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Calcination Effects and Photocatalytic Activity of Porous SiO₂-TiO₂ Material

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A porous SiO₂-TiO₂ photocatalyst was prepared through co-sol-gel method using PEG1000 template for photocatalytic degradation of methyl orange. Photocatalytic degradation was conducted after adsorption equilibrium to identify the contribution of both adsorption and photocatalytic degradation. The optimum calcination condition for the porous SiO₂-TiO₂ is 500 °C for 3 h. The adsorption of methyl orange on the photocatalyst has no apparent change in the whole temperature range. Nearly 96.5 % of the initial methyl orange is removed in 100 min under UV light irradiation with the existence of the porous SiO₂-TiO₂. Methyl orange degradation follows the first order kinetics equation. The azo and benzene structure are degraded into small molecules during photocatalytic oxidation process.

Keywords: TiO₂, SiO₂, Photocatalysis, Composite.

INTRODUCTION

One of the most concerned environmental problems is the pollution in air and aquatic system. Aside from the traditional air and water treating methods, some new techniques have found their application potential due to their special advantages such as high efficient and low cost. Photocatalytic oxidation of most of the existing environmental pollutants is a promising method, which in the research during the past decades has provided people a satisfactory way in dealing with the current environmental problems^{1,2}.

A research focus in this field is to find new photocatalyst that is stable, low cost and has high activity³. On the other hand, people also try to enhance the properties of currently widely investigated photocatalyst. Some researchers have developed some kinds of composite materials applicable in photocatalytic degradation process, such as SnO₂/TiO₂, Al₂O₃-TiO₂ and TiO₂-SiO₂⁴⁻⁶. Previous workers have also paid much effort on preparing porous TiO₂ in order to enhance photocatalytic activity⁷. Sol-gel is a widely applied method used for preparation of nano-sized TiO₂ photocatalyst. In order to improve the properties of the prepared photocatalyst, some kinds of techniques such as transition metal doping and composite photocatalyst have been used to enhance the activity of the prepared materials. Porous materials are regarded as one of the promising choice in improving performance on pollutant treatment. Mesoporous and macroporous materials accompanied with large specific surface area are considered to be effective in promoting photocatalytic oxidation efficiency.

To our best of knowledge, there was no literature reporting the preparation and properties of porous SiO₂-TiO₂ composite photocatalyst. In this paper, a porous SiO₂-TiO₂ photocatalyst was prepared through co-sol-gel method used for photocatalytic degradation of methyl orange. PEG1000 was used as a template.

EXPERIMENTAL

Sol-gel preparation: Porous SiO₂-TiO₂ catalyst was prepared according to a co-sol-gel process by the following method. Tetrabutyl titanate [Ti(OBu)₄, 2 mL] and ethyl silicate (0.0075 mL) were slowly added to ethanol under continuous magnetic stirring to obtain a mixed slurry and then PEG1000 template was added to the slurry. Another ethanol-water solution was added to the mixed slurry to hydrolyze tetrabutyl titanate and ethyl silicate after the mixture was stirred for 1 h. The resulting slurry was still under continuous magnetic stirring until it became a gel. The gel was dried at 90 °C for 12 h and calcined at the temperature indicated later. Finally, the catalysts were grinded into fine powders and stored in the dark.

Photocatalytic activity: Photocatalytic activity of the photocatalyst was evaluated by measuring degradation rate of aqueous methyl orange under UV irradiation. In each experiment, 0.03 g of the photocatalyst was put into 50 mL of 10 mg/L methyl orange aqueous solution in a 200 mL beaker. A 20 W UV lamp was suspended 11 cm above the solution. The lamp can irradiate UV light at wavelength of 253.7 nm with the intensity of 1100 μW/cm². In prior to turn on the lamp, the solution was magnetically stirred for 0.5 h to ensure adsorption

equilibrium. Methyl orange concentration was measured by a spectrophotometer (Shanghai Spectrum Instruments 721E) at its maximum adsorption wavelength of 466 nm. The suspensions were filtered through a Millipore filter (pore size 0.45 mm) before measuring. Irradiation time in the subsequent experiments was 0.5 h except for the prolonged examination.

RESULTS AND DISCUSSION

In order to prepare suitable porous material for the above mentioned purpose, template is always needed in the preparation process as the function of providing pore formation director. In this work, a porous SiO₂-TiO₂ photocatalyst was prepared through co-sol-gel method using PEG1000 as the template. Calcination temperature may affect crystal formation and phase change and it may also influence formation of porous structure and the removal of template, which will in turn affect property of the prepared material. Low temperature calcinating can lead to incomplete crystal formation and low activity. However, calcination at too high temperature may result in collapse of porous structure, crystallite growing and low activity as well.

Fig. 1 indicates methyl orange decoloration on the porous SiO₂-TiO₂ calcinated at different temperatures. The degradation rate increases with increasing calcination temperature in the temperature range from 400 to 500 °C and then it decreases with further increase of temperature. The optimum calcination temperature for the porous SiO₂-TiO₂ is 500 °C. At the same time, the adsorption of methyl orange on the photocatalyst has no apparent change in the whole temperature range.

