Preparation of Y-Ce Doped with TiO2 Photocatalyst in Microwave Ionic Liquids and Microwave Enhanced Photocatalytic Activity

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Abstract-Y and Ce co-doped TiO2 photo-catalysts were synthesized by microwave drying method and sol-gel method with room temperature ionic liquid as a reaction medium. The purpose of the experiment was order to improve the photo-catalytic activity and accelerate the degradation of pollutants. The structure and morphology of TiO2-Y-Ce 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 and phenol solution as simulated pollutants. The results showed that the TiO2-Y-Ce catalysts prepared at the optimum condition had higher photo-catalytic activity.

Keywords-Y-doped; Ce-doped; TiO2 photo-catalysts; Microwave enhancing effect; Photo-catalytic activity

I. INTRODUCTION

TiO2 semiconductor photocatalyst has the advantages of high catalytic activity, stability of chemical properties, environmental friendliness, and is widely used in the photocatalytic degradation of organic pollutants, sensors and other major areas [1, 2].

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 photocatalytic activity of the catalyst [3, 4].

The research group in ionic liquid medium by microwave auxiliary heating method of synthesis of rare earth yttrium and cerium Co doped TiO2 photo catalyst and with phenol and methyl orange solution as model pollutant. The effects of the photocatalytic degradation activity, in order to explore the effect of two kinds of rare earth elements Co doped on TiO2 photocatalytic degradation, further improve the rare earth elements doped on the modification of TiO2 photocatalyst catalytic activity.

II. EXPERIMENTAL SECTION

A. *Experimental Reagents and Instruments*

The main reagents: yttrium nitrate, cerium ammonium nitrate and other reagents, the preparation of ionic liquid and the structure test and characterization of the catalyst [5, 6].

B. *Preparation of TiO2-Y-Ce Catalyst*

The preparation of TiO2-Y-Ce photocatalyst for reference [5, 6].

C. *Photocatalytic Activity Test of TiO2-Y-Ce Catalyst*

In the reaction of TiO2-Y-Ce photocatalytic activity of photocatalytic degradation of methyl orange and phenol solution absorbance determination of reaction and catalyst of the visible light catalytic tests are detailed in reference [5, 6].

III. RESULTS AND DISCUSSION

D. *Effect of Yttrium and Cerium Doping on the Photocatalytic Activity of TiO2-Y-Ce*

TiO2-Y-Ce catalyst in the preparation process, in a fixed volume of ionic liquid is 3.0 ml, microwave drying power 210W, microwave drying time is 20min, calcination temperature of 650 DEG C, calcining time 3H conditions, to keep the percentage of n (Ce4 +) / N (Ti4 +) always is 0.075%, by changing the yttrium nitrate addition of different amount of yttrium dopant TiO2-Y-Ce catalyst, and methyl orange solution to simulate the degradation products, in a fixed UV irradiation time 1.0h conditions, study the influence of the amount of yttrium doping on the photocatalytic degradation of reactive and income results as shown in Figure 1; While the percentage of /n (Y3+) n (Ti4+) was 0.6%, and the other was the same as that of the above, the effect of cerium doping on the photocatalytic activity of the catalyst was investigated by changing the amount of ammonium nitrate.

From Figure 1 we can see that in the same amount of cerium doped, when yttrium addition amount of n (Y3 +) / N (Ti4 +) < 0.6%, the catalyst TiO2-Y-Ce on degradation of methyl orange solution rate with yttrium nitrate addition increased; When n (Y3+) /n (Ti4+) > 0.6%, the catalytic activity decreased with the increase of the amount of yttrium addition; And when the n (Y3 +) / N (Ti4 +) is 0.6%, TiO2-Y-Ce catalyst on degradation of methyl orange rate reached 99.8% of maximum has higher photocatalytic activity. The reason may be due to the coordination between the f orbitals and the degradation of the rare earth elements, which can improve the catalytic activity of TiO2 doped with rare earth elements. If the amount of yttrium nitrate is too high, too many yttrium can be deposited on the surface of TiO2, which is blocked by the electron hole transfer to the catalyst surface [7, 8].

From Figure 2 we can see that yttrium doping amount is the same, when CE is added, the amount of n (Ce4 +) / N (Ti4 +) < 0.075%, the catalyst TiO2-Y-Ce on degradation of methyl orange solution rate with cerium nitrate addition increased; When n (Ce4 +) / N (Ti4 +) > 0.075%, the catalytic activity but with cerium nitrate addition amount decreases with increasing; and when the n (Ce4 +) / N (Ti4 +) =0.075%, TiO2-Y-Ce catalyst on degradation of methyl orange rate reached 99.8% of maximum, the has higher photocatalytic activity.

