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Chemical Oxygen Demand of Oily Wastewater Treatment by Ti/CeO2

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In order to improve the recovery effect of oily wastewater, the chemical oxygen demand of oily wastewater treatment by Ti/CeO2 is studied in this paper. At first, thin film electrodes with photo catalytic activity are prepared to discuss the mechanism of catalytic oxidation organics of electrodes, proposing a method of photo catalytic oxidation degradation and anodic treatment. Then, this paper measures the current in the process of oxidizing organics to carry out more analysis.It is found that the decolorization rate of methylene blue solution is 97.3% and 88.8% after electrocatalytic degradation of methylene blue solution by electrodes.The depth mineralization selection coefficients of organics are 97.5% and 76.6%, respectively.It can be seen that the electrode prepared by anodizing-laser forging not only has stronger ability of photocatalytic oxidation, but also has higher selectivity for depth mineralization.

1. Introduction

Chemical oxygen demand is an important indicator for monitor to monitoring oily wastewater, and it is also one of the indicators of relative content of organics.The smaller the value, the lighter the water pollution.There are many methods for treating the chemical oxygen demand of oily wastewater, among which, the method of potassium dichromate reflux takes a long time with large sample consumption.

Based on this, most researchers are exploring a quick and easy analysis method to shorten the digestion time, but it still takes arelatively long time, generally about half an hour to an hour. Therefore, this paper discusses the mechanism of catalytic oxidation organics of electrodes on the basis of preparingthin film electrodes with photo catalytic activity, puts forward a method of photo catalytic oxidation degradation and anodic treatment, and then measures the current in the process of oxidizing organics for analysis.

2. Literature review

Mo et al. studied the performance improvement of chemical oxygen demand by cyclic voltammetry deposited carbon fiber felt/CeO_2-β-PbO_2 electrode (Mo et al., 2016). The influence of the strong interaction of Ti and CeO_2(111) on the structure of Ti/CeO_2(111) was systematically studied by density functional theory. It was found that Ti atoms were dispersed in the hollow position of CeO_2 (111) to form surface TiOx species instead of aggregated to form Ti metal clusters. Therefore, the interaction of Ti-CeO_2 was produced. This interaction was much stronger than the Ti-Ti interaction (Yao et al., 2016). A highly efficient and stable Au/CeO_2-TiO_2 photocatalyst was prepared by microwave assisted solution method. Even after calcination at 550 °C for 6 h, CeO_2 can stabilize nano gold crystals well and has strong metal carrier bonding. The Au-$Ce^{(3+)}$ interface was formed and used as the anchoring point of the O_2 molecule. More adsorbed oxygen reacts with the photogenerated electrons on the surface of TiO_2 to generate more superoxide radicals for NO oxidation, thereby improving efficiency (Zhu et al., 2015). O_2 was also captured at the periphery of the Au/TiO_2.

The NO molecules at the TiO_2 site were initially transported to the active peripheral sites on the TiO_2 surface by diffusion. It helps the O-O bond dissociate and react with oxygen at these peripheral locations. Therefore, these limited gold nanocrystals can continuously expose the active center of oxidized NO. These synergistic effects create an efficient and stable system for the decomposition of NO pollutants (Geng et al., 2017). A

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series of Ni/X%CeO_2-Y%TiO_2 composite catalysts were prepared by impregnation method. It was found that the Ni/CeO_2-TiO_2 catalyst with the best Ce/Ti ratio showed excellent activity and stability in dry reforming. XPS analysis, H_2 TPR and reverse water gas shift reaction (RWGS) experiments confirmed that the high dispersion of the Ni site on the surface of the support can increase the catalytic activity. The high reducibility of the catalyst improves the stability of cata (Kim et al., 2015).

