

Original Research

CuO/Al₂O₃ Catalyst Preparation Conditions for Removal of Nitrobenzene by Heterogeneous Fenton-Like System

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Abstract

In order to effectively remove nitrobenzene-containing wastewater, nitrobenzene was degraded by heterogeneous Fenton system in this study. CuO/Al₂O₃ catalysts were prepared by different methods and conditions. The characteristics of CuO/Al₂O₃ were analyzed by BET, X-ray diffraction (XRD) and scanning electron microscope (SEM). Among them, the specific surface area, pore volume and pore size of CuO/Al₂O₃ were characterized by BET; the phase and crystallinity of the CuO/Al₂O₃ were determined by XRD; the surface morphology of the CuO/Al₂O₃ was observed by SEM. Nitrobenzene concentration was determined by HPLC. The nitrobenzene-containing wastewater was degraded by a heterogeneous Fenton-Like system catalyzed with prepared CuO/Al₂O₃. The results showed that the optimal preparation method of the catalyst was the deposition precipitation method. The optimal conditions of the catalyst were as follows: the loading content of CuO was 5%, the calcination temperature of CuO was 400°C, the calcination time of CuO was 3 h, and the calcination temperature of Al₂O₃ carrier was 400°C. The removal rate of nitrobenzene reached 84.37% under this condition. This study shows that the nitrobenzene could be effectively degraded in a heterogeneous Fenton-like system catalyzed by CuO/Al₂O₃.

Keywords: CuO/Al₂O₃ catalyst, heterogeneous Fenton-like system, nitrobenzene, preparation method, wastewater

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Introduction

Nitrobenzene is a highly toxic substance with a relatively stable chemical structure [1-3]. It is one of the difficult biodegradable organic matters. In recent years, Fenton technology has been widely used to remove nitrobenzene. However, the response range of pH is limited in the traditional homogeneous Fenton system ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) [4-5]. Meanwhile the required amount of Fe^{2+} is large and it is easy to be lost, then the effluent color is deep and the subsequent sludge production is difficult to treat [6-8]. In order to solve the above problems, the researchers put more focus on the multi-phase Fenton technology. And development of new catalysts and optimization of reaction conditions become a hot topic [9-11].

Regarding copper as a heterogeneous catalyst, catalytic performance is good and cost is low. A previous study found that $\gamma\text{-Cu}/\text{Al}_2\text{O}_3$ has a good degradation effect on aromatic organic pollutants [12-15]. But it has been limited in water treatment processes due to the longer reaction time, the larger amount of copper dissolved and the H_2O_2 . Aluminum is an active metal. When aluminum is exposed to air, an oxide film with a thickness of about 0.5 nm is formed on the surface, protecting the metal aluminum from further corrosion [16-18]. Aluminum is very soluble in strong alkali, and also soluble in dilute acid. In the heterogeneous catalysts production process, alumina as a carrier to participate has excellent effects. The type of γ -alumina is with a large specific surface area and high porosity, so it has good adsorption capacity. In the industry, γ -alumina is often used as a carrier in the production of a catalyst [12].

Preparation methods of catalysts mainly contain deposition precipitation, co-precipitation and equal volume impregnation [19-20]. The deposition precipitation method is to add a metal solution to a suspension of a carrier (usually a metal oxide particle), and to form a uniformly mixed suspension under stirring. While controlling the pH of the solution, the metal element of interest is supported on the carrier. According to the experience of previous researchers, this method could usually produce a catalyst with a large specific surface area [21]. The co-precipitation method means that at least two kinds of cations are contained in the solution. They are uniformly distributed in the solution, and a precipitating agent is added for precipitation reaction. Thereby a uniform precipitation of various components are obtained. The equal volume impregnation method first mixes sodium carbonate solution, sodium lauryl sulfate and aluminum chloride solution. Then a carrier is obtained by sedimentation, filtration, washing, drying, calcinations and so on [22].

In this study, $\text{CuO}/\text{Al}_2\text{O}_3$ catalysts were prepared by the above-mentioned three methods. Combined with the degradation efficiency of nitrobenzene in a Fenton-Like system, the optimal preparation method of the catalyst

was selected. Under this condition, the impact factors during the preparation of the catalyst were studied. The optimal production conditions of the $\text{CuO}/\text{Al}_2\text{O}_3$ catalyst were obtained according to the characterization results of the technology and the degradation efficiency of the nitrobenzene.

Material and Methods

Nitrobenzene was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. $\text{CuO}/\text{Al}_2\text{O}_3$ catalysts were prepared by deposition precipitation, co-precipitation and equal volume impregnation. Then the CuO loading content, CuO calcination temperature, CuO calcination time, and the Al_2O_3 carrier calcination temperature during the preparation of the catalysts were investigated.

