promising future. In this paper, we present a new method to prepare the $\text{TiO}_2\text{-MoO}_3$ nano-composite photo-catalyst. The catalysts obtained have much higher photo-catalytic activity than those previously reported (Komandur, 2001; Jeon, 2000). Methyl orange could act as the typical example for environmental organic pollutants and are chosen as the research substrate due to its high toxicity, complex structure and non-biodegradability. Therefore, we prepared nano- TiO_2 species with different Mo content to investigate the effect of doping concentration and calcination temperature on the catalytic activity. It has been found that the photo-catalyst prepared by SCFD have the characteristics of small size, narrow distribution, good dispersivity and high catalytic activity.

1 Experimental

1.1 Preparation of nano-sized TiO_2 by SCFD

1.1.1 Preparation of TiO_2 gel by sol-gel method

TiCl_4 solution (0.3 mol/L) was mixed with surfactant (0.3%), after stirring ammonia (3 mol/L) was added to the mixture at the rate of 2 ml/min at the room temperature until pH 7—8 was reached. The suspension obtained was then placed for 20 h without stirring, the TiO_2 gel was finally obtained.

1.1.2 Phase transfer

The TiO_2 gel was washed with water until no Cl^- could be detected and separated by centrifugation. The water in the gel was replaced by absolute ethanol to afford alcogel.

1.1.3 Preparation of TiO_2 aerogel by SCFD

The alcogel was transferred into an autoclave, after addition of absolute ethanol, the temperature was raised at a rate of 100 °C/h. The mixture was kept under the supercritical condition of alcohol (262 °C, 8.5 MPa) for 30 min. Removing the solvent, followed by sweeping with nitrogen, cooling naturally to room temperature give TiO_2 as aerogel.

1.2 Preparation of nano-sized $\text{TiO}_2\text{-MoO}_3$

TiO_2 aerogel was added to the $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ solution, after stirring $\text{HCl-CH}_3\text{COOH}$ was added slowly to the suspension until the pH

1—2 reached. After drying in oven at 60 °C for 24 h, the grey-black solid was grinded to fine powder and calcined at 500 °C for 1 h and $\text{TiO}_2\text{-MoO}_3$ nano-composite particles of different Mo content (0.0%, 0.3%, 0.6%, 0.9%, 1.3%) was obtained.

1.3 Particle characterization and chemical composition determination

The contents of Mo and Ti were measured by atomic absorption spectrophotometer (Z-8000).

X-ray diffraction measurements were performed using a Shimadzu HR6000X (copper target X tube, pressure 40.0 kV, current 30.0 mA, scan angle 5—80°).

The surface morphologies and particle sizes were determined by transmission electron microscopy (TEM, Hitachi-800).

A Shimadzu UV-2100S (scanning range 200—800 nm) was employed to measure the absorbance spectra of samples.

1.4 Evaluation of photo-catalytic activity

The photo-catalytic activities of the particles were examined using a self-designed photo-catalytic reaction device. It consists of three layers of concentric, cylindrical quartz flask with an ultraviolet lamp (9 W, wavelength: 254 nm, intensity: 5860 $\mu\text{W}/\text{cm}^2$) in the middle (Fig. 1). Methyl orange aqueous solution (20 mg/L) is used as degradation solution. The concentration of catalyst is 1 g/L. The air is introduced from the bottom of the reaction solution at the rate of 30 ml/min, the temperature is controlled within the range of 25 ± 1 °C. Stirring is kept to make sure the catalyst was dispersed evenly in the reaction solution. A small volume of the reaction solution was periodically withdrawn. After centrifugal separation, the absorbance of this solution is measured with 752 spectrophotometer at 464 nm wavelengths. The photo-catalytic activity was identified as the degradation rate of methyl orange.

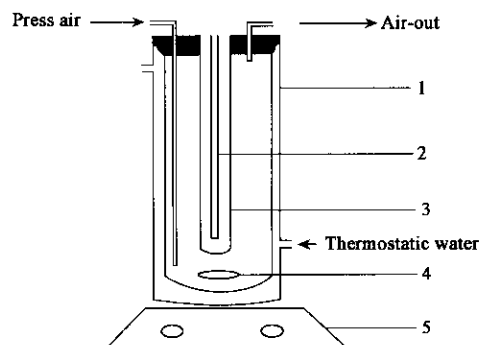


Fig. 1 Apparatus of photocatalytic reaction
1. jacketed thermostatic vessel; 2. UV-lamp; 3. quartz tube; 4. magnet; 5. magnetic stirring apparatus

