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PHOTOCATALYTIC DECOMPOSITION OF METHYLENE BLUE DYE IN AQUEOUS SOLUTION IN THE PRESENCE OF WO₃-DOPED TITANIUM DIOXIDE

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It has been investigated the photocatalytic decomposition of industrial dye Methylene blue (MB) in the presence of the heterogeneous photocatalyst nano-titanium dioxide (TiO₂), doped by tungsten oxide (WO₃), TiO₂ /WO₃, under UV-irradiation (λ = 253.7 *nm*). The photocatalyst preparation method by wet impregnation of titanium oxide nano-powder with ammonium paratungstate was simplified by us in comparison with the known ones.

It has been shown, that doping of TiO_2 with WO₃ leads to considerably higher photocatalytic activity of the WO₃/TiO₂ composit as against to pure TiO_2 . The mechanism of the removal of MB in the presence of TiO_2/WO_3 photocatalyst may be assumed to involve following two processes: photocatalytic oxidative destruction and adsorption of the substrate on the surface of the catalyst.

Figs. 3, table 1, references 8.

Introduction

Currently, wide use of chlorinated derivatives of mono- and polycyclic hydrocarbons in different areas, including chemical, agricultural and dye industries, causes serious ecological and environmental problems. Contaminated water bodies no longer cope with significant pollution through the natural process of water self-purification, so water purification from toxic halogen-containing organic contaminants is an actual health and environmental task.

Currently, the most promising are photocatalytic water treatment technologies, which have advantages due to their simplicity, profitability, the possibility of using sunlight. The latter is especially important, since energy saving technologies have an unconditional advantage. From this point of view, heterogeneous photocatalysts based on photosensitive carriers were widely used. Generally, transition metal oxides could be used as adsorbents or catalysts to remove organic pollutants from water. The photocatalytic process using TiO_2 photocatalyst is very promising for application in the water purification, because many organic compounds can be decomposed and mineralized by the proceeding oxidation and reduction processes on TiO_2 surface. The most commonly tested compounds for decomposition through the photocatalysis are phenols, chlorophenols, pesticides, herbicides, benzenes, alcohols, dyes, pharmaceutics, humic acids, organic acids, and others [1-3]. TiO_2 is the most commonly used photocatalyst, because it is nontoxic, chemically stable, cheap, and very efficient.

Earlier we investigated the photocatalytic oxidation of some chlorinecontaining organics in aqueous solution in the presence of catalyst based on the photosensitive support TiO_2 [4.5.6].

Over the past years, coupled semiconductors, especially TiO_2 composites, have been extensively studied for organics degradation and catalytic applications due to their coupled effect. Incorporation and doping of other species into TiO_2 can improve the electronic or photoelectrochemical characteristics of TiO_2 .

In this work, as an example of potential application, the us-prepared nano-TiO₂ doped by WO₃ (TiO₂ /WO₃) was used as heterogeneous catalyst in wastewater treatment. Methylene blue (MB), a common dye in the textile industry, was chosen as a typical organic waste.



Methylene blue

Experimental

TiO₂/WO₃ ($n_{Ti}:n_W=4:1$) catalyst was synthesized by impregnation of semiconductor TiO₂ nanoparticles (Sigma-Aldrich, anatase, 50 m^2/g , 21 nm) with ammonium paratungstate solution followed by calcination (500°C).

The phase composition of TiO₂ and TiO₂/ WO₃ catalyst was measured by XRD in DRON-0.5 diffractometer with CuK α lamp (1000, 2000 *imp/sec*). The morphology of the photocatalysts surface and content of WO₃ in TiO₂/ WO₃ catalyst were evaluated by SEM (VEGA TS 5130MM) measurements with EDS analysis. The size of WO₃ particles were also calculated by the P. Scherrer equation. BET surface area, pore volume, pore size were measured in Gemini VII Version 3.03 Analyzer from Micromeritics.

Diffuse reflectance spectra of TiO₂ and TiO₂/WO₃ powders were taken in UV-Vis spectrometer SPECORD-M-40-UV-VIS. SiO₂/WO₃ ($n_{Si}:n_W = 4:1$) composite based on nonconductor SiO₂ (300 m^2/g) was prepared in the same 312 way as TiO₂ /WO₃. Experimental setup consisting of photochemical reactor (quartz, 30 *mL*) with a magnetic stirrer and optical junction for UV-irradiation ($\lambda = 253.7 \text{ nm}$), Hg-lamp (DRT-230, Russia), were used.

Reaction mixture was 10 mL of water solution of MB (1.25 mg/L), containing 0.05g of the TiO₂ /WO₃ catalyst. Consumption of MB in solution was monitored by C Φ -46 and Agilent Technolodies Cary 60 UV-Vis spectrophotometeres.

