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# **Preparation of catalyst CuO/CeO<sub>2</sub> in multiphase Fenton** technology

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Abstract. The performance of the catalyst in the multiphase Fenton system is particularly important. It will directly affect the rate of hydroxyl radical generation during the multiphase Fenton reaction which is the main material for oxidative degradation of organic matter in wastewater. Therefore, it is necessary to select a suitable catalyst to construct a multiphase Fenton system. In this study, the preparation of CuO/CeO<sub>2</sub> catalyst in multiphase Fenton technology was discussed. The effects of CuO loading, calcination time and calcination temperature on CuO/CeO<sub>2</sub> were investigated. The best preparation conditions for the catalytic performance of the catalyst were as follows: the loading of CuO was 7%, the calcination time was 3h and the calcination temperature was 400°C. The catalyst prepared under this condition can achieve a COD<sub>Cr</sub> removal rate of 34% for a plurality of Fenton processes.

#### 1. Introduction

The supported catalyst consists of an active metal or a metal oxide and a carrier. The active metal is the basis of the performance of the catalyst, which determines the reaction rate and reaction direction. At present, domestic and foreign research on catalysts has made rapid progress in transition metals and their oxides, and is divided into catalysts containing noble metals and catalysts containing non-precious metals.

Compared with other metal catalysts, precious metal catalysts have many advantages, but at the same time, they have problems of poor stability, high price, and easy sintering into blocks at high temperatures, so the application of precious metal catalysts is limited. However, the price of the transition metal and its oxide supported on the catalyst carrier is much lower (copper, zinc, iron, nickel, etc.), and it is easier to obtain and has better catalytic performance. At the same time, it also has the advantages of precious metals and avoids its shortcomings. It is currently a hot spot in the field of multiphase Fenton catalysts.

Zhou Lingvun [1] used a multiphase Fenton system composed of CuO and  $H_2O_2$  under low temperature conditions to catalyze the oxidation of dye wastewater and degrade the reactive brilliant red X-3B in water.

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The results show that the multiphase Fenton system composed of CuO and  $H_2O_2$  can oxidize reactive brilliant red X-3B quickly and efficiently, and the oxidative degradation rate can reach 99%. Qiu et al. [2] used transition metal oxides as catalysts to form a heterogeneous Fenton system with  $H_2O_2$ , oxidized wastewater containing acid red dye, and discussed the performance, catalytic effect and preparation conditions of the catalyst.

The results show that CuO has the strongest catalytic performance in the system compared with the catalytic ability of metal oxides of Ni, Mn and Zn. Therefore, the transition metal oxide CuO was selected as the active component of the heterogeneous Fenton catalyst.

# 2. Preparation method of CuO/CeO<sub>2</sub>

 $CeO_2$  has good oxygen storage and oxygen release capacity, but it is generally not used as a catalyst alone, but as a carrier in combination with other highly stable oxides. Among them, the supported catalyst  $CuO/CeO_2$  is widely used because of its low cost and high activity. Here are a few common methods for preparing  $CuO/CeO_2$ .

# 2.1. Surfactant synthesis method

Surfactants are often used as templating agents because of their good structural distribution. The templating agent-assisted synthesis method means that the added templating agent can modulate the pore structure to obtain a catalyst having a high specific surface area. After 2005, surfactants were applied to prepare catalyst supports and non-silicon aluminium material catalysts with high specific surface area.

For the preparation of multi-component non-silicon-aluminium material catalysts, it is difficult to obtain a regular and uniform pore structure in normal preparation, because in the calcination stage, the valence state of the transition metal changes, resulting in collapse of the pore walls, failing to obtain an ideal mesoporous material.

However, by adding a surfactant during the production process, a catalyst having a large specific surface area and a regular mesoporous structure can be obtained.