2 Results and discussion

2.1 Results from XRD measurements

2.1.1 Effect of calcinations temperatures on surface morphologies and particle size

X-ray diffraction date of TiO₂-MoO₃ (0.6%), prepared by SCFD with calcinations at 400 °C, 500 °C and 600 °C respectively, are shown in Fig.2. It can be seen that TiO₂ was obtained only as anatase type crystal, which has diffraction peaks at 3.52Å°(101), 1.89Å°(200) and 2.38 Å°(004). There is no transformation from anatase type to rutile type could be observed after the heat treatment. This confirms the report that TiO₂ by SCFD exists only as anatase type crystal(Zhang, 1999). At the same time, there is no diffraction peaks from MoO₃ could be found in XRD of TiO₂-MoO₃ composite photo-catalyst. With the increase of the heat treatment temperature, the position of the diffraction peaks remain almost the same, the intensity becomes stronger, the peak of the strongest diffraction peak(101) sharpens, all these have shown that the crystal structure appears more intact without the transformation of the crystal type after calcinations.

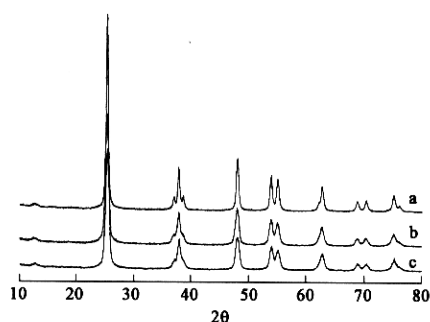


Fig.2 XRD pattern of various sample particles
a. 600 °C; b. 500 °C; c. 400 °C

The average radius of the particles is calculated with Scherer equation to be 12.20 nm, 12.84 nm, 18.11 nm, respectively for species prepared at 400 °C, 500 °C, and 600 °C calcinations. This clearly showed that the size of the particles grows with the increase of the calcinations temperature. No observance of MoO₃ diffraction peaks indicated that the MoO₃ phase is present in a highly dispersed or amorphous state on the surface of TiO₂.

2.1.2 Effect of Mo doping concentrations on TiO₂-MoO₃ surface morphologies and particle sizes

The contents of Mo in TiO₂-MoO₃ composites particles were determined by atomic absorption spectrophotometer to be 1.3%, 0.6%, 0.3%. XRD results of these particles are given in Fig.3. There is no influence for the crystal structure of TiO₂ as the content of Mo increase from 0.3% to 1.3%, the diffraction peaks can still not be observed in these cases. These results provided the same conclusion that the MoO₃ phase is present in a highly dispersed or amorphous state on the surface of TiO₂.

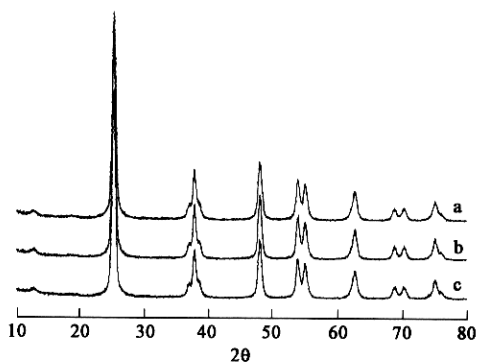


Fig.3 XRD pattern of various sample particle
a. 0.6%; b. 1.3%; c. 0.3%

2.2 Results from TEM measurements

The TEM pictures of TiO₂ and TiO₂-MoO₃ composite particles are shown in Fig.4. The powders obtained by SCFD, both the pure TiO₂ (Fig.4a) and the composite particles(Fig.4b) are observed to be 10—15 nm in size. On the other hand, the aerogel powders from SCFD were found to have very good dispersivity, there are distinct net-like structures between particles. Under the condition of SCFD, the powder could be dried in the absence of surface tension and keep the original structures of alcogel to give nano particles which have small size, large surface area and good dispersivity.