Specific surface area, pore volume and pore size distribution of $\text{CuO}/\text{Al}_2\text{O}_3$ were characterized by BET under the condition of liquid nitrogen temperature and pretreated to a pressure of 1×10^{-4} Pa at 120°C . The crystal structure of $\text{CuO}/\text{Al}_2\text{O}_3$ catalysts was determined by X-ray diffraction (XRD), while Cu targeted $\text{K}\alpha$, the target voltage and current were 40 kV and 40 mA, respectively. The surface morphology of $\text{CuO}/\text{Al}_2\text{O}_3$ catalysts was measured on a scanning electron microscope (SEM) under the condition of 20 kV accelerating voltage, 10 mm working distance, and 5000 times magnification. Nitrobenzene concentration was determined by HPLC.

Results and Discussion

Effect of Preparation Methods on Characteristics of $\text{CuO}/\text{Al}_2\text{O}_3$ and Degradation Efficiency of Nitrobenzene in a Fenton-Like System

In general, the catalytic activity of a catalyst is related to the specific surface area. Larger specific surface area can provide more active reaction centers for catalytic reactions. Then the degradation efficiency of pollutants could be improved. The specific surface area, pore volume and pore size of $\text{CuO}/\text{Al}_2\text{O}_3$ under three different preparation methods are shown in Table 1.

As can be seen from Table 1, the effect of preparation methods on specific surface area, pore volume and pore size of $\text{CuO}/\text{Al}_2\text{O}_3$ were significant. The specific surface area, pore volume and pore size of $\text{CuO}/\text{Al}_2\text{O}_3$ prepared by deposition precipitation method were $333 \text{ m}^2/\text{g}$, $0.19 \text{ cm}^3/\text{g}$ and 2.55 \AA , respectively. The specific surface area under deposition precipitation was largest among three preparation methods. The pore volume and pore size under deposition precipitation were smallest, which may be related to the change of the pore structure of the carrier caused by the secondary calcinations during sample preparation process. The pore size distributions of three preparation methods were similar. The most suitable apertures were 1.5 to 2.5 nm.

X-ray is a common means of material characterization that allows analysis of the crystalline structure and phase of a material [23-25]. As can be seen from Fig. 1a), all samples have 4 distinct Al₂O₃ diffraction peaks at 28.2°, 35.5°, 48.6° and 66.7°. Meanwhile, the diffraction peak of CuO might be at 38.8° and 61.5°, which was fine and diffuse. Other diffraction peaks were not observed, implying that no new substance was produced during the catalytic process. In addition, the intensities of diffraction peaks under different precipitation methods were different, indicating that the CuO/Al₂O₃ catalysts prepared by different methods have different extents of crystallization.

It can be seen that the surface morphology of the catalyst prepared by different methods was very different (Fig. 2). Under deposition precipitation and equal volume impregnation conditions, the surface morphology of the catalysts was irregular, but relatively smooth. And the crystal shape was obvious. The dispersion of CuO particles was good, which is beneficial to the improvement of degradation efficiency. The catalyst prepared by the co-precipitation method failed to form a distinct and regular crystal structure, which was mainly in the presence of an amorphous phase due to the mixing of CuO and Al₂O₃. This result was consistent with the diffused diffraction peak of

