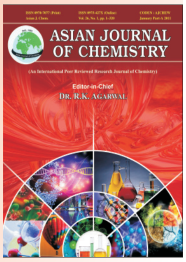
Asian Journal of Chemistry; Vol. 26, No. 19 (2014), 6431-6434

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.16416



Fe/CeO_2 Catalysts for Highly Efficient Degradation of Congo Red at Low Temperature

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Received: 24 September 2013; *Accepted*: 21 February 2014; *Published online*: 16 September 2014; AJC-15933

Fe/CeO_2 catalysts were prepared by combining with sol-gel and impregnation method. The structures of catalysts were characterized by X-ray diffraction. The results showed that the addition of Fe into CeO_2 unaffected the crystalline structure of CeO_2 and Fe emerged highly dispersed state. In the range of 5-35 °C, the 2 wt. % Fe/CeO_2 catalyst towards 10 mgL^{-1} azo dyes Congo Red by catalytic wet hydrogen peroxide oxidation (CWPO) displayed highly catalytic activity. Furthermore, at room temperature (25 °C), the degradation percentage of Congo Red was 96 % with the amount of 0.05 g catalyst and 0.02 M H_2O_2 (30 wt. %) after reacting 40 min. At the same time, the repetitive experimental results of catalyst have shown that the catalyst had excellent stability.

Keywords: Catalytic oxidation, Iron, Cerium oxide, Hydrogen peroxide, Congo red.

INTRODUCTION

With the development of modern industries, the limited water resources of human beings suffered from serious pollution. The removal of the toxic and hazardous chemicals from water has become an important task of environmental protection. The traditional water treatment methods had some drawbacks, such as the large consumption of energy, secondary pollution, incomplete degradation, *etc.*[1-4]. At present, the degradation of organic pollutants by TiO_2-based photocatalytic is the hot spot in field of the current materials and catalysis research[5]. However, the photo-catalysis technology have several pivotal problems[6-7]: (1) The quantum yield was very low (about 4 %) and no more than 10 %. It is difficult to deal with the industrial wastewater of large quantities and high concentrations. (2) The low utilization of solar energy, The photo-catalysts can only absorb the ultraviolet part of sunlight and did not make use of the visible part of sunlight. Furthermore, the ultraviolet component is only 5 % of the sunlight. (3) Photo-catalyst is difficult to support catalyst evenly and firmly on the surface of different materials under the premise of maintaining a high catalytic activity and meeting specific physical and chemical properties which the separation and regeneration of catalyst was very hard. Therefore, photocatalytic technology widely used in industry had been greatly restricted and the catalytic oxidation technology without the comsuption of extra energy has been paid much attention.

Compared with the photo-catalytic techniques, CWPO technology with H_2O_2 as the oxidant can produce $OH^{\bullet}$ with strong oxidation ability under the function of the catalyst, which can effectively destroy the molecular structure of pollutants. It can ease the reaction conditions and reduce processing costs[8,9]. Studies have also shown that the research and development of the highly efficient and stable heterogeneous catalyst is the key, which CWPO can use under the normal temperature and pressure conditions[10]. In the present study, Fe/CeO_2 catalysts were prepared by combining with sol-gel and impregnation method. The catalytic oxidation degradation toward the refractory azo dye of Congo red has been carried out. It has shown that the catalysts have demonstrated excellent catalytic activity under the room temperature even or low temperature (5 °C).

EXPERIMENTAL

Cerium(IV) nitrate (A.R.), ferric(III) nitrate (A.R.), glacial acetic acid (A.R.), hydrochloric acid (A.R.), pluronic P123 (MW = 5500) and ethanol (A.R.) were purchased from Sinopharm Chemical Reagent Co. Chemicals were used as received without further purification. Fe/CeO_2 catalysts were prepared by combining with sol-gel and impregnation method.