Results and discussion

The photocatalytic activity of the prepared catalyst was studied for a model reaction of the well-known industrial dye Methylene blue decomposition under irradiation with a UV lamp. This lamp emits the radiation with a maximum at around 253.7 *nm*. MB aqueous solution was exposed to UV-irradiation in air, in the presence of the prepared TiO_2/WO_3 catalyst, as well as pure TiO_2 and without them, in different time intervals. Experimental results of the consumption of MB are presented in Fig.1.



Fig.1. Consumption of Methylene blue under UV-irradiation in the presence of (a) $- TiO_2/WO_3$, (b) $- TiO_2$, (c) - only UV- irradiation, without (a), (b).

Curve (a) in Fig.1 corresponds to TiO_2/WO_3 catalyst, the curve (b) corresponds to the photochemical decomposition of MB on the surface of "pure" TiO_2 (without WO₃). The simple comparison of two curves indicates a significant increase of the consumption of MB in the presence of the mentioned catalyst (Fig.1.b). Under the same conditions, but in the absence of the WO₃, the photooxidation of MB on "pure" TiO_2 is a relatively slow process (Fig.1.b). The above facts indicate the catalytic character of the overall process in the presence of the TiO_2/WO_3 catalyst.

It is shown, that doping of TiO_2 with WO₃ leads to considerably higher catalytic activity of the TiO_2 /WO₃ catalyst as against to pure TiO_2 . Particularly, during 2 *min* of exposition 91,3% of MB was removed and after 10 *min* it practically disappeared completely. Note, that photocatalytic activity of WO₃ itself in the mentioned reaction was shown to be negligible.

With the purpose of additional confirmation the photocatalytic nature of the reaction decomposition of MB in the presence of TiO₂/WO₃ catalyst, this reaction was also studied in the presence of a composite based on a nonconductor SiO₂. Experimental results of the consumption of MB in the presence of nonconductor SiO₂ and SiO₂/WO₃ composite are presented in Table. The results obtained in the presence of SiO₂ and SiO₂/WO₃, both with and without irradiation, indicate that in the presence of a composite based on a nonconductor, MB is consumed as a result of adsorption on a SiO₂ surface. The reaction of photocatalytic decomposition of MB does not proceed. Note, the specific surface of SiO₂ (300 m^2/g) is 6 time more than of TiO₂ (50 m^2/g).

Table

	SiO ₂ (in dark) SiO ₂ ,UV-irradiation		SiO ₂ /WO ₃	SiO ₂ /WO ₃ , UV-irradiation
Irradiation time, <i>min</i>	0 10 30 60	10	10	10
D (optical density)	0.654 0.207 0.202 0.203	0.083	0.147	0.128
Consumption of MB, %	68.9 69.0 64.6	85.7	75.2	77.9

Consumption of methylene blue (MB) under UV-irradiation in the presence of SiO₂ and SiO₂/WO₃

The composition of the photocatalysts and the particle size were determined using photographs of a VEGA TS 5130MM scanning electron microscope (SEM) equipped with an INCA Energy 300SEM microanalytical system. Images of the surface in secondary and reflected electrons with a magnification of $50x \div 20000x$ were obtained to determine the morphology of the sample surface. Images in secondary electrons (SE) were used to localize the areas of analysis. In Fig. 2 SEM photographs of nonmodified TiO₂ (a) and TiO₂/WO₃ photocatalyst before (b) and after (c) the reaction are presented.



Fig.2. SEM photographs of nonmodified TiO_2 (a) and TiO_2 / WO_3 photocatalyst before (b) and after (c).

Some agglomerates of primary TiO₂ particles are larger than TiO₂ doped with WO₃ consisting of smaller particles. Apparently doping of TiO₂ with tungsten oxide causes a decrease in the catalyst particle size, mainly due to a decrease in the tendency of TiO₂ particles to form agglomerates. The effect of a decrease in the particle size of TiO₂/WO₃ composites in comparison with TiO₂ obtained by the sol-gel method was also noted by other authors [4]. From the EDS analysis, the measured Ti was 31.05 at%, O 68.95 at% for TiO₂ and Ti 28,32 at%, W 4,85 at% and O 66,83 at% for TiO₂/WO₃. The UV-visible spectra of the measured TiO₂ and WO₃-TiO₂ photocatalysts are shown in Fig. 3. As can be seen from Fig. 2, modification of TiO₂ with WO₃ causes an increase in the absorption of light in the visible range up to 520 *nm*.



Fig.3. UV-Vis diffuse reflectance spectra of TiO₂ / WO₃ catalyst and TiO₂.

