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PREPARATION AND PHOTOCATALYTIC ACTIVITIES OF NANOCOMPOSITES OF MCNTs/TiO_2 AND MCNTs-PHOSPHOTUNGSTIC ACID/TiO_2

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Abstract
Loading multi-walled carbon nanotubes(MCNTs) and/or Phosphotungstic acid (HPW) with TiO_2 was performed by sol-gel method. The photocatalytic activities of them were evaluated via experiment on ultraviolet light degradation methyl orange. It was found that either MCNTs/TiO_2 or MCNTs/HPW/TiO_2 nanocomposites exhibits a higher photocatalytic activity than that of pure TiO_2.An optimum value reached at the HPW/TiO_2 molar ratio is 0.08 in the presence of 0.025g MCNTs. With this co-doped catalyst composites, the decomposition ratio of methyl orange solution reaches 93.7% after 2.5h photocatalytic reaction, compared to 64.9% for pure TiO_2 and 83.7% for MCNTs/TiO_2.
Key words: TiO_2; photocatalysis; Phosphotungstic acid(HPW); multi-walled carbon nanotube (MCNTs).

1. Introduction

Numerous studies have shown that TiO_2 nanoparticles have been extensively investigated as the promising state-of-the-art photocatalysts due to their strong oxidizing ability, low toxicity, low cost and facile synthesis since it was reported in 1972 [1], however, any practical improvement in the photocatalytic efficiency of TiO_2 must overcome the poor quantum yield of the catalyst, which is caused by the rapid recombination of the photogenerated electrons and holes [2] .

At the moment, the photocatalyst of TiO_2 supported by Keggin-type polyoxometalates have been intensively investigated for the degradation of various organic pollutants and gases. At the same time, this kind of the catalysts can also be used to produce hydrogen by water splitting [3],especially supported by HPW of Keggin structure. The Keggin structure made the HPW show higher catalytic activities than the conventional acid catalysts. Keggin structure is similar to the zeolites which have the structure of cage [4].The catalytic reaction can acts both on the surface and interior of the HPW [5].So the HPW of the Keggin series have the high efficiency. Furthermore, the energy band of structure of HPW is similar to the TiO_2, which can affect the characteristic of TiO_2.The TiO_2 modified by HPW have gained the value in the field of photocatalysis nowadays [6-7].

Among all the modified materials of TiO_2, there are much attention paid on the carbon nanotubes [8-9].It was reported that the photocatalytic activity of the composite catalyst have an obvious improvement because of the more large specific surface area and stronger electron transport ability [10].Combination of TiO_2 and carbon nanotubes will increase the photocatalytic activity of TiO_2, studies has showed [8,10-11].

In this article, a new kind of catalyst was synthesized by sol-gel method, which contains both TiO_2 and HPW, furthermore, MCNTs also included. We use HPW and MCNTs to modified TiO_2, then the catalysts were used to degrade the methyl orange for its photocatalytic performance.

2. Materials and Methods

2.1 Materials

Phosphotungstic acid, absolute ethanol was bought from Tianjin Fuyu Chemical Co., Ltd; Tetrabutyl orthotitanate were bought from Tianjin Guangfu Fine Chemical Research Institute; Multi-walled carbon nanotubes was bought from Shenzhen Nano Port Ltd.

2.2 Oxygen functionalization of multi-walled carbon nanotubes (MCNTs)

In this paper, we used the nitric acid for the MCNTs oxygen functionalization. Appropriate amount of multi-walled carbon nanotubes were dispersed in $HNO_{3,}$ the mixed solution of MCNTs and HNO_3 after sonicated for 2 hours was obtained. Then we transferred the mixed solution into the three-necked flask for 4 hours' reflux.