General procedure[11]: The desired amount of cerium(IV) nitrate, glacial acetic acid and hydrochloric acid were added into ethanol, then added in P123 (MW = 5500) after sufficient mixing, continued aging 20 h after the formation of the thinfilm-like gel, finally calcinated 6 h in muffle furnace at 400 °C (2 °C min^{-1}) for getting the CeO_2 sample. The Fe/CeO_2 catalysts were obtained by adding certain amount of CeO_2 samples into the different concentration of ferric (III) nitrate solution, dryed 2 h in vacuum and calcined 2 h at 400 °C.

The XRD patterns of samples were recorded on a Rigaku D/max-2400 diffractometer operated at 40 kV voltage and a 200 mA current with CuK_α radiation. UV-visible absorption spectra were measured on a Hitachi U-3010 spectrophotometer with a 1 cm quartz cuvette. The catalytic reaction of decomposition of Congo red was carried out in a 50 mL two-double beaker and the temperature was controlled by a circular condenser system with ethanol as fluid.

RESULTS AND DISCUSSION

Fig.1 shows the XRD Spectrum of the several representative catalysts. In Fig. 1(a) the CeO_2 appeared the relatively strong diffraction peaks at 2θ (28. 5°, 33.0°, 47. 4°, 56.3°). These peaks correspond to (111), (200), (220) and (311) crystal planes (JCPDS:81-0792) of cubic fluorite structure of CeO_2. After the Fe species loaded on CeO_2, the spectra of Fe/CeO_2 catalysts (Figs. 1b-1d) were similar to that of pure CeO_2. It can also be seen that the peak intensity of Fe/CeO_2 have not weakened compared as that of pure CeO_2, it shows that the crystal structures of CeO_2 were still maintained after loaded the Fe. Furthermore, the characteristic diffraction peaks of related iron oxide species were not detected. This may be due to the quantity of the loaded Fe was relatively low and highly dispersed[12].

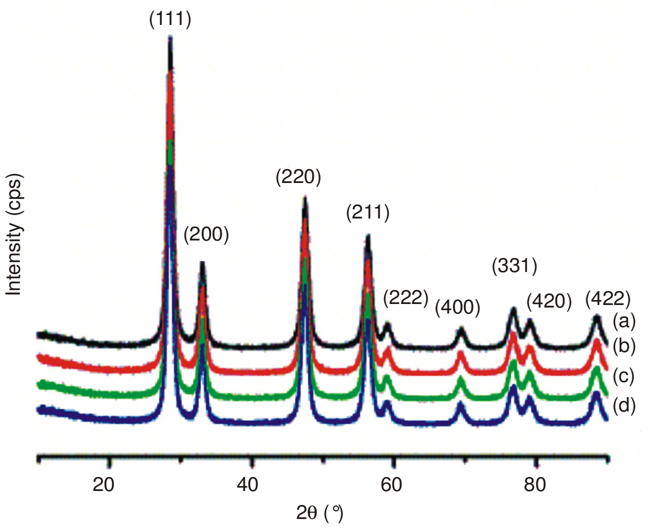


Fig. 1. XRD patterns of the representative catalysts, (a) CeO_2 (b) 1 wt. % Fe/CeO_2 (c) 2 wt. % Fe/CeO_2 (d) 3 wt. % Fe/CeO_2

Fig. 2 shows the dependence of the degradation rate of Congo red on the quantity of Fe of Fe/CeO_2 catalysts after reacting 40 min at 25 °C. It can be seen that the 2 wt.% Fe/CeO_2 catalyst shows the highest activity, the degradation percentage of Congo red was 96 %. When the load is more than 2 wt. %, the degradation rate of Congo red began to fall. It indicates the load of the 2 wt % Fe was the optimalizing in present system.