Conclusion

The method of wet impregnation, which is simplified in comparison with the known ones, was used to prepare a photocatalyst based on nanotitanium dioxide, doped with tungsten oxide. Doping WO₃ into TiO₂ increased its absorption of light, adding to the visible range. Although it is known that the formation of OH radicals on the surface of TiO₂/WO₃ photocatalysts is higher than on TiO_2 [8], this is not the main factor affecting the rate of MB decomposition. It is obvious that the noticeable adsorption of MB on the surface of the photocatalyst and its ability to absorb both UV and visible light are responsible for the increasing of the photocatalytic properties of the doped photocatalyst with the composition (n_{Ti} : $n_W = 4$: 1), as a result of which the decomposition of MB in an aqueous solution was achieved up to 99% in just 10 min. The doping of WO₃ into TiO₂ also caused a decrease of its particle size, which could also contribute to a greater dispersion of TiO₂ in water, thus increasing the surface available for MB adsorption. The expansion of the light absorption limit of the photocatalyst to the visible light region is of great importance for sensitized photocatalysis, and the photocatalyst itself is effective in the process of removing MB from aqueous solutions.

ՄԵԹԻԼԵՆԱՅԻՆ ԿԱՊՈԻՅՏ ՆԵՐԿԱՆՅՈԻԹԻ ՖՈՏՈԿԱՏԱԼԻԶԱՅԻՆ ՏԱՐՐԱԼՈԻԾՈԻՄ WO3-ԴՈՊԻՆԱՑՎԱԾ ՏԻՏԱՆԻՈԻՄԻ ԵՐԿՕՔՍԻԴԻ ՆԵՐԿԱՅՈԻԹՅԱՄԲ ՋՐԱՅԻՆ ԼՈԻԾՈԻՅԹՈՒՄ

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Ուսումնասիրվել է մեԹիլեն կապույտ (ՄԿ) արդյունաբերական ներկանյուԹի ֆոտոկատալիզային քայքայումը ջրային լուծույԹում` Հետերոդեն ֆոտոկատալիզատորի` տիտանի նանոերկօքսիդ` (TiO₂) Հավելված (doped) վոլֆրամի օքսիդով (WO₃), (TiO₂/WO₃) ներկայուԹյամբ, ուլտրամանուշակադույն ճառադայԹման (λ=253.7 նմ) տակ:

Ֆոտոկատալիզատորի պատրաստման եղանակը` տիտանի երկօջսիդի նանոփոչին ամոնիումի պարավոլֆրամատով Թաց ներծծմամբ, մեր կողմից պարզեցվել է Համեմատած Հայտնի մեԹողների Հետ: Ցույց է տրվել, որ TiO₂-ի վրա WO₃-Հավելումը (դոպինգը) Հանդեցնում է TiO₂/WO₃ կոմպոզիտի ֆոտոկատալիտիկ ակտիվուԹյան զգալի բարձրացմանը` ի տարբերուԹյուն մաջուր TiO₂-ի: Արվել է եզրակացուԹյուն, որ TiO₂/WO₃ ֆոտոկատալիզատորի առկայուԹյան դեպքում ՄԿ-ի Հեռացման մեխանիզմը ներառում է Հնտևյալ երկու պրոցեսները` ֆոտոկատալիզային օջսիդային քայքայում և աղսորբցիա` կատալիզատորի մակերևույԹի վրա:

ФОТОКАТАЛИТИЧЕСКОЕ РАЗЛОЖЕНИЕ КРАСИТЕЛЯ МЕТИЛЕНОВОГО ГОЛУБОГО В ВОДНОМ РАСТВОРЕ В ПРИСУТСТВИИ ДИОКСИДА ТИТАНА, ДОПИРОВАННОГО WO₃

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Исследовано фотокаталитическое разложение промышленного красителя метиленовый синий (MC) в водном растворе, в присутствии гетерогенного фотокатализатора, нанодиоксида титана (TiO₂), допированного оксидом вольфрама (WO₃), (TiO₂/WO₃), при УФ-облучении ($\lambda = 253.7 \ hm$). Метод приготовления фотокатализатора влажной пропиткой нанопорошка оксида титана паравольфраматом аммония нами был упрощен по сравнению с известными. Показано, что допирование диоксида титана обеспечивает значительно более высокую фотокаталитическую активность композиту TiO₂/WO₃ по сравнению с чистым TiO₂. Сделано заключение о том, что механизм удаления MC в присутствии фотокатализатора TiO₂/WO₃ включает следующие два процесса: фотокаталитическую окислительную деструкцию и адсорбцию субстрата на поверхности катализатора.

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