Study on Microwave-hydrothermal and Sol-gel Method Synthesis of Er-doped TiO_2 Photo-catalyst and its Photo-chemical Performance

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Abstract—Er-doped TiO_2 photo-catalysts were synthesized by microwave-hydrothermal and sol-gel method. The purpose of the experiment was order to improve the photo-catalytic activity and accelerate the degradation of pollutants, for example methyl orange. The structure and morphology of TiO_2-Er were characterized with XRD, IR and SEM. The photo-catalytic activity was respectively investigated by microwave irradiation (MW) and ultraviolet irradiation (UV) and microwave irradiation with ultraviolet irradiation (MW-UV) with the photo-catalytic degradation of methyl orange solution as simulated pollutants. The results showed that the TiO_2-Er catalysts prepared at the optimum condition had higher photo-catalytic activity.

Keywords—Er-doped TiO2 photo-catalysts; microwave-hydrothermal; Microwave enhancing effect; Photo-catalytic activity; sol-gel method.

I. INTRODUCTION

Nano-crystalline titania is a photo-catalyst which has attracted considerable attention for its potential use in environmental cleaning[1]. In particular, lanthanide-ion doped titania samples have been shown to increase photo-catalytic efficacy of selected reaction[2,3]. Because of the rare earth elements unique to the electronic structure of the 5d space, it can provide a good electron transfer orbit for the formation of the TiO2 light. Therefore, TiO2 can effectively inhibit the electron hole recombination and broaden the absorption spectrum, so as to improve the photo-catalytic activity of the catalyst [4].

The research group in ionic liquid medium by microwave auxiliary heating method and microwave-hydrothermal of synthesis of rare earth element erbium doped TiO2 photo catalyst and with methyl orange solution as model pollutant. The effects of the photo-catalytic degradation activity, in order to explore the effect of two kinds of methods on TiO2 photo-catalytic degradation, further improve the rare earth element doped on the modification of TiO2 photo-catalyst catalytic activity.

II. EXPERIMENTAL SECTION

A. *Experimental Reagents and Instruments*

The main reagents: erbium nitrate and other reagents, the preparation of ionic liquid and the structure test and characterization of the catalyst [4.5].

B. *Preparation of TiO_2-Er Catalyst*

The preparation of TiO2-Er photo-catalyst for reference [4.5].

C. Photo-catalytic Activity Test of TiO_2-Er Catalyst

In the reaction of TiO2-Er photo-catalytic activity of photo-catalytic degradation of methyl orange solution absorbance determination of reaction and catalyst of the visible light catalytic tests are detailed in reference [4,5]。

III. RESULTS AND DISCUSSION

D. *Effect of erbium Doping on the Photo-catalytic Activity of TiO_2-Er*

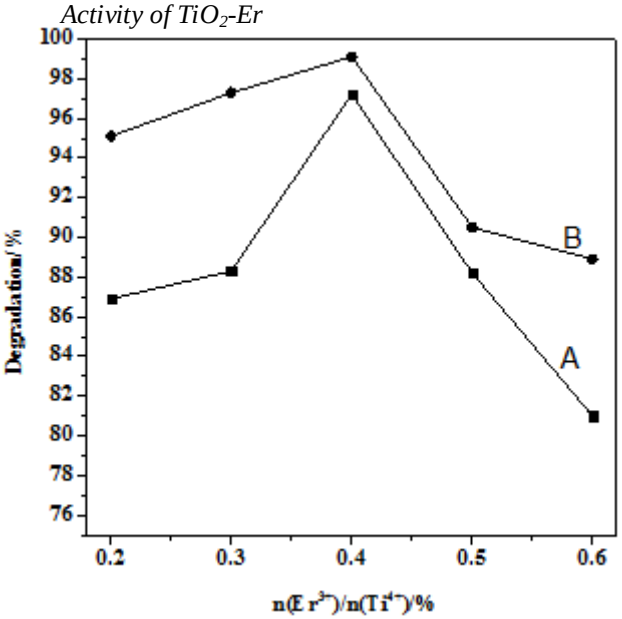


Figure 1. The influence of Er-doped amount $n(Er^{3+})/n(Ti^{4+})$ for two kinds of TiO_2-Er on the degradation rate of methyl orange (A: sol-gel B: microwave-hydrothermal)