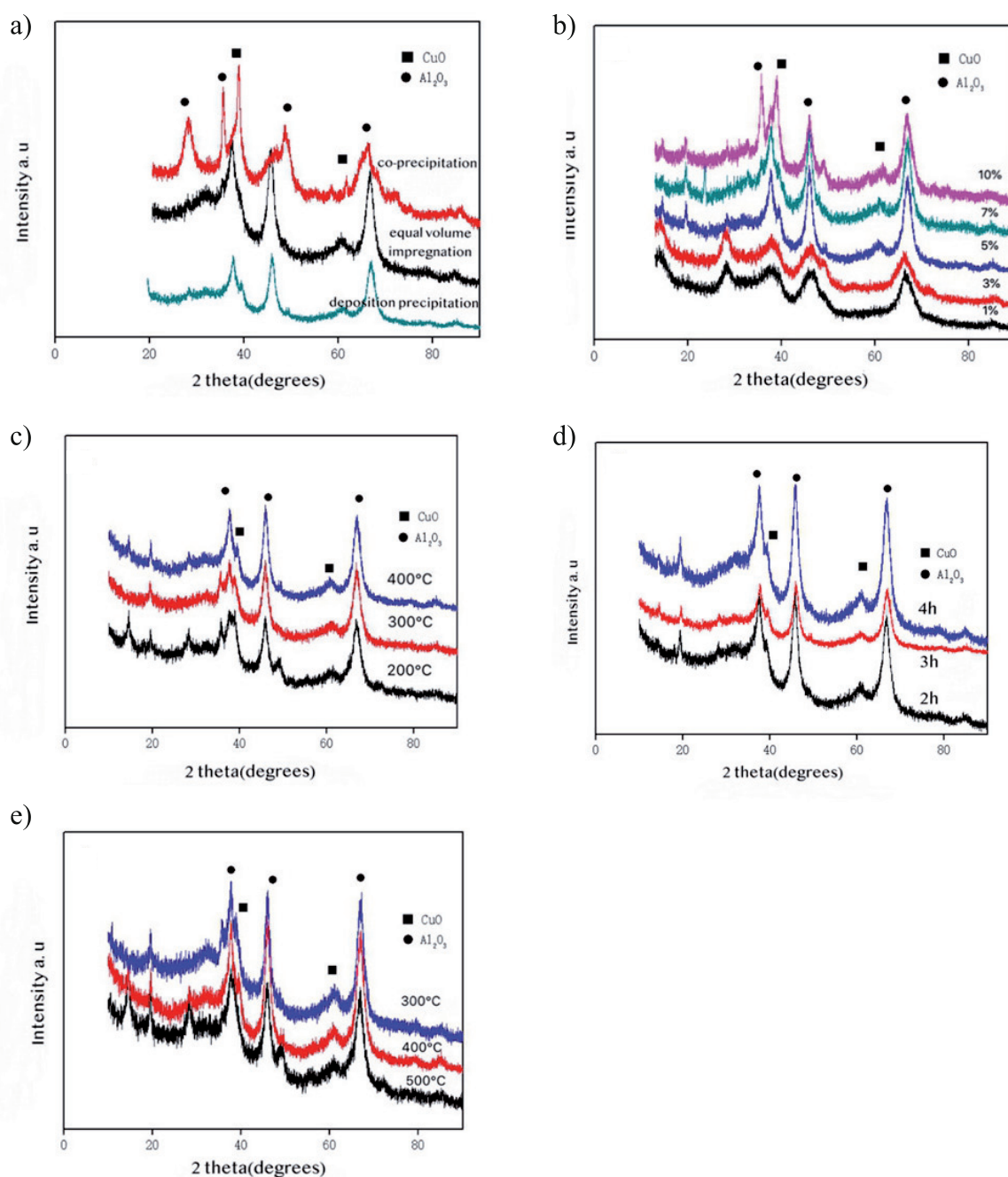


Fig. 1. Effect of preparation methods a), CuO loading content b), CuO calcination temperature c), CuO calcination time d) and Al₂O₃ calcination temperature e) on X-ray diffraction patterns of CuO/Al₂O₃.

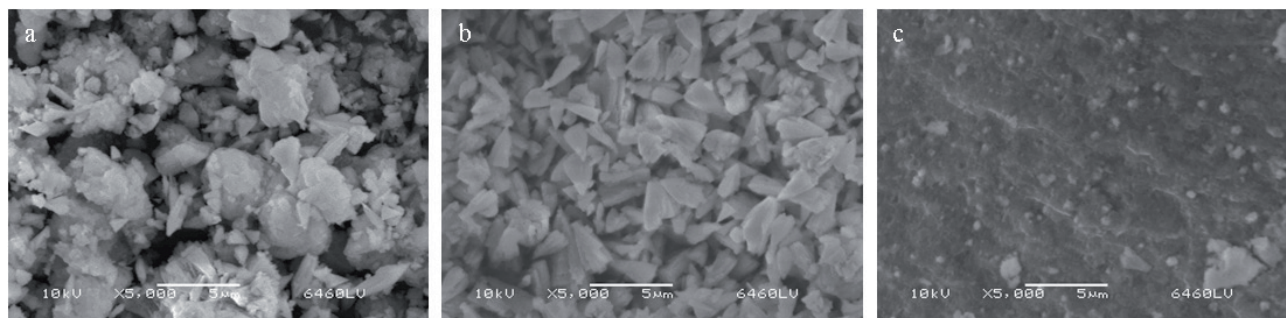


Fig. 2. Effect of preparation methods on SEM of $\text{CuO}/\text{Al}_2\text{O}_3$ (a. deposition precipitation; b. equal volume impregnation; c. co-precipitation).

Al_2O_3 . At the same time, CuO was encapsulated in the Al_2O_3 bulk phase and could not be used for the catalytic reaction.