2.3 Catalysts preparation

The catalysts were synthesized by sol-gel method. Typically, 0.025g MCNTs were first added to 40ml ethanol, then sonicated for one hour, this is denoted Solution A. In solution B, appropriate amount of phosphotungstic acid to achieve HPW/TiO_2 molar ratios of 2/100, 4/100, 6/100, 8/100 were dissolved in 40ml distilled water with stirring, respectively. In another process, 10 ml tetrabutyl orthotitanate was added to 10 ml ethanol drop by drop with stirring. This is denoted Solution C; Furthermore, the solution D contains 40ml ethanol, 10 ml distilled water and 2 ml nitrate was also prepared. Then, solution B was added to solution A with another half an hour sonicated, which then dropwised into the mixed solution of C and D, the black wet gel was obtained. Continue stirring for another 2 hours, then it was allowed to stand for 6 hours, after this procedure, the mixed solution was put into oven at 373K for 24 hours. Then the obtained powders were placed in a muffle furnace at 673K for 2 hours. Corresponding to their HPW/TiO_2 ratios (2/100, 4/100, 6/100, 8/100), the samples were denoted HTC2,HTC4,HTC6, HTC8.Simlary, without solution B the sample of TiO_2/CNTS were obtained .Without solution A ,the pure titanium dioxide was obtained. This two were denoted TC ad T, respectively.

2.4 Photocatalytic capability testing

The catalysts photocatalytic capability testing experiments were carried out in a obscura which contained a 300W mercury lamp which was placed in the quartz cold trap. Typically, the appropriate amount of the samples were dispersed in 50 ml methyl orange solution of 10 mg/L with magnetic stirring, a 300W mercury lamp irradiated on the other side. Before irradiation, the condensed water should be flowed through the quartz cold trap.

3. Results and discussion

3.1 Effect of the MCNTs, TiO_2 and MCNTs-TiO_2 on photodegradation rate of the methyl orange

This experiment studied the effects of the MCNTs, TiO_2 and MCNTs-TiO_2 on photodegradation rate of the methyl orange at the conditions of reaction time 2.5h, catalyst dosage 0.1g and methyl orange 50ml. The results showed that three catalysts shares the same trend that it rises as the reaction time increases. Especially, the MCNTs-TiO_2 exhibits the best appearance of photodegradation, which can reach 83.7%.

Studies [12] have shown that the absorption on the surface of the TiO_2 is one of the most important conditions for the degradation of the solution. Adding the absorption of that increased the electron transfer between the solution molecules and titanium dioxide, the rate of photocatalysts also follows the same trend. As a conclusion, the nanocomposites shows the best result.

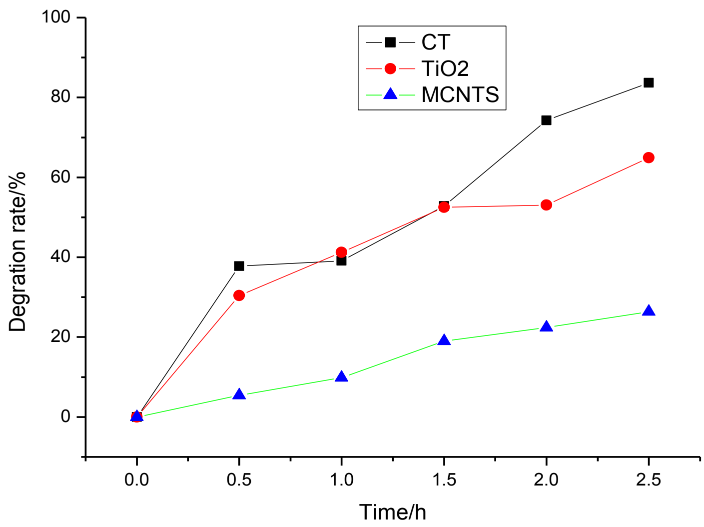

Fig 1.The photodegradation rate of MCNTs, TiO_2, MCNTs-TiO_2 with an amount of 100mg of the methyl orange degradation

3.2 Effect of the HPW amount on photodegradation rate of the methyl orange

This experiment studied the effect of the HPW amount on photodegradation rate of the methyl orange at the conditions of reaction time from 0.5h to 2.5h, catalyst dosage 0.1g and methyl orange 50ml. The results showed that the degradation rate rises as the MCNTs-HPW//TiO_2 ratios increases. However, the exception is HTC8. When the reaction time reaches 1h, it shows poor performance about the degradation of the methyl orange. After the reaction time reaches 2.5h, HTC8 exhibits the best performance about this experiment, obviously. Compared to both TiO_2 and MCNTs-TiO_2, the catalysts of various MCNTs-HPW/TiO_2 ratios exhibit better performance, which can reach 93.7% after 2.5h reaction.