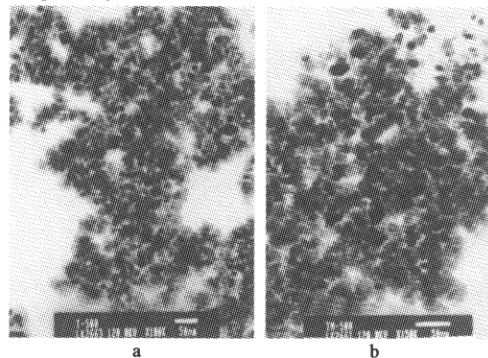


Fig.4 TEM photograph of various sample particles
a. TiO₂, 500 °C; b. TiO₂-MoO₃, 500 °C

2.3 UV-Vis spectra

The UV-Vis spectra of TiO₂ and TiO₂-MoO₃ (0.6%) by SCFD and followed by calcinations at 500 °C are shown in Fig.5. It could be seen from Fig.5a that the red-shift(about 15 nm) takes place in the spectra of TiO₂-MoO₃ due to the lower energy gap. Semiconductors absorb light below a threshold wavelength, the fundamental absorption edge, which is related to the energy gap via(Hagfeldt, 1995):

$$\lambda_g(\text{nm}) = 1240/E_g(\text{eV}).$$

The energy gap of the particles is calculated equation to be 3.43 eV, 3.56 eV, respectively for TiO₂-MoO₃ (0.6%) and pure TiO₂ species prepared, and then decreased to 0.14 eV. This result met the aim of the study to absorb more of the solar spectrum reaching the earth as small amount of Mo is added.

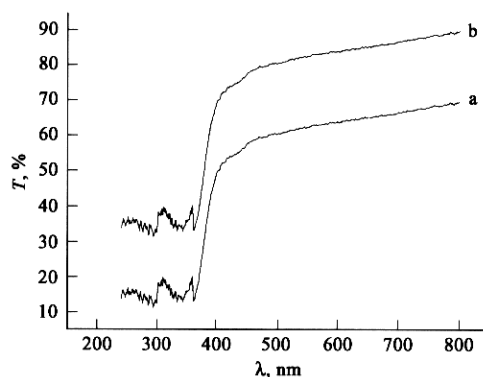


Fig.5 UV-Vis spectra of TiO₂-MoO₃
a. TiO₂-MoO₃; b. TiO₂

2.4 Effect of the longer wavelength on the photo-catalytic activities

The evaluation experiments were carried out in an ultraviolet lamp (11 W, wavelength: 365 nm, intensity: 1102 μW/cm²) using methyl orange aqueous solution (20 mg/L) as the degradation solution. The degradation rate of TiO₂ and TiO₂-MoO₃ (0.6%) by SCFD and followed by calcinations at 500 °C are shown in Fig.6 (The concentration of catalyst is 1 g/L). The degradation rate of TiO₂-MoO₃ (0.6%) is higher than that of the pure TiO₂.

It is shown in Fig.6a that the TiO₂-MoO₃ nano composite catalyst has better methyl orange degradation rate than pure TiO₂ catalyst in the radiation of long wavelength violet light. This higher catalytic activity is probably because the addition of Mo decreases the energy gap of TiO₂, which has been demonstrated by the red shift in its absorption spectra in

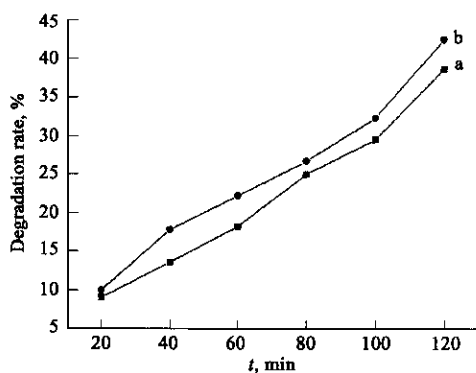


Fig. 6 Effect of the longer wavelength on photocatalysis
a. TiO₂; b. TiO₂-MoO₃

2.3. The quantum size effect could be ignored due to the similar particle sizes as the result of measurement in 2.2.

2.5 Effect of Mo doping concentrations on the photo-catalytic activities

Fig. 7 shows the catalytic activities of TiO₂-MoO₃ nano-composite catalysts (Mo doping concentration are 0.0%, 0.3%, 0.6%, 0.9%, 1.3% respectively) which are prepared by an impregnation technique. The addition of Mo can increase the photo-catalytic activities of these particles, which are much higher than that of the pure TiO₂. When the content of Mo is 0.3% to 0.6%, the addition of Mo can increase the photo-catalytic activities of these particles. When the content of Mo is 0.9% and 1.3%, the addition of Mo can decrease the photo-catalytic activities of these particles. The catalyst containing 0.6% Mo is the best with the degradation rate of methyl orange at 100% in 1.2 h.