Control of experimental conditions: the reaction temperature was 25°C , the dosage of the catalyst was 500 mg/L , the dosage of H_2O_2 was 25 mmol/L , the concentration of nitrobenzene was 10 mg/L , the initial pH was 6, and the reaction time was 180 min. The catalysts prepared by different methods were investigated for their effects on the degradation of nitrobenzene. The

results are shown in Fig. 3a). The effect of preparation methods on nitrobenzene degradation efficiency was significant. The removal efficiency of nitrobenzene by catalysts prepared by deposition precipitation method could reach 84.37%. While the removal rates of the equal volume impregnation method and the co-precipitation method were 57.82% and 45.05%, respectively. This phenomenon corresponded to the largest specific surface area, obvious crystal form, high degree of regularity, smooth catalyst surface and good dispersion degree of

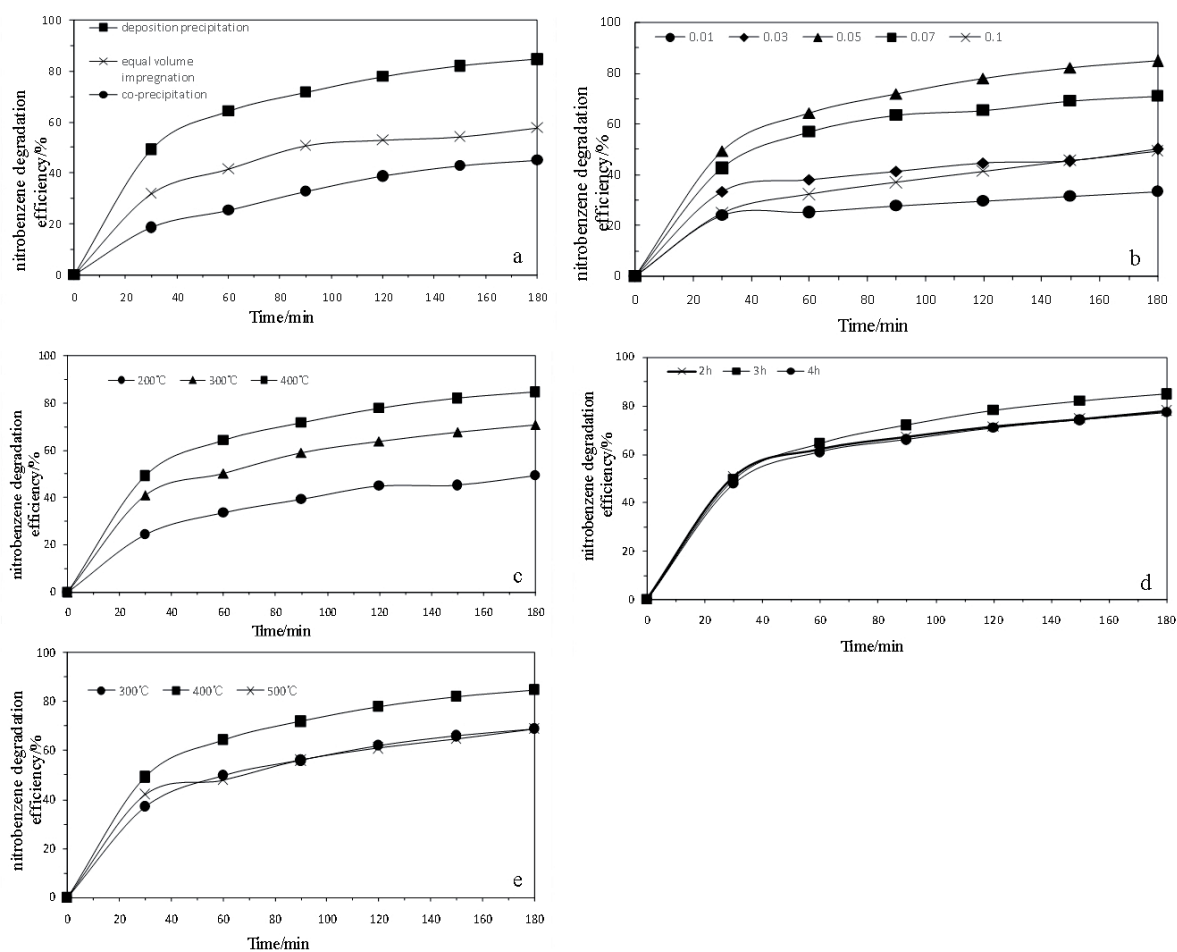


Fig. 3. Effect of preparation methods a), CuO loading content b), CuO calcination temperature c), CuO calcination time d) and Al_2O_3 calcination temperature e) on nitrobenzene degradation efficiency.

Table 1. Effect of preparation methods, CuO loading content, CuO calcination temperature, CuO calcination time and Al₂O₃ calcination temperature on specific surface area, pore volume and pore size of CuO/Al₂O₃ by BET.