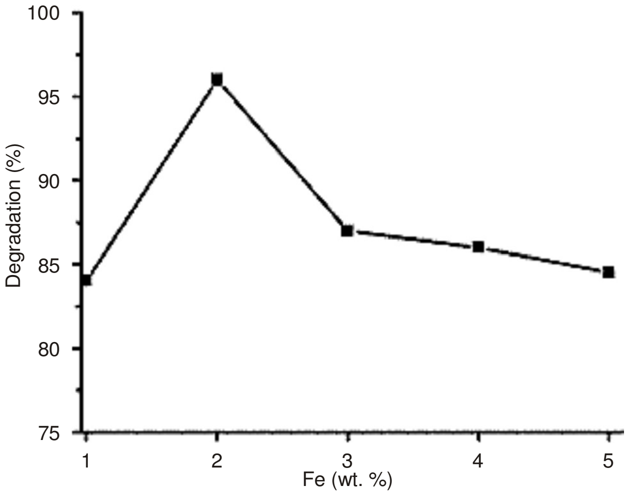


Fig. 2. Effects of Fe content in Fe/CeO_2 catalysts on Congo red degradation, Reaction conditions: V(Congo red solution) = 50 mL, C_0(Congo red) = 10 mg/L, m(Fe/CeO_2) = 0.05g, $C_0(H_2O_2)$ = 0.02 M

At 25 °C, the catalytic activity of 2 wt. % Fe/CeO_2 catalyst towards azo dyes Congo red was carried out at different time. UV-visible spectral scanning profiles and digital photos were show in Fig. 3(a) and 3(b), respectively. The dotted line stand for the results of H_2O_2 reacting with Congo red after 40 min without catalysts (Fig. 3a).

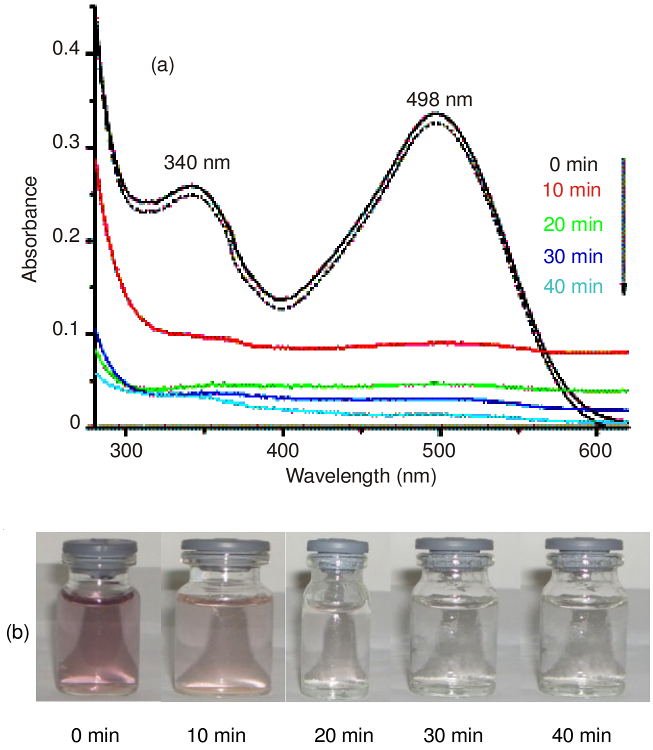
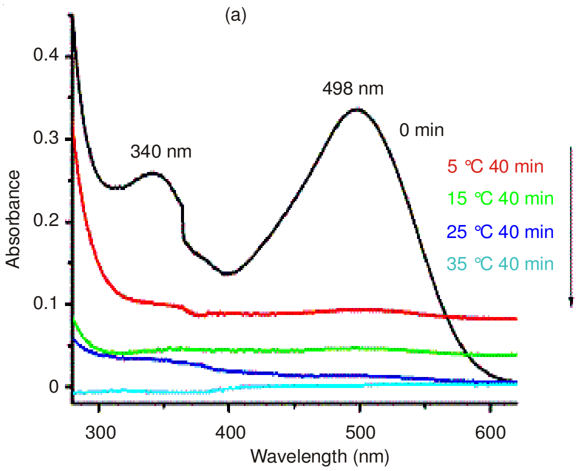