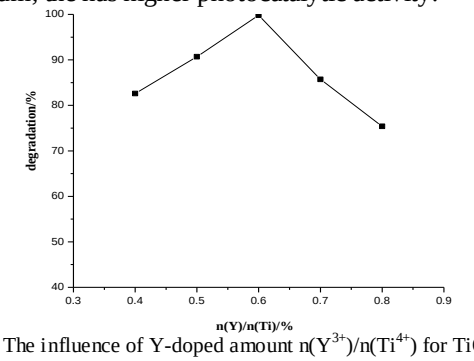

Figure.1 The influence of Y-doped amount $n(Y^{3+})/n(Ti^{4+})$ for TiO_2-Y-Ce on the degradation rate of methyl orange

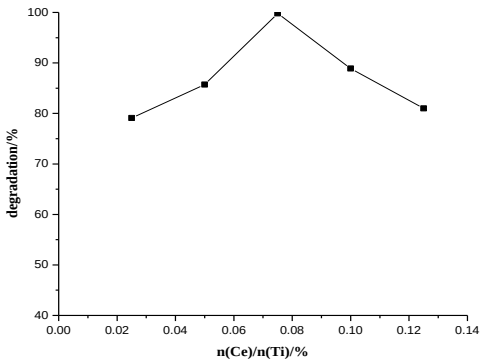

Figure.2 The influence of Ce-doped amount $n(Ce^{4+})/n(Ti^{4+})$ for TiO_2-Y-Ce on the degradation rate of methyl orange

E. Comparison of TiO2-Y, TiO2-Ce and TiO2-Y-Ce Three Catalysts

Table 1 Degradation rate of methyl orange and phenol for TiO_2-Y, TiO_2-Ce and TiO_2-Y-Ce catalysts by MW，UV and UV-MW for 1h

The degradation rate	TiO_2-Y		TiO_2-Ce		TiO_2-Y-Ce	
	η_1	η_2	η_1	η_2	η_1	η_2
MW	3.9%	3.9%	3.9%	3.9%	3.9%	3.9%
UV	89.8%	73.4%	98.6%	96.6%	99.5%	97.6%
UV-MW	93.6%	81.8%	99.3%	97.2%	99.8%	98.5%

Under the optimum conditions, three kinds of catalysts 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 / TiO2-Y-Ce / TiO2-Y / TiO2-Ce / catalyst with single rare earth element or cerium rare earth element is significantly higher than that in the same degradation conditions. The reason may be due to the Ce4+ and Y3+ Co doped Ce4+, TiO2-Y-Ce is the electron acceptor, which can capture the electron and hole the pairs, and the Y3+ valence state is lower than that of Ti4+, and the electron hole pair can reduce the catalyst surface. In addition, from table 1, the degradation rate of TiO2-Y-Ce catalyst in UV-MW was also significantly higher than that of MW or UV. This shows that microwave irradiation has the effect of enhancing the TiO2-Y-Ce degradation of pollutants. Under the constant temperature condition, the degradation rate of 298K 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 TiO2-Y-Ce 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 photocatalytic activity of the catalyst. This indicates that the microwave radiation heating is beneficial to the synthesis of Co doped TiO2-Y-Ce catalyst, and also has the function of enhancing the photocatalytic degradation of the Co doped TiO2-Y-Ce catalyst for simulating the pollutant.

Table 2 for the three kinds of catalysts and phenol degradation rate of methyl orange under solar light irradiation 4h.

Table 2 Degradation rate of methyl orange and phenol for TiO_2-Y, TiO_2-Ce and TiO_2-Y-Ce catalysts by the sun light for 4h

Degradation rate	TiO_2-Y	TiO_2-Ce	TiO_2-Y-Ce
η_1	93.8%	96.8%	97.6%
η_2	87.6%	89.4%	90.5%

According to Table 2, the degradation activity of the three catalysts in the solar irradiation is still the highest,

which indicates that the TiO2-Y-Ce catalyst has good photocatalytic activity under the sun light. The possible reason is that the absorption range of TiO2 and Ce^{4+} after Y^{3+} doping is increased, which is favorable for the generation of charge carriers, which can improve the photocatalytic activity of TiO2-Y-Ce catalyst.