		Specific surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (Å)
Preparation methods	Deposition precipitation	333	0.19	2.55
	Co-precipitation	252	0.41	5.43
	Equal volume impregnation	286	0.22	3.11
CuO loading content	1%	345	0.36	1.02
	3%	339	0.35	2.26
	5%	333	0.19	2.55
	7%	325	0.18	3.21
	10%	307	0.15	4.26
CuO calcination temperature	200°C	341	0.21	3.51
	300°C	332	0.20	3.55
	400°C	333	0.19	2.55
CuO calcination time	2 h	254	0.24	3.68
	3 h	333	0.19	2.55
	4 h	284	0.22	3.35
Al ₂ O ₃ calcination temperature	300°C	337	0.20	3.03
	400°C	333	0.19	2.55
	500°C	260	0.20	3.07

the catalyst prepared by the deposition precipitation method [26-27]. In summary, the best preparation method for the catalyst was the deposition precipitation method.

Effect of CuO Loading Content on Characteristics of CuO/Al₂O₃ and Degradation Efficiency of Nitrobenzene in a Fenton-Like System

The CuO/Al₂O₃ catalyst was prepared by deposition precipitation method. In order to investigate the influence of CuO loading content, the CuO loading content was 1%, 3%, 5%, 7% and 10%, respectively.

It can be seen from Table 1 that as the CuO content increased, the specific surface area of the catalyst decreased. The reason might be that the increase of CuO content aggregated in the catalyst, resulting in the crystal grain size became larger. At the same time, the pore volume of the catalyst became smaller with the increase of CuO content, because the pores were blocked by the CuO content.

As can be seen from Fig. 1b), when the loading content of CuO increased, the diffraction peak of CuO gradually became sharp and the peak shape was notable. When the loading content of CuO was less than 5%, the diffraction peak of CuO was not obvious. The 28.2°, 35.5°, 48.6° and 66.7° diffraction peaks were the peaks of Al₂O₃. While the CuO loading content was

more than 5%, the CuO diffraction peaks at 38.8° and 61.5° became relatively obvious and sharp, indicating that the crystal form of the catalyst was significant and the crystal grain size became larger. This phenomenon was consistent with the results detected by BET. The diffraction peaks were all peaks of CuO and Al₂O₃, no new phase was formed.

As shown in Fig. 4, the surface morphology of the catalysts changed with the increase of CuO content. Among them, the catalysts with CuO content of 5% and 7% had a smooth surface, good crystallization effect, low degree of regularity and good dispersion, which was beneficial to the improvement of catalytic performance. While the CuO content reached 10%, the particle size of CuO/Al₂O₃ catalyst was larger than in other catalysts, and the degree of regularity was high, which was not conducive to catalytic oxidation performance.

As can be seen from Fig. 3b), when the CuO contents were 1%, 3%, 5%, 7%, and 10%, the nitrobenzene degradation efficiencies were 33.26%, 49.91%, 84.73%, 70.7%, and 49.2%, respectively. The nitrobenzene degradation efficiencies reached the maximum when the CuO content was 5%. When the CuO content was less than 5%, the degradation efficiency increased as it increased. The reason may be that when the CuO content increased, the active component of the catalyst also increased, which was beneficial to the degradation reaction [28]. When the

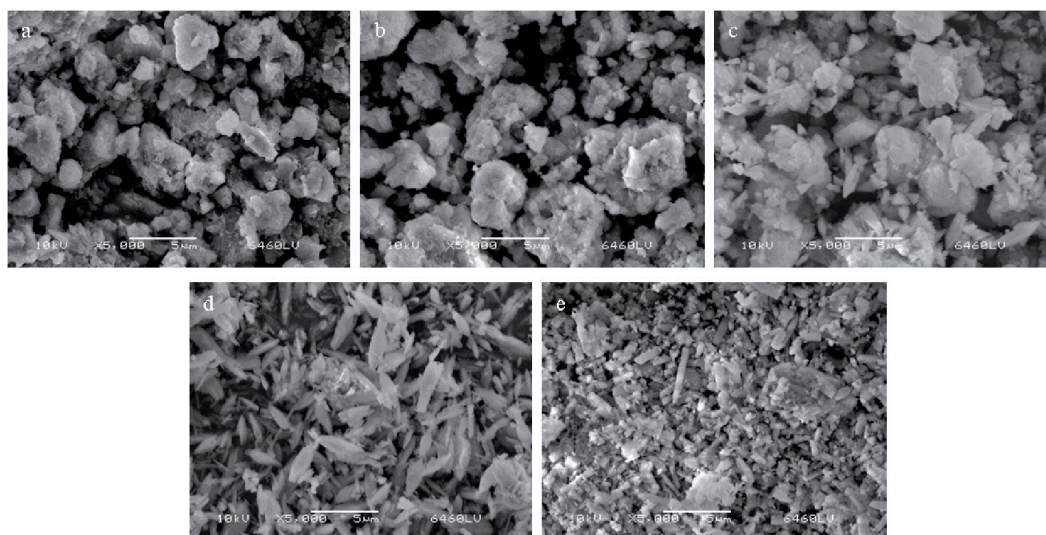


Fig. 4. Effect of CuO loading content on SEM of CuO/Al₂O₃: a) 1% CuO; b) 3% CuO; c) 5% CuO; d) 7% CuO; e) 10% CuO.