Fig. 3. (a) UV-visible spectra of Congo red at 25 °C at different time (Note: the black dotted line is the comparison experiment, reaction time: 40 min.). (b) The digital photoes of corresponding time. Reaction conditions: V(Congo Red solution) = 50 mL, C_0(Congo Red) = 10 mg/L, m(2 wt.% Fe/CeO_2) = 0.05 g, $C_0(H_2O_2)$ = 0.02 M

It indicated that H_2O_2 does not react with Congo red without catalysts. Meanwhile, in Fig. 3(a), the two obvious absorption bands of Congo red solution have been displayed at 498 nm and 340 nm[13]. The absorption band of 498 nm was related to the azo-bond of molecules and the large conjugated system of dye molecules. Aromatic hydrocarbons or polycyclic aromatic hydrocarbons interacted with some chromophores generated the absorption peaks which displayed in the 340 nm. The absorption peak intensity of 498 nm rapidly decreased with the reaction proceeding, the absorption peak almost disappeared after reacting 40 min. It shows that the azo-bond of molecules has been destroyed in this stage. The absorption peak of 340 nm was gradually weakened, but the peak width became a little larger. It shows that the ring structure of aromatics or polycyclic aromatic hydrocarbons has not been destroyed completely in the initial decolourization stage and maybe generated the different aromatic compounds[13]. However, with the process of reaction, they were almost disappeared completely after 40 min. At the same time, Fig. 3(b) shows the colour of Congo red solution form red quickly turned into light red and became colourless finally in the degradation process, which shows that the azo-bond of molecular structure may be broken and the conjugated chromogenic of dye molecules structure was destroyed. It was consistent with the result of UV-visible spectroscopy (Fig 3a).

At the same conditions, in the range of 5-35 °C, the degradation rate of Congo red after reacting 40 min has also been studied. The results are shown in Fig. 4(a) and 4(b).



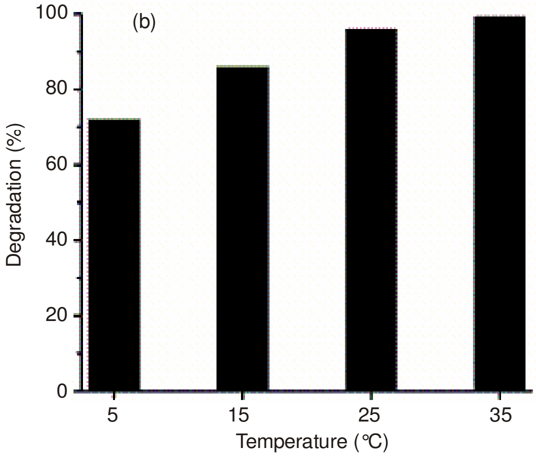


Fig. 4. (a) UV-Visible spectra of Congo red at different temperature. (b) The degradation of Congo red at different temperature. (The reaction conditions are the same as Fig. 3)

Fig. 4 (a) shows that the results of the degradation of Congo red were excellent in the range of reaction temperature. When the temperature was 5 °C, The UV-visible absorption peaks of Congo red have decreased greatly. When the temperature was 25 °C or higher, the UV-visible absorption peaks of Congo red have almost disappeared completely. As shown in Fig. 4(b), the degradation rate of Congo red was 72 % at 5 °C, with temperature increasing to 25 °C, the degradation rate of Congo red was 96 %, which was consistent with the result of UV-visible spectroscopy. Furthermore, the final degradation rates of Congo red at 25 and 35 °C were almost similar, which indicates the degradation of Congo red was almost finished at 25 °C after reacting 40 min.

Fig. 5 shows the correlation of times and degradation of Congo red at 25 °C. It shows that the result of the degradation rate of Congo red of second time compared with that of the first time decreased 2 %. The result of third time compared with that of the first time, the degradation rate of Congo red decreased about 4 %. These showed the activity of catalyst was decreased a little with the increasing of time. This may be generate small amount of organic intermediates which were very difficult to degradate in the wet oxidation process and occupied the part active sites of catalysts. Therefore, the activity of catalysts was decreased. However, the degradation rate of Congo red was still beyond 85 % after using four times. It shows that the repeated performance of catalysts was excellent in the reaction system and the catalyst possessed high stability.