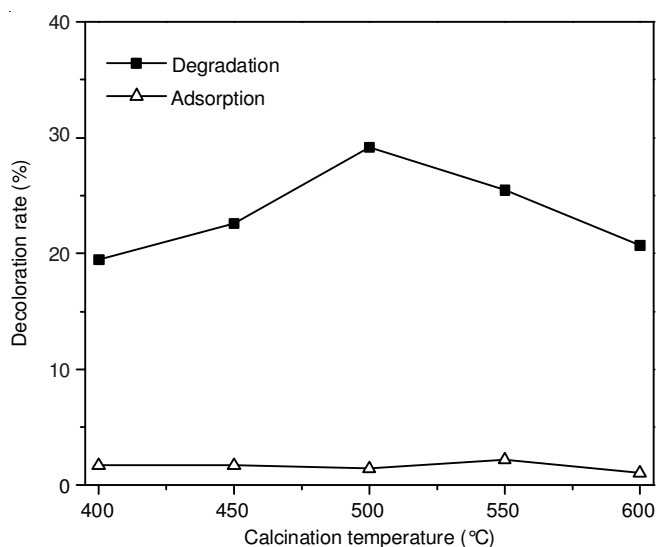


Fig. 1. Effect of calcination temperature on photocatalytic activity and adsorption of porous TiO₂-SiO₂ composite material

The porous SiO₂-TiO₂ was calcinated at 500 °C for different time in order to investigate their adsorption and degradation activities (Fig. 2). The adsorption capacity has nearly no variation with the change of calcination time from 2 to 5 h and the degradation activity has a maximum value after 3 h of calcination. The photocatalyst calcinated at 500 °C for 3 h can lead to 29.2 % degradation of the initial methyl orange in 0.5 h. It also indicates that nearly most of decoloration of the dye is due to photocatalytic degradation process. Adsorption

of the dye can only contribute a small portion to the overall decoloration. Crystallite formation mainly depends on calcination temperature, while calcination time is responsible for crystal growing as well as removal of organic substances in the material. Structure and porosity of the material can be influence by both calcination temperature and time. The suitable thermal treatment condition is 3 h at 500 °C for the prepared porous SiO₂-TiO₂.

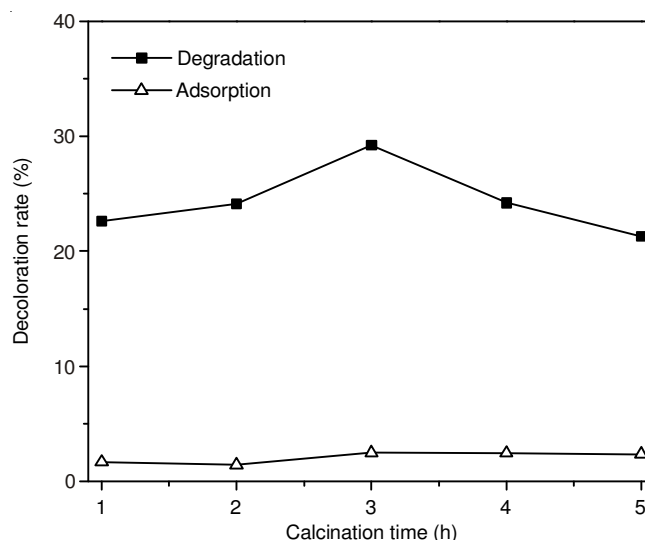


Fig. 2. Effect of calcination time on photocatalytic activity and adsorption of porous TiO₂-SiO₂ composite material

Methyl orange adsorption equilibrium curve on the porous SiO₂-TiO₂ is shown in Fig. 3. The adsorption amount of methyl orange increases to the maximum value in the first 10 min. No obvious variation can be found with further increase of adsorption time. The highest adsorption rate is less than 2.5 %, which is quite small compared to photocatalytic degradation efficiency. In this work, the solution containing methyl orange and photocatalyst was thoroughly stirred to reach adsorption equilibrium. Photocatalytic degradation was conducted after adsorption equilibrium to identify the contribution of both adsorption and photocatalytic degradation.