CuO content was higher than 5%, the degradation efficiency showed a downward trend, mainly because the surface of the catalyst was in a massive structure, and agglomeration occurred. That was not conducive to the catalysis reaction. At the same time, the specific surface area was getting smaller and smaller, and the active center required for the reaction to proceed was also reduced, which was also a disadvantage to the degradation reaction. Based on the above results, the optimal CuO loading content should be 5%.

Effect of CuO Calcination Temperature on Characteristics of CuO/Al₂O₃ and Degradation Efficiency of Nitrobenzene in a Fenton-like System

The CuO/Al₂O₃ catalyst was prepared by deposition precipitation method. In order to investigate the influence of CuO calcination temperature, the CuO calcination temperature was 200°C, 300°C and 400°C, respectively.

When the calcination temperature of CuO was 200°C, 300°C and 400°C, the specific surface area was 341 m²/g, 332 m²/g and 333 m²/g, respectively (Table 1). Correspondingly, the pore volume was almost 0.20 cm³/g

in three calcination temperatures of CuO. In general, the pore volume was not much different in value. When the calcination temperature of CuO was 200°C and 300°C, the pore size was equivalent. However, the pore size dropped significantly while the calcination temperature of CuO was 400°C.

As shown in Fig. 1c), the phases exhibited by the catalysts were CuO and Al₂O₃. When the calcination temperature of CuO was 200°C, the peaks were weak and the distribution was relatively dispersed, indicating that the catalyst had no good catalytic performance. As the calcination temperature of CuO increased, the diffraction peaks became sharp and obvious, indicating that the crystal shape of the catalysts was obvious with the increase of temperature.

As shown in Fig. 5, the effect of CuO calcination temperature on the surface morphology of the catalysts was significant. The surface of the catalysts prepared at 200°C and 300°C was relatively rough, unevenly distributed, and poorly crystallized, while the surface morphology prepared at 400°C was relatively smooth and the surface particle size was uniform. These phenomenon exhibited a loose structure, a low degree of regularity, and good dispersion. This was good for catalytic performance.

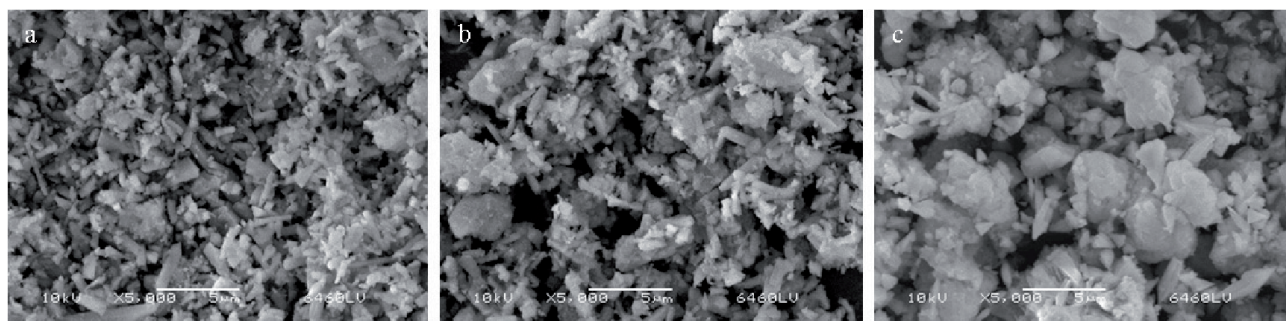


Fig. 5. Effect of CuO calcination temperature on SEM of CuO/Al₂O₃: a) 200°C; b) 300°C; c) 400°C.

In the process of preparing the catalyst, it is necessary to thermally decompose the compound by high-temperature calcination, removing impurities and moisture. Then the active component was retained, forming large specific surface area and crystal catalyst. In this study, the CuO/Al₂O₃ catalysts, prepared at different CuO calcination temperatures, were combined with H₂O₂ to form a heterogeneous Fenton system to degrade the nitrobenzene.

Fig. 3c) shows that when the CuO calcination temperatures were 200°C, 300°C and 400°C, the corresponding degradation efficiencies were 49.32%, 70.82% and 84.73%, respectively. The degradation efficiencies tended to increase as CuO calcination temperature increased. This was consistent with the characterization results of poor crystal shape, rough surface, dispersibility and low degree of regularity under lower CuO calcination temperatures. According to the analysis of the characterization results and the degradation efficiencies, the optimum calcination temperature of CuO was 400°C.

