Influence of Silicon Content on the Photocatalytic Activity of Methyl Orange by TiO$_2$-SiO$_2$ Composite Aerogels

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Abstract. TiO$_2$-SiO$_2$ aerogel has been synthesized at an ambient pressure with a silica-precursor of waterglass and a titania-precursor titanium tetrachloride with a variable silicon content (10%, 20%, 30%) by sol-gel method/surface modification. The photocatalytic performance of these materials was tested by degrading the methyl orange following UV light irradiation at $\lambda = 465$nm. The experimental results have shown that the as-prepared aerogels have entirely consisted with anatase crystalline phase. With the increase of silicon content, the photocatalytic degradation capacity of the as-synthesized aerogels was decreased. When the silicon content is 10%, the best catalytic degradation effect was obtained, the decolorizing efficiency of MO is detected as 97.13% after 160 mins exposure to UV light irradiation.

Introduction

TiO$_2$ aerogel, with the characteristics of good stability, high catalytic activity, non-toxic, combined with the porous structure and high specific surface area of aerogel, has been considered one of the best photocatalytic materials\[1,2\]. However, it is difficult to obtain practical application because of its poor network structure. The results show that SiO$_2$ aerogel possesses strong network structure, high specific surface area and large pore volume. Therefore, it is common to improve the catalytic activity of TiO$_2$ aerogel by introducing SiO$_2$ into the TiO$_2$ sol\[3\].

Feng Jian et al.\[4\] studied the effect of silicon content on the structure and properties of Al$_2$O$_3$-SiO$_2$ aerogels. The results show that with the increase of silicon content, the gelation time of Al$_2$O$_3$-SiO$_2$ sol was extended, the aerogel density increases gradually, the structure made of polycrystalline boehmite favour a transition to amorphous SiO$_2$. When the silicon content is 6.1wt%~13.1wt%, the appropriate amount of silicon inhibits the phase transition of Al$_2$O$_3$-SiO$_2$ aerogel, and its specific surface area (339~445 m$^2$.g$^{-1}$) after 1000°C calcination is higher than that of pure Al$_2$O$_3$ aerogel (157m$^2$.g$^{-1}$). Li XW et al.\[5\] studied the microstructure of TiO$_2$-SiO$_2$ composite aerogels with different silicon content by using tetrabutyl titanate and TEOS as raw materials. The results indicate that with the silicon content increasing, the density of the composite aerogel becomes smaller, the specific surface area increases, the porosity enhances, and the phase transition temperature increases. Above all, Further research of silicon content influence on photocatalytic degradation of methyl orange is needed.

In this work, TiO$_2$-SiO$_2$ aerogel has been synthesized at an ambient pressure with waterglass and titanium tetrachloride via applying sol-gel method at low temperature/surface modification. The effect of silicon content of TiO$_2$-SiO$_2$ aerogels on photocatalytic activity under UV light irradiation was optimized for the degradation of Methyl orange (MO).
Experimental

Chemicals

Waterglass (Be°=37, ratio of Na$_2$O:SiO$_2$=1:3.3, Changzhou Yongfeng Chemical Co. Ltd., China), titanium tetrachloride (TiCl$_4$, ≥98.0%, Shanghai Lingfeng Chemical Co. Ltd., China), Sulphuric acid (H$_2$SO$_4$, Cancheng Chemical Co. Ltd., China), Chlorotrimethylsilane (TMCS, ≥98%, Chinese Medicine Group Chemical Reagent Co. Ltd.), n-Heptane (≥97%, Chinese Medicine Group Chemical Reagent Co. Ltd.), Ethanol (C$_2$H$_5$OH, ≥99.7%, Chinese Medicine Group Chemical Reagent Co. Ltd.) were used as received without any further purification. Strongly acidic styrene type cation exchange resin (Amberlite, D001) was used to exchange water glass solution to prepare silicon precursor. Distilled water was used in all experiments.