For microwave-hydrothermal method TiO2-Er catalyst in the preparation process, the percentage of n (Er3+) /n (Ti4 +) always is 0.4%,microwave power 600W, reaction temperature 160℃, reaction time 3h, calcination temperature of 650℃, calcining time 3h condition. For sol-gel method TiO2-Er catalyst in the preparation process, in a fixed volume of ionic liquid is 3.0 ml, microwave drying power 70W, microwave drying time is 10min, calcination temperature of 650℃, calcining time 3h conditions, the percentage of n (Er3+) / n (Ti4 +) always is 0.4%, to keep other conditions of the two methods same ,by changing the erbium nitrate addition of different amount of erbium dopant TiO2-Er catalyst, and methyl orange so

products, in a fixed UV irradiation time 60min conditions, study the influence of the amount of erbium doping on the photo-catalytic degradation of reactive and income results as shown in Figure 1.

From Figure 1 we can see that in the same amount of erbium doped, when erbium addition amount of n (Er^{3+}) /n (Ti^{4+})<0.4%, the catalyst TiO_2-Er on degradation of methyl orange solution rate with erbium nitrate addition increased; When n(Er^{3+}) /n (Ti^{4+})>0.4%, the catalytic activity decreased with the increase of the amount of erbium addition; And when the n(Er^{3+}) /n (Ti^{4+}) is 0.2%, the TiO_2-Er catalyst of microwave-hydrothermal method on degradation of methyl orange rate reached 99.1% , and the TiO_2-Er catalyst of sol-gel method on degradation of methyl orange rate reached 97.2% (Homemade device reaction in 60 min) of maximum has higher photo-catalytic activity. And TiO_2-Er photo-catalyst of microwave-hydrothermal method is significantly higher than sol-gel method in the same degradation conditions. The reason may be that microwave-hydrothermal method under the condition of high temperature and high pressure medium water in the critical state and Properties of reactants in the water and chemical reaction performance have very big change. So the activity of TiO_2-Er are improved greatly. Under the condition of microwave heating, the whole reaction system temperature can achieve crystallization temperature at moment. And greatly accelerated the speed of the synthesis and crystallization. In addition, the microwave-hydrothermal method is operable and adjustable. It is beneficial to low state, intermediate state and the generation of special valence compounds. And it can proceed ion doped on average[6-8].

E. Comparison with the TiO2-Er catalysts of microwave-hydrothermal and sol-gel methods

Table I Degradation rate of methyl orange for TiO_2-Er catalysts of microwave-hydrothermal and sol-gel methods by UV,MW and UV-MW for 50 min.

The degradation rate	Microwave-hydrothermal	Sol-gel
	η	η
MW	3.9%	3.9%
UV	99.8%	98.8%
UV-MW	100%	99.6%

Under the optimum conditions, two kinds of method were studied, and the degradation of the pollutants in MW-UV, UV and MW were investigated. The results were shown in Table 1. The catalytic activity of TiO_2-Er photo-catalyst of microwave-hydrothermal method is significantly higher than sol-gel method in the same degradation conditions. The reason may be due to the synergistic effect of UV and MW. Under the constant temperature condition (298K), the degradation rate was very low, and only a few of the simulated pollutants were degraded by microwave irradiation; Under the condition of UV irradiation, using microwave irradiation can improve the degradation rate of pollutants, which shows that the degradation rate of microwave and ultraviolet irradiation is higher than that of the ultraviolet irradiation or under microwave irradiation. Microwave radiation can increase the catalytic activity of TiO_2-Er catalyst, which may cause more • OH free radicals, which is beneficial to the degradation and mineralization of pollutants, and can also inhibit the electron hole recombination, so as to improve the photo-catalytic activity of the catalyst.