# 2.2. Coprecipitation method

The coprecipitation method refers to precipitating a solution of cerium nitrate and copper nitrate with a precipitant (Na<sub>2</sub>CO<sub>3</sub>) in an aqueous solution to obtain a precipitate, followed by centrifugation, washing, drying, and finally calcination to obtain a CuO/CeO<sub>2</sub> catalyst. Further, a mixed solution of potassium carbonate and potassium hydroxide can also be used as a precipitating agent to prepare a CuO/CeO<sub>2</sub> catalyst.

# 2.3. Deposition precipitation method

The deposition precipitation method refers to putting different metal oxides and carriers into a solution containing an active ingredient, adding an alkaline solution for neutralization, and selecting certain reaction conditions to deposit a metal oxide on the surface of the carrier to obtain a precipitate.

After the precipitate is obtained, it is centrifuged, washed, dried, etc., and finally calcined to obtain a  $CuO/CeO_2$  catalyst.Richter et al. [3, 4] precipitated  $Cu(OH)_2$  onto Y-type molecular sieves and activated it at high temperature to obtain a chlorine-free Cu/Y catalyst with better catalytic activity.

# 2.4. Impregnation method

The impregnation method refers to immersing  $CeO_2$  as a carrier in a  $Cu(NO_3)_2$  solution. After a period of time, the precipitate is separated for centrifugation, washing, drying, etc., and finally calcined to obtain a  $CuO/CeO_2$  catalyst.

Zhang Haitao et al. [5] prepared CuO supported catalyst by immersing  $Cu(NO_3)_2$  and then decomposing  $Cu(NO_3)_2$ . It was found that the catalyst prepared by activated carbon was catalytically active, and the surface of CuO and Cu<sub>2</sub>O was the main catalyst.

#### 2.5. Citric acid hydrothermal synthesis

Citric acid hydrothermal synthesis means adding citric acid to a mixed solution of  $CuC_2O_4$  and  $Ce_2(C_2O_4)_3$ , pouring the solution into a hydrothermal reaction kettle, and hydrothermal treatment at 150°C for 1 day. Then, the supernatant is removed and the precipitate is separated, followed by centrifugation, washing, drying, etc., and finally calcination to obtain a CuO/CeO<sub>2</sub> catalyst.

Shaikh et al. [6] prepared a CuO/CeO<sub>2</sub> catalyst with CuO attached to the surface of CeO<sub>2</sub> nanorods by hydrothermal synthesis to study the distribution effect of copper species on low temperature CO oxidation. Liu et al. [7] prepared a CuO/CeO<sub>2</sub> composite oxide catalyst by hydrothermal method and studied its catalytic decomposition of N<sub>2</sub>O. The CuO/CeO<sub>2</sub> mixed oxide catalyst was found to have higher oxidation activity than pure CuO and CeO<sub>2</sub>.

#### 2.6. Sol-gel method

The sol-gel method is a relatively common production method, which is divided into a hydrogen peroxide sol gel method and a urea sol gel method. Hydrogen peroxide hydrogel method refers to separately adding  $H_2O_2$  in a solution of cerium nitrate and copper nitrate, and then mixing the two solutions. After standing for a while, the supernatant is removed and the precipitate is separated, followed by centrifugation, washing, drying, and finally calcination to obtain a catalyst CuO/CeO2.

Ren Jun et al. [8] used copper nitrate and soluble starch as raw materials, and obtained CuO/AC catalyst through sol-gelation, high temperature carbonization and KOH activation. When the carbonization and activation temperatures were 500°C and 850°C respectively, and KOH: C was 1, the specific surface area of the catalyst reached 1690 m<sup>2</sup>/g, and the microporous pore volume was 72.4%, which was the highest.

#### 3. Experiment

The supported catalyst  $CuO/CeO_2$  supported by  $CeO_2$  was prepared by sedimentation precipitation method. The reagents used were analytically pure.

The sodium lauryl sulphate solution, the CeCl<sub>3</sub> solution and the NaOH solution were prepared for use. Stir the sodium lauryl sulphate solution for more than 40 minutes until the sodium lauryl sulphate is completely dissolved.