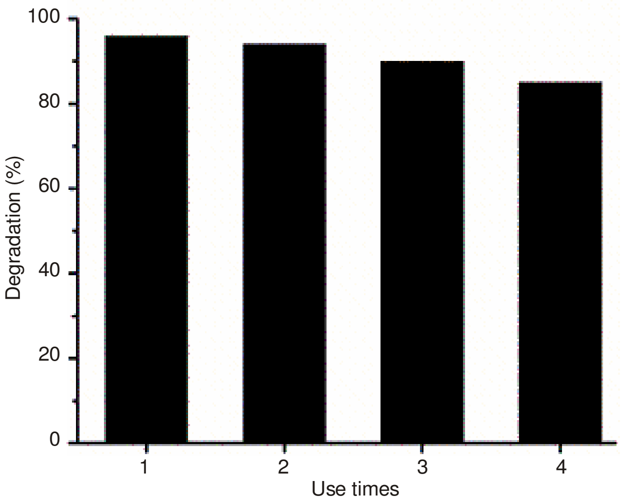


Fig. 5. Correlation of use times and degradation of Congo red, (The reaction conditions are the same as Fig. 3)

Conclusion

In conclusion, the Fe/CeO$_2$ catalysts were synthesized by combining with sol-gel and impregnation method. The 2 wt % Fe/CeO$_2$ catalyst has displayed high catalytic activity toward Congo red degradation in the range of 5-35 °C. The maximum degradation rate of Congo red can be achieved as much as 96 % at 25 °C after reacting 40 min. And the result of stability test has shown the catalyst possesses high stability. These results have also shown the catalyst has a potential application in wastewater treatment.

ACKNOWLEDGEMENTS

This work was supported by Natural Science Foundation of Guizhou Province (20072013, 20122284).

REFERENCES

1. K. Vinodgopal and P.V. Kamat, *Environ. Sci. Technol*., **29**, 841 (1995).
2. H. Hidaka, Y. Asai, J. Zhao, K. Nohara, E. Pelizzetti and N. Serpone, *J. Phys. Chem*., **99**, 8244 (1995).
3. Y.J. Zhang, L.C. Liu, L.L. Ni and B.L. Wang, *Appl. Catal. B*, **138-139**, 9 (2013).
4. J. Herney-Ramirez, M.A. Vicente and L.M. Madeira, *Appl. Catal. B*, **98**, 10 (2010).
5. K. Vinodgopal, D.E. Wynkoop and P.V. Kamat, *Environ. Sci. Technol*., **30**, 1660 (1996).
6. J.J. He, J.C. Zhao, T. Shen, H. Hidaka and N. Serpone, *J. Phys. Chem. B*, **101**, 9027 (1997).
7. G. Centi, S. Perathoner, T. Torre and M.G. Verduna, *Catal. Today*, **55**, 61 (2000).
8. M. Neamtu, C. Zaharia and C. Catrinescu, *Appl. Catal. B*, **48**, 287 (2004).
9. H.X. Fu, Z.P. Jiang and Y.J. Tan, *Chin. J. Catal*., **21**, 375 (2000).
10. A.M.T. Silva, R.R.N. Marques and R.M. Quinta-Ferreira, *Appl. Catal. B*, **47**, 269 (2004).
11. J. Fan, S.W. Boettcher and G.D. Stucky, *Chem. Mater*., **18**, 6391 (2006).
12. S.X. Yang, W.P. Zhu, Z.X. Chen, J.B. Wang and Y.R. Zhou, *Chin. J. Catal*., **27**, 329 (2006).
13. Z.Y. Sun, J.H. Du and H.S. Chen, *Spectrosc. Spect. Anal*., **26**, 1226 (2006).