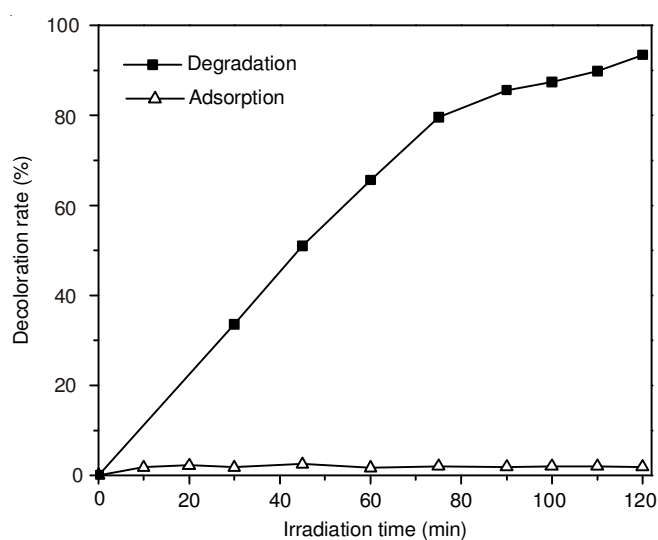


Fig. 3. Decoloration of methyl orange on porous SiO₂-TiO₂ as the factor of irradiation time

After an extending time of irradiation, the methyl orange solution containing the porous SiO₂-TiO₂ as photocatalyst can be fully degraded, as illustrated in Fig. 3. Nearly 96.5 % of the initial methyl orange is removed in 100 min under UV light irradiation with the existence of the porous SiO₂-TiO₂.

Fig. 4 Shows kinetics curve of photocatalytic degradation of methyl orange with extending irradiation time. After linear fitting of the data, the equation $\ln(C/C_0) = 4.99007 - 0.02521t$ can be obtained with $R^2 = 0.990$. It shows that methyl orange degradation follows the first order kinetics equation.

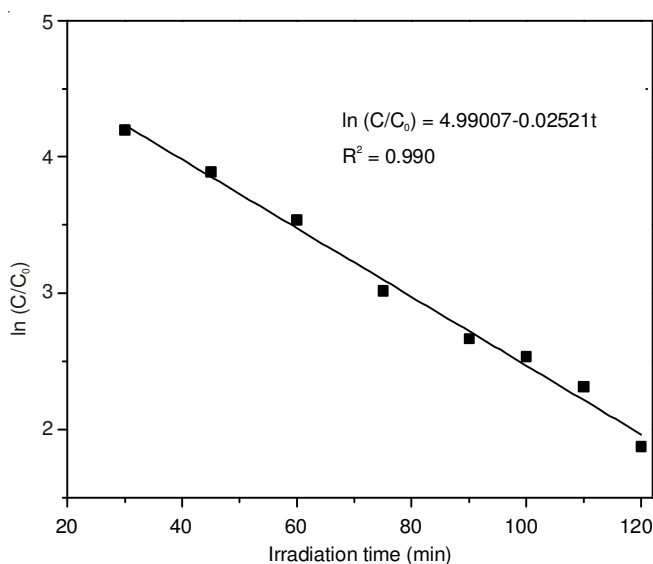


Fig. 4. Kinetics curve of photocatalytic degradation of methyl orange

UV-visible absorption curves of methyl orange solution during irradiation are presented in Fig. 5. Methyl orange solution has two major absorption peaks at 468 nm and 270 nm. The former absorption peak is in visible region and is often used to ascertain concentration of the dye. The two absorption peaks shrink with extending irradiation time during photocatalytic process. Nearly no absorption peaks can be found after 4 h of degradation. That means the azo and benzene structure of the dye are degraded into small molecules during photocatalytic oxidation process.

Conclusion

A porous SiO₂-TiO₂ photocatalyst was prepared through co-sol-gel method using PEG1000 as the template. The degradation rate increases with increasing calcination temperature in the temperature range from 400 to 500 °C and then it decreases with further increase of temperature. The photocatalyst calcinated

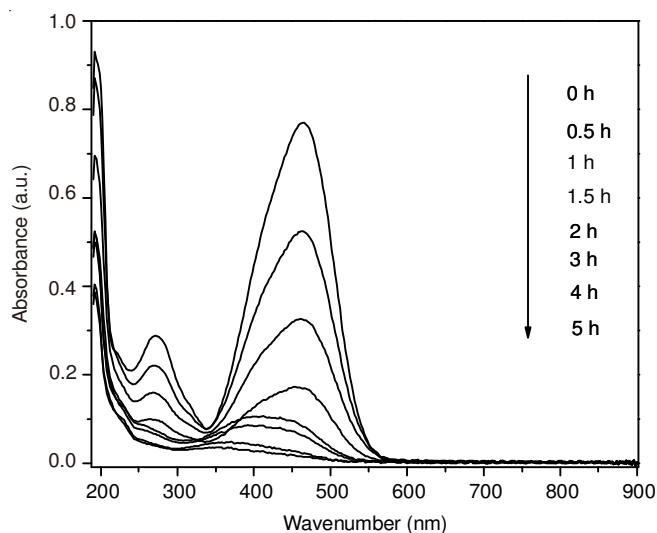


Fig. 5. UV-visible absorption curves of methyl orange solution during irradiation

at 500 °C for 3 h can lead to 29.2 % degradation of the initial methyl orange in 0.5 h. The adsorption of methyl orange increases to the maximum extent in the first 10 min. Nearly 96.5 % of the initial methyl orange is removed in 100 min under UV light irradiation with the existence of the porous SiO₂-TiO₂. The two absorption peaks of the dye shrink with extending irradiation time during photocatalytic process.

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