The fully dissolved CeCl<sub>3</sub> solution was slowly added to the sodium dodecyl sulphate solution using a peristaltic pump and stirring was continued for 30 to 40 minutes. Then, the prepared NaOH solution was slowly added to the solution by a peristaltic pump in the same manner. After the addition, the container was sealed with a plastic wrap and stirring was continued for 24 hours. Subsequently, the mixture is placed in an oven and crystallized at 90°C for 24h, then subjected to 3 to 5 centrifugation washing, 70°C vacuum drying for 12h, 400°C calcination for 4h (under dry air conditions) and natural cooling to normal temperature, etc., a CeO<sub>2</sub> carrier having a high specific surface area can be obtained.

A certain amount of CeO<sub>2</sub> carrier was dissolved in deionized water and stirred for 60 min until the CeO<sub>2</sub> support was completely dissolved in deionized water. he weighed Cu(NO<sub>3</sub>)<sub>2</sub> was added to the solution, and anhydrous Na<sub>2</sub>CO<sub>3</sub> was added to adjust the pH to maintain the pH at about 10. The container is sealed with plastic wrap, heated in a continuous water bath at 60°C for 3h, then washed by 3-5 times, vacuum dried at 100°C for 3h, calcined at 400°C for 3h (under dry air) and naturally cooled to room temperature, a CuO/CeO<sub>2</sub> catalyst having a high specific surface area can be obtained.

#### 4. Results and discussion

At room temperature 25°C, initial pH of 8, the addition of CuO loading of 5%, catalyst CuO/CeO<sub>2</sub> dosage of 1 g/L,  $H_2O_2$  dosage of 0.3 mol/L, reaction time of 120 min, COD<sub>Cr</sub> removal rate can reach 30%.

#### 4.1 Effect of CuO loading

As shown in figure 1, the removal rate of  $COD_{Cr}$  increases first and then decreases with the increase of CuO loading. When CuO loading is 7%, the removal rate of  $COD_{Cr}$  is the highest, which can reach 34%.

When the CuO loading is 1%, the COD<sub>Cr</sub> removal effect is the worst, only 18%. This is because the CuO loading is too low, the active material which plays a major role in the catalysis is reduced, and the catalytic activity is lowered.

When the CuO loading is too high, the pores of the catalyst carrier are blocked, resulting in incomplete contact and reduced catalytic performance.



**Figure 1.** Effect of different CuO loading on COD<sub>Cr</sub> removal efficiency.

Sample	Specific surface area	Pore volume	Pore size
	$(m^2/g)$	$(cm^{3}/g)$	(nm)
1% CuO	156	0.22	4.31
3% CuO	152	0.20	4.33
5% CuO	150	0.18	4.40
7% CuO	150	0.18	4.56
9% CuO	148	0.16	4.78

Table 1. Results of BET characterization of catalysts with different CuO loading.

According to table 1, as the CuO loading increases (1% CuO increases to 9% CuO), the specific surface area gradually decreases from  $156 \text{ m}^2/\text{g}$  to  $148 \text{ m}^2/\text{g}$ , and the pore volume gradually decreases from  $0.22 \text{ cm}^3/\text{g}$  to  $0.16 \text{ cm}^3/\text{g}$ , but the pore size gradually increases from 14.31 nm to 4.78 nm. This is because as the CuO loading increases, the CuO content in the pores of the catalyst carrier increases gradually, resulting in a decrease in pore volume and specific surface area, and a slight change in pore size [9].

It can be seen that too much or too low CuO loading will affect the catalytic performance of the catalyst. There are two possible reasons for this: On the one hand, as the CuO loading decreases, the amount of active component per unit mass of the catalyst is reduced, reducing the catalytic effect.

On the other hand, the structure of the catalyst changes as the CuO loading increases. When the CuO loading is too low, the catalyst has a high specific surface area and pore volume, but the active component is small, and the advantage of large specific surface area of the catalyst is not fully utilized, and the removal effect of  $COD_{Cr}$  is reduced.