Effect of CuO Calcination Time on Characteristics of CuO/Al₂O₃ and Degradation Efficiency of Nitrobenzene in a Fenton-like System

The CuO/Al₂O₃ catalyst was prepared by deposition precipitation method. In order to investigate the influence of CuO calcination time, the CuO calcination time was 2 h, 3 h and 4 h, respectively.

As shown in Table 1, the specific surface area of CuO/Al₂O₃ catalyst was up to 333 m²/g as the CuO calcination time was 3 h. When the calcination times were 2 h and 4 h, the specific surface areas were 254 m²/g and 284 m²/g, respectively. Under different CuO calcination times, the values of pore volume were similar, which were 0.24 cm³/g, 0.19 cm³/g and 0.22 cm³/g, respectively. While the pore size decreased to 2.55 Å when the CuO calcination time was 3 h.

Fig. 1d) shows that all of the diffraction peaks with different CuO calcination times were very sharp, indicating that the crystals and their dispersions were good. The XRD patterns of the catalysts were similar. The peaks were the diffraction peaks of CuO and Al₂O₃, indicating that no new phase was formed.

The SEM characterization results for the three catalysts with different CuO calcination times are shown in Fig. 6. The surface morphology of the catalysts was relatively rough under the conditions of 2 h and 4 h calcination times, while the surface morphology was relatively smooth when the calcination time was 3 h. All the catalysts of different CuO calcination times were with obvious crystal forms, good dispersion and low degree of regularity. It can be seen from the characterization results of BET, XRD and SEM that the catalytic performance of different CuO calcination times was very good. When the CuO calcination time was 3h, catalytic performance was the best.

As can be seen from Fig. 3d), when the calcination time increased from 2h to 4h, the nitrobenzene degradation efficiency first increased and then decreased. The degradation efficiency of nitrobenzene increased to a maximum of 84.37% as the CuO calcination time was 3 h. When the CuO calcination times were 2 h and 4 h, the nitrobenzene degradation efficiency was identical. The degradation efficiency increased when the calcination time was less than 3 h, indicating that an increase in calcination time contributed to an improvement in catalytic performance. However, when the calcination time exceeded 3 h, the removal rate of nitrobenzene decreased. The reason may be that when the calcination time was too long, the surface of the catalyst appeared to be charred [29-32]. This phenomenon was not conducive to the catalytic performance of the catalyst. Comprehensive characterization results and nitrobenzene degradation efficiency ensured that the best CuO calcination time was 3 h.

Effect of Al₂O₃ Calcination Temperature on Characteristics of CuO/Al₂O₃ and Degradation Efficiency of Nitrobenzene in a Fenton-like System

The CuO/Al₂O₃ catalyst was prepared by deposition precipitation method. In order to investigate the influence of Al₂O₃ calcination temperature, the Al₂O₃ calcination temperature was 300°C, 400°C and 500°C, respectively.

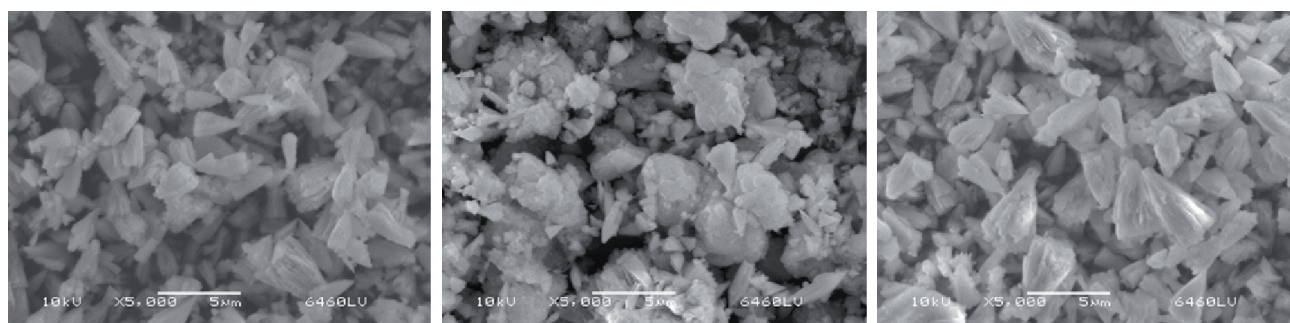


Fig. 6. Effect of CuO calcination time on SEM of CuO/Al₂O₃: a) 2 h; b) 3 h; c) 4 h