Synthesis of TiO$_2$-SiO$_2$ Gels

TiO$_2$/SiO$_2$ composite aerogels was synthesized by two-step method. First of all, the waterglass was diluted with deionized water, in which SiO$_2$ content of 10% v/v, 20% v/v, 30% v/v respectively, was used as the silica gel precursor. Then the cation exchange resin of strong acidic styrene was used to carry out ion exchange to obtain silicic acid of pH1-2. In the second step, Titanium sol was prepared by TiCl$_4$: ETOH in the molar ratio of 1:2, to this solution was added the mixture of silicic acid under constant stirring at 40°C and gelation was initiated by adding a 1M solution ammonium hydroxide (NH$_4$OH) at 1% v/v of the sol. The gelation-initiated sols were poured into polystyrene moulds, shortly after which the alcogels were covered with ethanol and aged overnight and labeled with WT-1, WT-2, WT-3 respectively.

Solvent Exchange/Surface Modification and Drying of TiO$_2$-SiO$_2$ Gels

Modification study was conducted to get aerogel materials with better features. After crystallization of gelation, the hydrogels were immersed into distilled water at 50°C for 24 h, and then soaked in the 50 vol%H$_2$O/ethanol solution and aged for 24 h at room temperature so as to strengthen the gel network. Further, the surface modification was performed by soaking gels in EtOH/TMCS/Heptane solution for 24 h at 50°C. After the reaction between the wet gel and EtOH/TMCS/Heptane solution were completed and pore water were extruded (exchanged by heptane) thoroughly, the modified wet gels were aged again for 24 h and then were dried at 150 °C for 2 h in the oven.

Photocatalysis of TiO$_2$-SiO$_2$ Gels

The aerogels prepared with strong hydrophobicity are not conducive to the adsorption and degradation of MO solution, therefore, the aerogels were calcined at 500°C for 2h. Photocatalytic activity evaluation of catalyst samples was using methyl orange as target pollutants. The photocatalytic degradation experiments were carried out in a beaker of a total volume of 100ml placed directly on the stirring platform. The powered aerogels (50mg) were putted into the 100mL methyl orange solution (10mg/L). The contents were kept constant stirring 1h to allow the solid-liquid equilibration. Then UV light was turned on using LED lamp for about 6 h during which time an aliquot (4mL) was extracted from reaction solution supernatant at every 15 minutes for product analysis with a UV spectrophotometer determination of methyl orange solution absorbance at 465nm. Comparative experiments were carried out under the same conditions of the gels without exposure to UV light.

Characterization

X-ray diffraction (XRD) was used to identify the crystallite phase present in TiO$_2$-SiO$_2$ aerogels and the data was obtained on an APEX II DUO X-ray diffractometer of Rigaku Corporation with a Cu Kα source at 40 mA and 40 kV. UV-Vis absorption features of the TiO$_2$-SiO$_2$ aerogels were studied on a spectrophotometer equipped with an integrating sphere over a wavelength range of 190-900 nm. Infrared spectroscopy (FT-IR) was used to study the chemical composition and the structure of the group. Microstructure was obtained on SEM analysis equipped with a FEI Nova Nano SEM 230 instrument (FEI, Hillsboro, Oregon, USA).
Results and Discussion

Structural and Morphological Study

Figure 1. The SEM of TiO\textsubscript{2}-SiO\textsubscript{2} aerogels(a)WT-1(b)WT-1(c)WT-1(d)WT-1 after 500°C calculations.

The SEM image of the aerogels prepared by different Si content is shown in Fig.1, which all exhibits similar porous network structure formed by cross linking nano scale skeleton particles. With the increase of silicon content, the porosity of the composite aerogel decreases, but the basic structure of the aerogel does not change obviously. From the Fig.1ac we can see the particle cluster phenomenon, which is formed by TiCl\textsubscript{4} alcoholsysis too quickly. Fig.1d shows the structure of the sample WT-1 is gradually intensive after 500°C calcination and the pore size is reduced. However, the porous structure itself is easy to collapse at high temperature, resulting in shrinkage and agglomeration of the skeleton particles, the contribution to the inhibition of aerogel sintering is not large, so the specific surface area of aerogel decreased.