The synergy between the Cr x-CeO_2 and Ti-PiLC supports was promoted due to the excellent texture/structural properties of Ti-PILC. The catalytic activity of butylamine oxidation on Ti-PiLc supported Cr x-Ce_2 catalyst was improved, especially for 8CrCe(6:1)/Ti PILC (12,20). All catalysts exhibited good NOx control quality, and the yield of NOx was limited to 1% within the T 98 range (Shi et al., 2015). The reaction mechanism of ruthenium oxide as an anode in a lithium ion battery (LIB) was not known. To solve this problem, nano LIB was constructed using a separate CeO_2/graphene composite as an anode in a transmission electron microscope (TEM). The lithiation/desulfurization cycle of CeO_2/graphene composites was carried out inside the TEM. The electrochemical process was simultaneously determined by high resolution TEM, electron diffraction and electron energy loss spectroscopy (Sun et al., 2013). Danilo et al. studied the stability of ruthenium, iridium, cerium, tin and antimony (Danilo et al., 2017). Wang et al. used a copper-based metal organic framework (Cu-MOF) as a raw material to synthesize a novel porous CuO/Cu_2O@CeO_2 anode by a simple two-step pyrolysis method. The MOF template pyrolysis of porous CuO/Cu_2O-CeO_2 anode materials for high performance lithium ion batteries was investigated (Wang et al., 2017). The electrochemical properties of Si/CeO_2/polyaniline composites as anode materials for lithium ion batteries were investigated. A series of polyaniline composites were synthesized as anode materials. Its initial coulombic efficiency reached 87.6%. Di- and polyaniline improved electrochemical performance (Bai et al., 2015).

In summary, Ti/CeO_2 and its related research have been extensively explored in terms of catalysts and electrochemical properties. As the demand for fuel and oil grows, the amount of water produced during the extraction process continues to increase, which becomes an environmental issue. Therefore, based on the above research, in order to improve the recovery treatment effect of oily wastewater, the chemical oxygen demand of Ti/CeO_2 anode treated oily wastewater was studied.

3. Principles and Methods

The oily wastewater treatment in the laboratory is as follows: a SPE column, which is a medical-grade propylene column, is prepared, and a gram of filler is filled between two polyethylene screen plates. A solid-phase microextraction (SPME) is prepared. Column: A medical-grade propylene column is selected and phenyl polyglycol sodium is filled between two polyethylene screen plates. Column pretreatment: In order to gain high recovery and good reproducibility, the SPE column must be pretreated prior to the usage. The purposes are to remove possible impurities in the filler and to dissolve the filler to improve the reproducibility of SPE. The filler without pretreatment or moistening by solvent may cause early penetration of solute to affect the recovery. The added methanol is operated to get through the SPE column. Then, the purified water replaces the methanol in the column. The flow rate is dripping. Sample: After the pretreatment, the water sample is added and passed through the column, and it is also kept dripping.A certain amount of samples are placed in a beaker. Then, different amounts of activated carbon are added according to the fact.It is put on a magnetic stirrer for stirring and adsorption for a certain period of time. After that, it is settled and filtered.

In nature, there are three crystal formations of TiO2, including rutile, Ruiqin Mine and Banqin Mine. Due to the instability of Banqin Mine TiO2, few studies have been conducted. At present, the most studied and widely used are the rutile and Ruiqin Mine, whose crystal structure is shown in Figure 1 and Table 1.

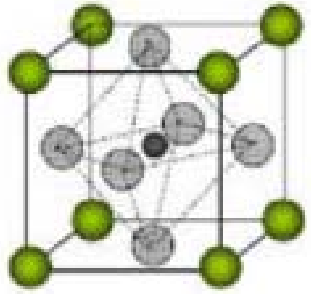

Figure 1: Rutile crystal structure

Table 1: Some characteristics of different structures of TiO2

	Ruiqin Mine	Rutile
Crystal system	Quartet	Quartet
Density	3.90	4.24
Lattice constant	3.73	4.59
Refractive index	2.53；2.49	2.62；2.90
Phase transition Temperature	640	1855
Microhardness	450	1000

In the practical application, TiO2powder is easy to agglomerate and difficult to recover, so researchers have been paying attention to the immobilization of the powder in recent years. The production of TiO2thin films is one of the biggest achievements. There are many methods for producingTiO2thin films, including solid phase method, gas phase method and liquid phase method.