Table II The TiO_2-Er catalysts of microwave-hydrothermal and sol-gel methods degradation rate of methyl orange under the sun light for 4h

Degradation rate	Microwave-hydrothermal	Sol-gel
η	99.0%	97.5%

According to Table 2, the degradation activity of the three catalysts in the solar irradiation is still the highest, which indicates that the TiO_2-Er catalyst of microwave-hydrothermal has good photo-catalytic activity under the sun light. The possible reason is that the absorption range of TiO_2 is increased when Er^{3+} doped, which is favorable for the generation of charge carriers, which can improve the photo-catalytic activity of TiO_2-Er catalyst.

F. Analysis the XRD, IR and SEM of two kinds of catalysts

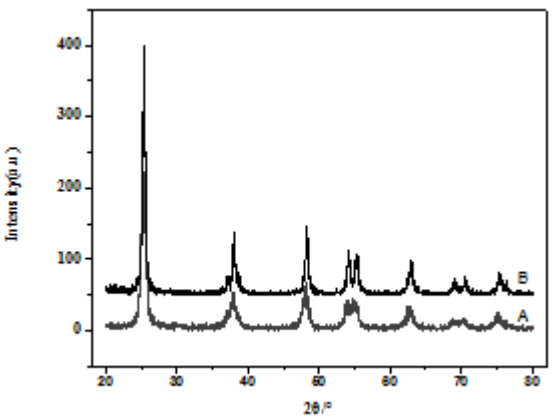


Figure 2. XRD patterns of two kinds of TiO_2-Er catalysts

(A: Sol-gel B: microwave-hydrothermal)

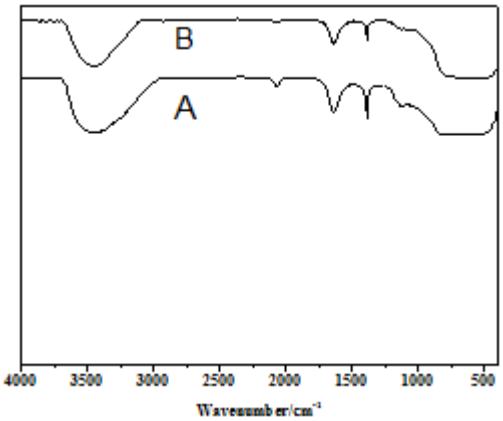
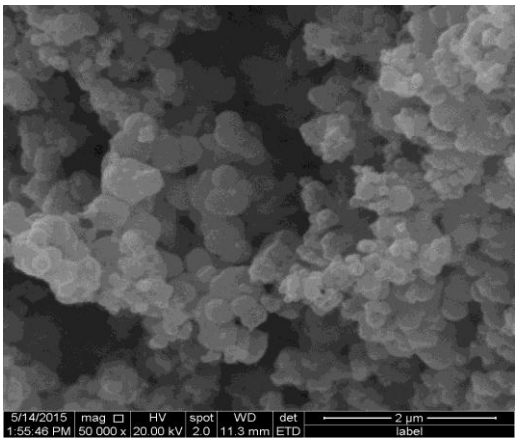
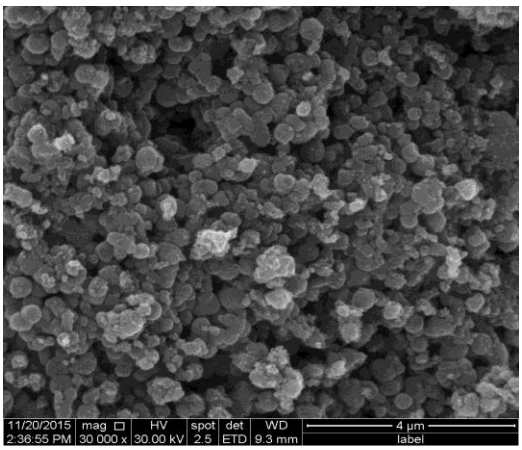