Therefore, the CuO loading is too low to achieve the best removal effect. When the CuO loading is too high, the specific surface area and pore volume are low, and the effective contact area of CuO and wastewater supported on the catalyst surface is reduced, so the removal effect of COD<sub>Cr</sub> is decreased.

#### 4.2 Effect of calcination temperature

It can be seen that the calcination temperature has a certain influence on the catalyst CuO/CeO<sub>2</sub>, and the overall COD<sub>Cr</sub> removal rate is between 20% and 35%. At a temperature of 400°C, the COD<sub>Cr</sub> removal rate is the highest, reaching 34%, while at temperatures below 400°C or above 400°C, the COD<sub>Cr</sub> removal rate is reduced. This is because, if the temperature is too low, the active material cannot be completely thermally decomposed, the impurities cannot be completely removed, and if the temperature is too high, the active material is sintered [10], thereby reducing the catalytic activity.



**Figure 2.** Effect of different calcination temperature on  $COD_{Cr}$  removal efficiency.

**Table 2.** BET characterization of catalysts at different calcination temperatures.

Sample	Specific surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore size (nm)
200 °C roasting	190	0.22	4.33
300 °C roasting	166	0.21	4.48
400 °C roasting	150	0.18	4.56
500 °C roasting	133	0.17	4.79
600 °C roasting	122	0.17	4.99

It can be seen from table 2 that as the calcination temperature increases, the specific surface area and pore volume gradually decrease, and the pore diameter gradually increases. The specific surface area is reduced from 190 m<sup>2</sup>/g at 200°C to 122 m<sup>2</sup>/g at 600°C. The difference is large, but the decrease and increase of pore volume and pore size are small, and the pore volume is reduced by 0.05 m<sup>3</sup>/g, while the pore size is increased by 0.66 nm. This indicates that the change in the calcination temperature mainly affects the specific surface area of the catalyst, and has little effect on the pore volume.

Combined with figure 2 and table 2, it can be concluded that the specific surface area and pore volume are the highest at 200°C, but the  $COD_{Cr}$  removal rate is the lowest, only 21%. At 400°C, the specific surface area and pore volume are compared with those at 200°C having a decrease, but the  $COD_{Cr}$  removal rate is the highest.

This is because when the calcination temperature is low, the active material is incompletely loaded, although the specific surface area is large, but the effective catalytically active substance per unit mass is small, and some residual substances also adhere to the catalyst surface, which restricts the catalytic performance of the catalyst. When the temperature is higher, the calcination temperature is higher than

the heat resistance limit of the catalyst, causing the catalyst to be sintered, the pore structure is destroyed, and the specific surface area and pore volume are reduced, the catalytic activity is lowered, and the  $COD_{Cr}$  removal rate is decreased.

#### 4.3 Effect of calcination time

It can be seen from figure 3 that as the calcination time increases, the removal rate of  $COD_{Cr}$  increases first and then decreases. The  $COD_{Cr}$  removal rate was the lowest when there was no roasting, only 18%; when the roasting time was 3h, the  $COD_{Cr}$  removal rate was the highest, reaching 33%, and the removal effect was better; after the calcination time is more than 3h, the  $COD_{Cr}$  removal rate shows a downward trend. This is because the calcination time is too short, the crystal size of the prepared catalyst surface is incomplete, and if the calcination time is too long, the pore structure of the catalyst is destroyed, and finally the  $COD_{Cr}$  removal rate can be changed.



**Figure 3.** Effect of different calcination time on COD<sub>Cr</sub> removal efficiency.

Sample	Specific surface area	Pore volume	Pore size
	$(m^2/g)$	$(cm^{3}/g)$	(nm)
not roasting	178	0.26	4.31
roasting 1h	173	0.23	4.46
roasting 2h	169	0.20	4.51
roasting 3h	150	0.18	4.56
roasting 4h	146	0.17	4.89

It can be seen from table 3 that as the calcination time increases, the specific surface area and pore volume are gradually decreasing, but the pore diameter is gradually increasing. When it is not calcined, the specific surface area of the catalyst is the largest, which can be 178 m<sup>2</sup>/g. However, the specific surface area has been decreasing with the increase of calcination time. When the calcination time reaches 4h, the specific surface area has been reduced to 146 m<sup>2</sup>/g, and the reduction amount is about 30 m<sup>2</sup>/g, and the pore size and pore volume are only changed by 0.58 nm and 0.09 cm<sup>3</sup>/g, which indicates that the calcination time mainly affects the specific surface area of the catalyst and has a weak influence on the pore volume.