The Ti net (99.7%, with an area of 3*3cm) is purchased from Shanghai Far East Equipment co., LTD. The butyl phthalate, ethanol, diethanolamine, polyethylene glycol, methylene blue and other reagents are purchased from Shanghai Chemical Reagent Company. All solutions are prepared from secondary distilled water. X-ray diffraction analysis is performed on the D8ADVANCE automatic X-ray diffractometer (from Brukeraxs, Germany). The X-ray is Cu-Ka ray, and the 2A angle is increased from 10 to 70 degrees with 0.030. The AC impedance experiment is performed at the CHI660A electrochemical workstation (of American CHI Company). The electrochemical experiment is performed on a potentiostat (from Jiangsu Electro analytical Instrument co., LTD.) with a three-electrode system. The working electrode, pair electrode and reference electrode are Ti/CeO2 modified electrode, platinum electrode and saturated calomel electrode, respectively. The 30-watt ultraviolet lamp (from Shanghai) is placed outside the quartz cup reactor (5ml) (as shown in Figure 2).

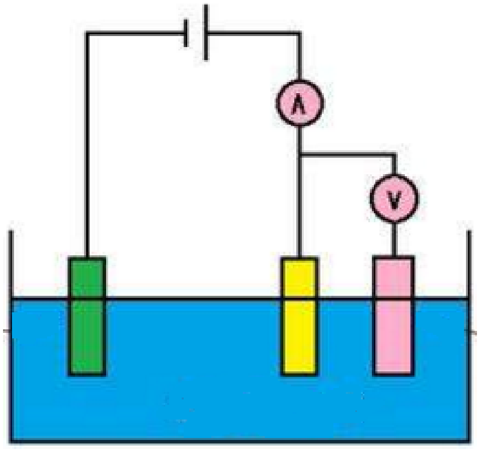

Figure 2: Experimental system

The Qin substrates are washed in hydrofluoric acid separately and flushedwith distilled water. The TiO2 filmis generated on the surface of the Qinsubstrate by anodizing. In the anodizing system, a copper sheet of the same size as the Qin substrateis used as the cathode. The whole anodizing process can be divided into two stages. The first stage maintains a constant current density of 100 mA cm-2 until the voltage rises to the set value of 150 V. In the second stage, the anodizing voltage is kept at 150V until the current gradually decays to about 40 mA cm-2. The prepared TiO2 film electrode is flushed with distilled water. The treated Qin net is scanned at a speed of 2.0 mm s-1 with a diameter of 2.0mm and a power of 5000mW for 30minutes to generate a TiO2 film on the surface of Tisubstrate.

The experiment applies a three-electrode system. Ti electrode is used as the working electrode, saturation calomel electrode as the reference electrode, and Pt electrode as the pair electrode. Electrodes are placed in the quartz electrolytic cell, which is added methylene blue solution with a certain concentration. The ultraviolet light is opened and positive potential is applied on the working electrode by a potentiostat. The photocatalytic degradation of methylene blue solution is carried out. The air is injected into the reaction system through an airway, which can not only control the dissolved oxygen content in the reaction system, but also play a role in stirring.

4. Results and Analysis

Figure 3 shows the XRD characterization of pure titanium substrate, in which the main diffraction peak coincides with the main diffraction peak of pure Qin. Figures 2B and 2C are XRD characterizations of TiO2 film prepared by anodizing-laser forging and anodizing-muffle furnace forging (both for 30 minutes). They show that the major diffraction peaks of XRD characterizations of TiO2 film prepared by anodizing-laser forging are stronger than those of Ruiqin Mine TiO2. This indicates that both methods can be used to produce Ruiqin Mine TiO2 particles on the surface of Tisubstrate. However, as the laser as the heat source can concentrate the energy on the surface of sample, the efficiency of forging is improved to promote that the amorphous TiO2is crystallized into Ruiqin Mine TiO2.