Figure 2. FT-IR spectra of aerogels (a) WT-1(b) WT-2(c) WT-3.
The FT-IR spectra of the aerogels is shown in Fig.2, where the presence of Si-O-Si[6,7] is observed at 1096 cm$^{-1}$, 1801 cm$^{-1}$, while the Si-O-Ti bond is located at 950 cm$^{-1}$. The formation of Ti-O-Si bond is due to the substitution of Ti into a SiO$_2$ network. 452 cm$^{-1}$ is the absorption peaks of Ti-O-Ti bonds and there is increasingly sharp with the increase of titanium content. The absorption peaks near 2963 cm$^{-1}$ is correspond to CH$_3$ groups. The presence of the CH$_3$ groups has been attributed to the wet gel silanization effect[8] and shows hydrophobicity of samples. The vibrational features at 3445 cm$^{-1}$ and 1634 cm$^{-1}$ are due to the surface OH groups. With the increase of silicon content, the absorption peak of Si-O-Si group is more and more obvious, and the intensity of the Ti-O-Ti bond absorption peak is accordingly enhanced. Compared with fig.3, we can found that the absorption peak of CH$_3$ group has been almost disappeared, and the absorption peak intensity of OH group has been enhanced, which illustrates the sample WT-1 after heat treatment showed hydrophilic, which is conducive to the adsorption of methyl orange degradation.

![Figure 3. FT-IR spectra of the sample WT-1 after 500°C calculations.](image)

![Figure 4. XRD patterns of the as prepared samples (a)WT-1(b) WT-2(c) WT-3.](image)

The XRD patterns for WT-1, WT-2, WT-3 typically showed three diffraction peak at $2\theta$ = 25.31°, 37.96°, 48.02° and 54.28°, corresponding to crystal plane of TiO$_2$(101), (004), (105) and (204)[9-11], which proved the aerogels obtained possess anatase phase. With the increase of silicon content, the intensities of the diffraction peaks of the samples were strengthened and the crystallinity increased, which is attributed to the condensation of silicate ion in the condition of higher silicon content. Fig.4 shows the XRD spectra of the sample WT-1 calcined at 500°C. Compared with the untreated WT-1, the main peak is getting higher, narrower, which demonstrates the anatase phase generated more complete, and the grain size increases.

![Figure 5. XRD patterns of the sample WT-1 after after 500°C calcinations.](image)
Evaluation of Photocatalytic Activity

![Graph](image)

Figure 6. Degradation of methyl orange in the presence of TiO2-SiO2 aerogels.

The photocatalytic activity of composite aerogels at different Si content was assessed by investigating the degradation of MO aqueous solution. According to Fig.6, the negligible change in the concentration of MO solution is occurred in the presence of composite aerogels under UV light via using catalysts. In the initial period of time, the concentration of methyl orange solution decreased rapidly, the downward trend is gradually slowing down with the illumination time prolonging. When the samples are exposed to UV light for 60 min irradiation, the decolorizing efficiency reached 68.44%, 45.69%, 42.88% respectively, which is because TiO2 gel skeleton strength gradually enhanced, the surface area is significantly increased with the introduction of SiO2. When the mole fraction of SiO2 was 10%, the best catalytic degradation effect was obtained. The catalytic degradation rate of 160min was increased from 54.57% to 97.13% compared with that a mole fraction of 30%.

Conclusion

In summary, TiO2-SiO2 aerogels were synthesized utilizing sol-gel method at various silicate content. The as-prepared aerogels exhibits obvious anatase phase and the diffraction and emission peaks broadened with the content of Si. All TiO2-SiO2 aerogels exhibit excellent photoactivity as evidenced by degradation of MO. With the Si content increasing, the decolorizing efficiency enhanced. When the silicon content is 10%, the best catalytic degradation effect was obtained, the decolorizing efficiency of MO is detected as 97.13% after 160 mins exposure to UV light irradiation.

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Reference