Cai *et al.* have found that the phosphoric acid can affect the surface area, acidity, light-absorbing capacity of TiO_2 [13]. Similary, as a kind of the strong acid, HPW also have the similar band structure of TiO_2,so there exists the synergies between HPW and TiO_2. Due to the special performances of the Keggin structure, HPW have a strong ability to accept electrons, which capture the electrons that generated by TiO_2 absorbing photons. Since the effective export of the photo-generated electrons, not only promoted the separation of the electron-hole pair, but also reducing the chance of the electron-hole recombination, improving the photocatalytic activity of the composite catalysts. Furthermore, the existence of the MCNTs also enlarges the reaction surface area of both HPW and TiO_2, which also improves the photocatalytic performance.

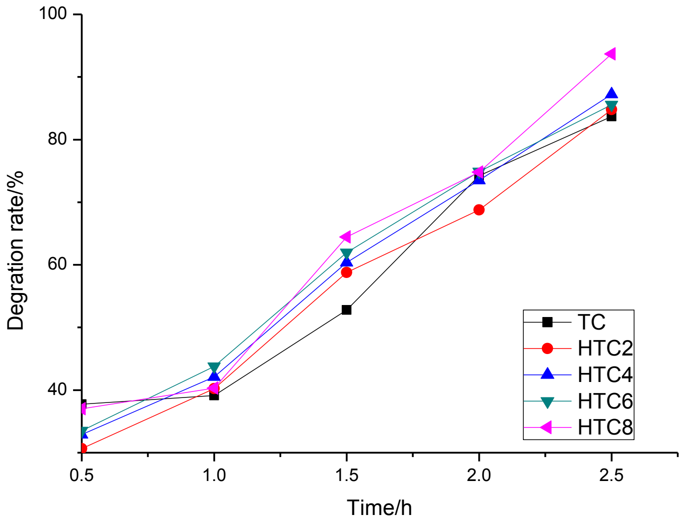

Fig 2. The photodegradation rate of various MCNTs-HPW//TiO_2 ratios with an amount of 100mg of the methyl orange degradation.

3.3 Effect of catalyst dosage on photodegradation rate of the methyl orange

This experiment studied the effect of catalyst dosage on photodegradation rate of the methyl orange at the conditions of reaction time 2h, catalyst dosage from 0.01g to 0.2g and methyl orange 50ml.The results showed that the photodegradation rate shares the same trend with the catalyst dosage rises from 0.01g to 0.15g, beyond the 0.15g, the rate began to decrease, but with a high result, relatively. From this trend, more catalysts not only did no help to the degradation of the methyl orange, but also will bring more problems and side effects. The reason maybe that HPW which was loaded on the MCNTs and TiO_2 shares the same trend with catalyst dosage rises, therefore more HPW will be dissolved in methyl orange solution and began did effect on the dissolved oxygen which can influence the procedure of the degradation [14].The mechanisms have been reported by Ozer *et al.* [15].

4. Conclusions

In summary, new catalysts that both Phosphotungstic acid and multi-walled carbon nanotubes supported TiO_2 nanocomposites have been successfully synthesized via sol-gel method and were examined for the degradations of the methyl orange. We can concluded that either HPW or MCNTs supported can improve the photocatalytic activity of TiO_2, but the HPW and multi-walled carbon nanotubes co-supported TiO_2 one shows better property. In particular, under the conditions that the molar ratio of HPW/TiO_2 reaches 0.08 and meanwhile contains 0.025g of MCNTs, do the nanocomposites exhibit the best result.

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