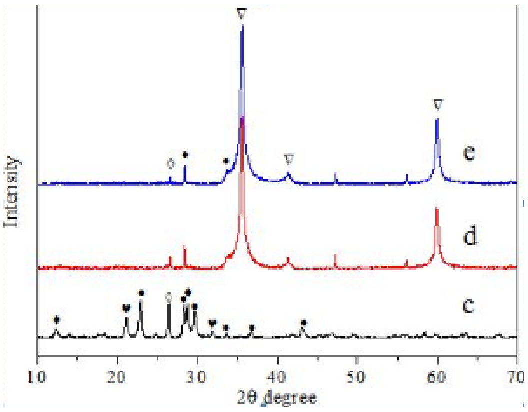

Figure 3: XRD characterization of pure titanium substrate

Electrochemical impedance spectroscopy (EIS) is an electrochemical measurement through the electrode perturbation with a small alternating voltage or current. Based on the EIS data and the simulated equivalent circuit of electrode, the corresponding electrode reaction parameters can be calculated, including electrode impedance, double layer capacitance, surface electron transfer resistance, solution resistance and other data. On the Faraday EIS, the entire electrochemical system can be simulated by the Randles equivalent circuit, in which Ret is the working electrode surface electron transfer resistance, Zw the Warburg impedance, Cdl the double layer capacitance of electrode surface, RS the solution resistance. The Nyquist map of this circuit consists of a semicircle and an oblique line (as shown in Figure 3). The semicircle part as the high frequency area is controlled by the electron transfer process, of which its diameter is equal to the electrode play. In this experiment, the surface electron transfer resistance Retis measured according to the Nyquistmap of Ti / TiO2 electrodes scanned by CHI660A workstation to conduct a preliminary study on the photocatalytic performance of TiO2 film.

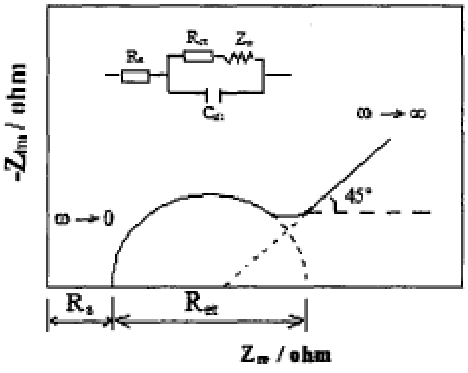

Figure 4: Nyquist map of the experimental circuit

As shown in Figure 4, the anode current is very small with a little influence of working voltage without the ultraviolet irradiation. This is primarily due to the TiO2 film on the electrode surface is a semiconductor oxide with a relatively large surface electron transfer resistance. While the TiO2 film produces a large number of photo-generated carriers under the ultraviolet irradiation. These photo-generated carriers (mainly photo-electrons) can flow to the external circuit under an external voltage, producing the photocurrent. When the anode potential is lower, that is less than +0.5 V, the anode photocurrent increases with the increase of voltage. When the anode potential increases to a certain value, that is greater than +0.5V, the photocurrent tends to saturate. In addition, the corresponding saturated voltage will increase with the increase of added organics (MB) concentration.

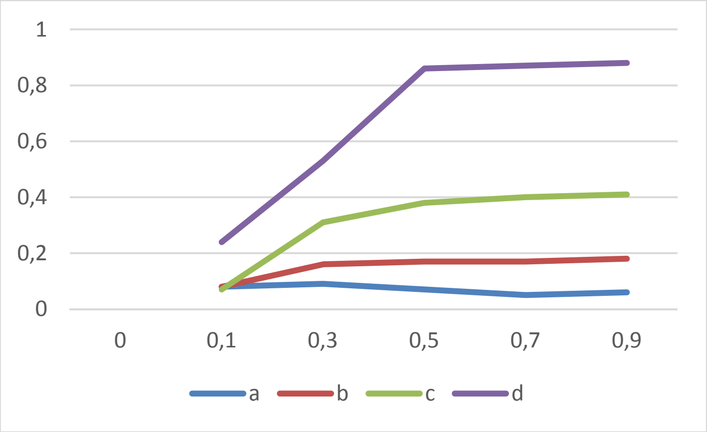

Figure 5: The illumination typical voltammograms of MB at TiO2/ Ti photoelectrode with and without UVin containing different concentrations of MB at pH 10.0: (a) without MB in dark; (b) withoutunder illumination; (c) under illumination; (d) 0.025

The results show that after electro catalytic degradation of methylene blue solution by electrodes, the decolorization rate of methylene blue solution is 97.3% and 88.8%, respectively. The depth mineralization selection coefficients of organics are 97.5% and 76.6%, respectively.

5. Conclusion

The results show that the decolorization rate of methylene blue solution is 97.3% and 88.8% after electro catalytic degradation of methylene blue solution by electrodes. The depth mineralization selection coefficients of organics are 97.5% and 76.6%, respectively. According to the experimental results, it can be seen that the electrode prepared by anodizing-laser forging not only has stronger ability of photo catalytic oxidation, but also has higher selectivity for depth mineralization.

It is worth noting that Mini personal computers can be widely used in the future research, which can complete the collection by compiling FFT computing software and adopting A/D converter with high speed and accuracy.

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