Combined with figure 3 and table 3, it can be seen that the calcination time has a certain influence on the specific surface area of the catalyst, which in turn affects the  $COD_{Cr}$  removal rate. When the catalyst calcination time is 3h, the specific surface area of the catalyst is 150 m<sup>2</sup>/g, which is not the

maximum nor the minimum, but the  $COD_{Cr}$  removal rate is the highest at this time, which can reach 33%, which is much higher than the  $COD_{Cr}$  removal rate at the maximum specific surface area. This is because the non-calcination or the calcination time is too short, the active material is insufficiently supported on the surface of the catalyst, and the effective active material content per unit mass of the catalyst is small, and the catalyst specific surface area is large, but the  $COD_{Cr}$  removal rate is low.

If the calcination time is too long, the already formed catalyst structure is sintered and damaged due to the calcination time exceeding the limit, resulting in a decrease in the specific surface area of the catalyst, and thus an effective contact with the contaminant in a limited time is reduced, resulting in a decrease in the  $COD_{Cr}$  removal rate.

These results indicate that the calcination time of the catalyst  $CuO/CeO_2$  is not shorter or longer, and different adjustments need to be made according to actual conditions. Based on the above discussion, it was finally chosen to prepare the catalyst  $CuO/CeO_2$  with a calcination time of 3h.

# 5. Conclusion

In the experiment,  $CuO/CeO_2$  supported by  $CeO_2$  was prepared by sedimentation precipitation method. During the preparation process, the content of CuO will affect the content of CuO and the amount of  $Cu^{2+}$  dissolved and dispersed in the unit mass catalyst.

The temperature and calcination time can change the appearance and structure of the catalyst, which in turn affects the catalytic activity of the catalyst. Therefore, after investigating the influence of CuO loading, calcination time and calcination temperature on the CuO/CeO<sub>2</sub> catalyst, the best preparation conditions of the catalyst were as follows: CuO loading was 7%, calcination time was 3h, calcination temperature is 400°C, the catalyst prepared under these conditions can achieve a  $COD_{Cr}$  removal rate of 34%.

# References

- [1] Zhou L Y and Guo W 2013 J. Industrial Water Treatment **33** pp 61-64
- [2] Qiu Z M and Liu X C 2003 J. Journal of Safety and Environment 03 pp 50-53
- [3] Richter M, Fait M J G, Eckelt R, Schreier E, Schneider M, Pohl M M and Fricke R 2007 J. Appl Catal B: Environ. 73 pp 269-28
- [4] Richter M, Fait M J G, Eckelt R, Schneider M, Radnik J, Heidemann D and Fricke R 2007 J Catal. 245 pp 11-24
- [5] Zhang H T, Wang S F, Zhao X Q and Wang Y J 2004 J. Hebei Univ Technol. 33 pp 36-40
- [6] Shaikh T H, Elizaveta A, Kefu Z et al. 2018 J. Applied Surface Science 455 pp 132-143
- [7] Liu Z M, He C X, Chen B H, et al. 2017 J. Catalysis Today 297 pp 78-83
- [8] Ren J, Guo C J, Li L L and Li Z 2013 J. Chin J Catal. 34 pp 1734-1744
- [9] Ranga G R, Ranjan H S and Braja G M 2003 J. Colloids and Surfaces A: Physicochemical and Engineering Aspects 220 pp 261-269
- [10] Chen Y N and Meng M 2015 J. Chemical Industry and Engineering. **32** pp 1-5+12