Figure 3. IR spectra of two kinds of TiO_2-Er catalysts
(A: Sol-gel B: microwave-hydrothermal)

XRD, IR and SEM of two kinds of TiO_2-Er analysts are shown in Figure 2, figure3 and figure 4. According to observed in Figure 2, diffraction angle 2θ =25.33°, 37.88° , 48.06° near, two kinds of doped TiO_2 catalyst have obvious main diffraction peaks appear, they with the standard card anatase TiO_2 peak than consistent. The two kinds of catalysts, were prepared by microwave-hydrothermal and sol-gel methods. The particle sizes of TiO_2-Er were calculated according to Scherrer formula, and the particle sizes of them were 10.65 and 9.35 nm respectively.



A



B

Figure 4. SEM images of two kinds of TiO_2-Er analysts
(A: Sol-gel B: microwave-hydrothermal)

According to the IR spectra of two catalysts (Figuere 3), The two kind of TiO_2-Er in the 3446cm^{-1}, respectively, near the 1631cm^{-1}, Ti-OH, and wide absorption band at 501 cm^{-1} type corresponding to the anatase TiO_2 in Ti-O stretching vibration，Among them, 1631cm^{-1} and 3446cm^{-1} appear to absorb larger peaks, which represent the characteristics of O-H bond stretching vibration and bending vibration caused by the surface of TiO_2 catalyst. Compared with the peak of the three catalysts, TiO_2-Yb-Er catalyst has a strong absorption peak at 1631cm^{-1} and 3446cm^{-1}, which indicates that the surface hydroxyl adsorption of the catalyst of microwave-hydrothermal is more than that TiO_2 of sol-gel. Under the interaction of microwave and ultraviolet light, the surface of the catalyst was changed to form OH, and the content of. OH, and the content of the catalyst had an effect on the activity of the catalyst. In addition, hydroxyl radical or oxidant can promote the adsorption of O_2 into O_2^-, HO_2^- and other active groups, so as to promote the photo-catalytic degradation of organic pollutants. Therefore, the TiO_2-Er of microwave-hydrothermal catalyst has more surface hydroxyl groups, which shows that it has high photo-catalytic activity. At 1500~1300 cm^{-1} within the scope of the absorption peak was caused by -CH_3 symmetric deformation caused by vibration. Although most of the organic solvent in the process of heat treatment can eliminate, but IR analysis showed that the surface is still a small amount of residual organic matter.

From the SEM diagrams of two kinds of catalysts (Figuere 4), the Nano-particles of two kinds of TiO_2-Er catalysts were obviously refined. The morphology of the nanoparticles was nearly spherical and the particle size was nanometer. The specific surface area was larger, which could make full contact with the simulated pollutants, so that the photo-catalytic activity of the catalysts could be improved[9-11].

IV. CONCLUSION

The microwave-hydrothermal method as a new method is combined the traditional hydrothermal synthesis method with the microwave field. It use of microwave as the heat source, reaction medium in the special can be through the pressure in the reaction kettle of the microwave field, and through microwave heating make a reaction to the environment of high temperature and high pressure, to dissolve usually difficult soluble or insoluble substances and recrystallization, then separation and heat treatment products. In this study TiO2-Er were synthesized through the microwave-hydrothermal and sol-gel methods with the addition of 0.4%(in mole) erbium into reactor container. And TiO2-Er photo-catalyst of microwave-hydrothermal method is significantly higher than sol-gel methods in the same degradation conditions. Microwave-hydrothermal method is a new kind of preparation method. As a plus field introduced microwave can make the solution in a short period of time be evenly heating, to eliminate the influence of temperature gradient greatly, at the same time has the potential to precipitate germination nucleation in an instant, and TiO2 colloidal particles crystallization occurred quickly, thus obtain uniform particle size of ultrafine Nano TiO2 powder.

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