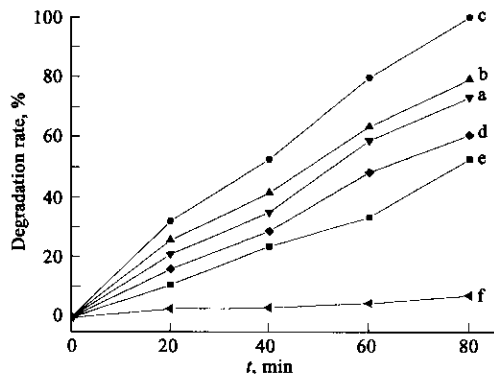


Fig. 7 Effect of Mo concentration on photo-catalysis
a. 0.0; b. 0.3; c. 0.6; d. 0.9; e. 1.3; f. contrast

When new particles are subjected to light, the valence electrons of TiO₂ are excited to the conduction band, resulting in the separation of electrons and holes, the hydroxy radicals are produced when holes react with hydroxy. The isolated MoO₃ is believed to play a key role in the acceptance of those excited electrons from TiO₂. In the presence of MoO₃ particles, Mo of high valence could be reduced by the electrons on TiO₂ conduction band (Lee, 1993), at the same time, the electrons of MoO₃ could combine with oxygen absorbed on TiO₂ to form oxygen anion. The effective separation of electrons and holes and the decrease of charge recombination thus enhance the catalytic activities of catalysts.

Excess positive charges on the surface of TiO₂ can be regarded as the result of the addition of Mo of high valence. This also produces more acidic positions on the surface. The acidity of composite photo-catalysts is quite important in the improvement of its catalytic activities (Papp, 1994). However, as the concentration of Mo is too high, the heterogeneous particles could form between MoO₃/TiO₂ and MoO₃, the two chemically different crystals. The connecting of their conduction bands and valence bands makes it easier for the photoelectrons to combine with holes, and the photo-catalytic activity will definitely decrease. In Fig. 7, it is clear that the addition of small amount of Mo can increase the activity significantly, as the trend has been shown from c to d. When the Mo doping concentration is lower than 0.3%, the

number of electron and hole is not enough for the effective separation, the catalytic activity of catalysts is not high. This is the same case as the concentration exceeds 1.3%, the decrease of TiO₂ active centers reduces the absorbance of light. The best concentration of MoO₃ is found to be 0.6%. TiO₂ powder samples (Pegussa P25) were calcined at 500°C for one hour, the degradation rate of methyl orange reaches 60.1% in 1.2 h irradiation time.

2.6 Effect of calcinations temperatures on the photo-catalytic activities

The TiO₂-MoO₃ (0.6%) composite particles was heated at 400°C, 500°C, 600°C for one hour, respectively, the photo-catalytic activities of these catalysts were studied through methyl orange degradation tests in 1 h irradiation time and the results are shown in Fig. 8.

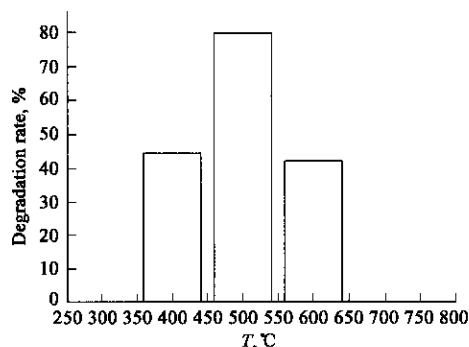


Fig. 8 Effect of heated-temperature on photo-catalysis

Treatment at 500°C gives the catalyst of best activity, at the lower calcinations temperature, the surfaces of the catalyst were still coated by some organic compounds (such as alcohols, surfactants), thus the active centers were covered and results into lower catalytic activity. As the temperature increases, decomposition of the impurities will expose more active centers on the surface. However, when the calcinations temperature rises to 600°C, the growth of the powder from 12.84 nm to 18.11 nm leads to decrease of the surface area and thus the photo-catalytic activities.

3 Conclusions

TiO₂-MoO₃ nano-composite catalyst prepared by SCFD and an impregnation technique, has the advantage of small size, narrow distribution, large surface area and good dispersivity. The red-shift happens in the ultraviolet absorbance spectrum of TiO₂-MoO₃ nano-composite catalysts due to the decrease of energy gap, this enhances the utility of sunlight. The addition of suitable amount of Mo can increase the surface acidity of TiO₂ and thus improve its catalytic activity.

The optimum doping concentration of MoO₃ in TiO₂-MoO₃ nano-composite catalysts is found to be 0.6%. The activity of catalyst increases by two times, and the degradation rate of methyl orange reaches 100% in 1.2 h irradiation time.

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