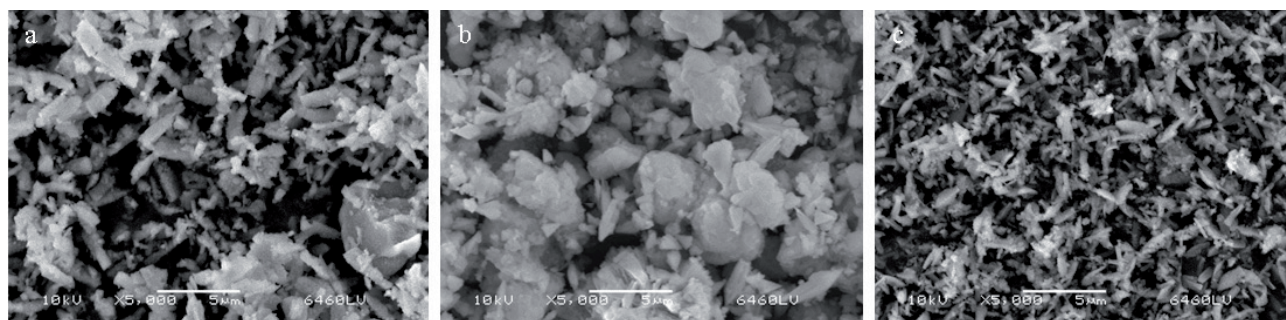


Fig. 7. Effect of Al_2O_3 calcination temperature on SEM of $\text{CuO}/\text{Al}_2\text{O}_3$: a) 300°C; b) 400°C; c) 500°C.

As shown in Table 1, when the calcination temperatures of Al_2O_3 were 300°C, 400°C and 500°C, the specific surface areas of the catalysts were 337 m^2/g , 333 m^2/g and 260 m^2/g , respectively. The specific surface area decreased as the Al_2O_3 calcination temperature increased. However, the change of the calcination temperature of Al_2O_3 had little effect on the pore volume and pore size of the $\text{CuO}/\text{Al}_2\text{O}_3$ catalyst.

The XRD characterization results were as shown in Fig. 1e). The Al_2O_3 calcination temperature had a certain effect on the XRD characterization of the catalyst. When the calcination temperature of Al_2O_3 was 300°C, 400°C and 500°C, all of the peak shapes were sharp, indicating that the crystallization effect of the three conditions were good. When the Al_2O_3 calcination temperatures were 300°C and 400°C, the CuO characteristic peaks of the catalyst were stronger and narrower. Simultaneously, the grain size was also larger. This was consistent with the BET results.

The SEM results can be seen from Fig. 7 that the effect of Al_2O_3 calcination temperature on surface morphology of the catalyst was significant. When the Al_2O_3 calcination temperature was 300°C and 500°C, the surface morphology of the catalyst was relatively rough. Meanwhile, the catalyst surface was unevenly dispersed and had a high degree of regularity as the Al_2O_3 calcination temperature was 300°C. When the Al_2O_3 calcination temperature was 400°C, the surface morphology of the catalyst was smooth, the dispersion was high, and the degree of regularity was low and showing good catalytic performance. This was consistent with the BET and XRD results.

As can be seen from Fig. 3e), when the Al_2O_3 calcination temperatures were 300°C, 400°C and 500°C, nitrobenzene degradation efficiencies were 69.32%, 84.37% and 69.54%, respectively. Under 300°C and 500°C Al_2O_3 calcination temperatures, the nitrobenzene degradation curves were similar and consistent with the similar characteristics result of $\text{CuO}/\text{Al}_2\text{O}_3$ catalysts. When the calcination temperature of the Al_2O_3 carrier was 400°C, the degradation efficiency of nitrobenzene increased to 84.37%. Therefore, based on the above characterization results and the degradation efficiency of nitrobenzene, the optimal Al_2O_3 calcination temperature was 400°C.

During the process of nitrobenzene degradation, phenols, aniline and organic substances with the amino-group were the main intermediate products [33]. At the end of the reaction, some light molecular substances such as ester organics were the final products [33].

Conclusions

A $\text{CuO}/\text{Al}_2\text{O}_3$ catalyst was prepared by different methods and conditions. The characteristics of $\text{CuO}/\text{Al}_2\text{O}_3$ catalyst were analyzed by BET, XRD and SEM. At the same time, using the prepared catalyst and H_2O_2 to form a heterogeneous Fenton-like system, the nitrobenzene-containing wastewater was degraded. The optimal preparation conditions were as follows: the optimal preparation method of the catalyst was deposition precipitation, the loading content of CuO was 5%, the calcination temperature of CuO was 400°C, the calcination time of CuO was 3 h, and the calcination temperature of Al_2O_3 was 400°C. The removal efficiency of nitrobenzene reached 84.37% under optimal conditions. These results show that $\text{CuO}/\text{Al}_2\text{O}_3$ is an effective catalyst for the removal of nitrobenzene in a heterogeneous Fenton-like system.

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Conflict of Interest

The authors declare no conflict of interest.

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