F. Analysis of XRD, IR and TiO2-Y-Ce of SEM catalyst

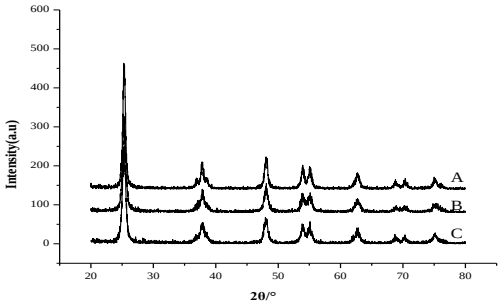

Figure.3 XRD patterns of TiO_2-Y，TiO_2-Ce and TiO_2-Y-Ce catalysts

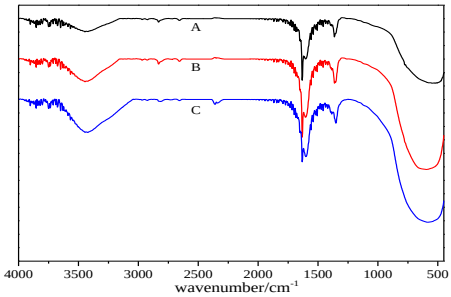

Figure.4 IR spectra of TiO_2-Y，TiO_2-Ce and TiO_2-Y-Ce catalysts

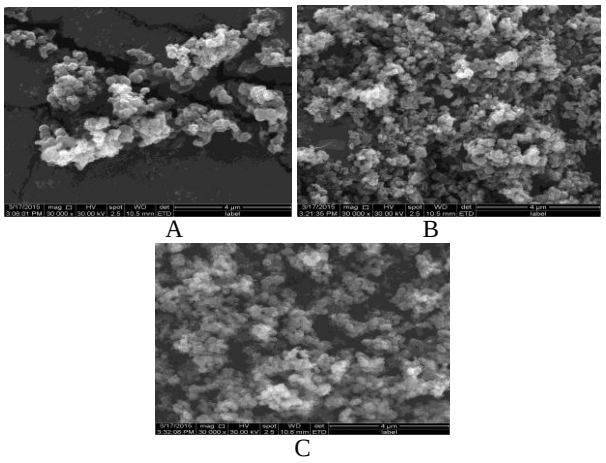

Figure.5 SEM images of TiO_2-Y，TiO_2-Ce and TiO_2-Y-Ce catalysts

SEM, IR and XRD of TiO_2-Y, TiO_2-Ce and TiO_2-Y-Ce three catalysts are shown in Figure 3, figure 4 and figure 5. According to observed in Figure 3, diffraction angle 2 theta =25.30 degrees, 37.8 DEG, 48.14 degrees near, three kinds of doped TiO_2 catalyst have obvious main diffraction peaks appear, they with the standard card anatase TiO_2 peak than consistent. The three kinds of catalysts, TiO_2-Y, TiO_2-Ce and TiO_2-Y-Ce, were prepared by the method. The particle sizes of, and TiO2-Y were calculated according to Scherrer formula, and the particle sizes of TiO_2-Ce, and TiO_2-Y-Ce were 11.58, 12.81 and 12.68nm respectively.

According to the IR spectra of three catalysts (Fig. 4), TiO_2-Y-Ce and TiO_2-Y in the 3446cm^{-1}, TiO_2-Ce and, respectively, near the 1631cm^{-1}, Ti-OH, and Ti-O-Ti bond stretching vibration peak near the 592cm^{-1}; 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-Y-Ce catalyst has a strong absorption peak at 1631cm^{-1} and 3446cm^{-1}, which indicates that the surface hydroxyl adsorption of Co doped catalyst is more than that of single element doped TiO_2; 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 O2 into O2-, HO2- and other active groups, so as to promote the photocatalytic degradation of organic pollutants. Therefore, Co doped TiO2-Y-Ce catalyst has more surface hydroxyl groups, which shows that it has high photocatalytic activity.

From the SEM diagrams of three kinds of catalysts (Fig. 5), the nano particles of TiO2-Y, TiO2-Ce and TiO2-Y-Ce three kinds of 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 photocatalytic activity of the catalysts could be improved[9.10].

IV. CONCLUSION

Optimum conditions for preparation of rare earth element yttrium and cerium Co doped TiO2-Y-Ce catalyst by microwave assisted ionic liquid medium: $n(Y^{3+})/n(Ti^{4+})$=0.6% 、 $n(Ce^{4+})/n(Ti^{4+})$=0.075%, Ionic liquid dosage 210W, microwave drying power 3.0mL, microwave drying time 20min, calcination temperature 650, calcination time 3h. Under the condition of TiO2-Y-Ce photocatalyst, in MW, UV and UV-MW conditions after degradation of methyl orange and phenol solution 1.0h, methyl orange drop and phenol degradation rate in the UV-MW under the condition of is the best. The structural analysis of the catalyst showed that the activity of TiO2-Y-Ce catalyst was greater than that of TiO2-Y or TiO2-Ce catalyst, and the size of the photocatalytic activity of the three was: TiO2-Y-Ce > TiO2-Ce > TiO2-Y.

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