Study on catalyst stability based on morphology and structure characterization

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Abstract. In this experiment, the dissolution concentration of metal ions, SEM, TEM, and XRD were used as the stability evaluation index of the catalyst, and the activity and stability of the catalyst were further comprehensively evaluated. The catalyst Pd-catalyst was used to treat simulated printing and dyeing waste-water by CWAO method. The results shows that the morphology and structure of the Cu-Fe-Pd-La/γ-Al₂O₃ (ratio 1:1:1:3) catalyst do not change significantly before and after the CWAO reaction, indicating that the experimentally prepared Pd-catalyst has better stability.

1. Introduction

Treatment of printing and dyeing waste-water is a big problem in today's sewage treatment industry. The composition of printing and dyeing waste-water is complex, high in concentration, and high in color. With the development of the fine chemical industry, especially in recent years, the improvement of people's living standards and the upgrading of the pursuit of beauty have greatly improved the output and quality of textiles. The use of dyes is developing in the direction of anti-photolysis, anti-oxidation and anti-biodegradation, resulting in more and more serious environmental pollution of printing and dyeing waste-water [1-2]. However, as the country's requirements for waste-water discharge indicators become higher and higher, the traditional physical, biochemical, physicochemical, and general chemical methods cannot meet the treatment requirements of printing and dyeing waste-water [3]. For the above-mentioned treatment methods of printing and dyeing waste-water, the filtration method, precipitation method and air flotation method in the physical method mainly remove particulate suspended matter and easily sinkable impurities. The adsorption method cannot remove hydrophobic dyes in water, while the membrane separation method has no good effect on soluble dyes. The biochemical method has a poor effect on decolorization and difficult-to-biochemical substances.

In the physicochemical method, the chemical coacervation method generates a large number of secondary pollutants, the electrocoagulation method has low processing efficiency and there is a problem of electrode passivation; and the oxidation efficiency of ozone oxidation, Fenton reagent oxidation and photocatalytic oxidation is low.

Catalytic wet oxidation is an advanced oxidation method for treating high-concentration refractory organic waste-water [4]. Japan, the United States, and the European Union countries have done a lot of research work on the treatment of organic waste-water by CWO and have industrial-scale applications [5], but China has relatively little research in this area. In the existing CWO technology for treating printing and dyeing waste-water, there is a secondary pollution problem in which a large amount of
metal is lost. Studying the stability of CWAO catalysts has important theoretical and practical significance.

2. Experimental part

2.1. Experimental materials
Research object: Experimental object
Catalyst: Supported four-component catalyst, Cu-Fe-Pd-La/Al₂O₃.
Reagents: palladium chloride solution, copper nitrate, iron nitrate, lanthanum nitrate, etc.
Water sample: Methyl orange aqueous solution with COD₄ concentration of 2000 mg/L.

2.2. Characterization of catalyst
Morphology: Scanning Electron Microscopy (SEM). In order to determine the effect of the preparation process on the catalyst performance, the surface morphology of the catalyst was characterized by German ZEISS Uriga FIB-SEM scanning electron microscope (SEM).
Structural Characterization: (1) X-Ray Diffraction Analysis (XRD), conducted by Japan Rigaku D/max-RB X-ray Diffraction (XRD), at 40 kV voltage, 100 mA current, and 6 °/min scan rate, reveals the crystal phase structure, particle size, and cell parameters of the catalyst, which is convenient for further analysis of the structure and composition of the catalyst. (2) Thermogravimetric-differential thermal analysis (TG-DTA), using Japan Seiko EXSTAR-7000 synchronous thermal analyzer (TG-DTA), carrying samples in Al₂O₃ crucibles to study the thermal stability of the catalyst; The analysis of TG-DTA is based on the mass change of the catalyst precursor at 0–950 °C to infer the factors such as the loss of water in the catalyst precursor, the decomposition of metal salts, the further decomposition of metal oxides, the collapse of the skeleton, etc. The above factors provides a basis for determining the calcination temperature for the preparation of the catalyst.
Stability Characterization: ICP-OES is an inductively coupled plasma emission spectrometer, which can be used for the qualitative and quantitative analysis of more than 70 metal elements and some non-metal elements in samples.

3. Results and discussion

3.1. Recyclability of the catalyst
In the first and second applications of the catalyst Cu-Fe-Pd-La/γ-Al₂O₃ (ratio 1:1:1:3), simulated printing and dyeing waste-water with a COD₄ of 2000 mg/L. At 90 minutes of the CWAO reaction, The data are showed in Figure 1 and Figure 2.

![Figure 1. Decolorization rate of waste-water in first and second use.](image-url)
It can be seen from the data in Figure 1 and Figure 2 that in the first and second application of the catalyst, the decolorization rate of the waste-water differs by about 0.5 %, and the COD difference is about 0.55 %. It can be seen that the catalyst was relatively stable, and the catalyst in repeated use had good stability.

3.2. ICP Characterization
In an attempt to investigate the stability of each element in the Cu-Fe-Pd-La/γ-Al₂O₃ catalyst composition, simulated water samples are processed at a reaction temperature of 180 °C, an oxygen partial pressure of 2.5 MPa, and a catalyst amount of 4 g/L. The dissolution concentration of the metal ions in the treated effluent for 90 minutes is measured and the results are showed in Figure 3.

It can be seen from Figure 3 that the stability of the element Fe is relatively poor, and the stability of Cu is relatively good. At a reaction time of 90 minutes, the concentration of Cu in the waste-water is about 0.4 mg/L.
3.3. SEM and TEM characterizations of catalysts

In this set of experiments, the optimally prepared Cu-Fe-Pd-La/γ-Al$_2$O$_3$/550 °C catalysts are used to investigate their stability before and after use. The SEM photos of Cu-Fe-Pd-La/γ-Al$_2$O$_3$ catalyst before and after use are showed in Figure 4 (a)-(b); The TEM photos of Cu-Fe-Pd-La/γ-Al$_2$O$_3$ catalyst before and after use are showed in Figure 5 (a)-(b):

![SEM photos of Cu-Fe-Pd-La/γ-Al$_2$O$_3$ catalyst before and after reaction](image1)

Figure 4. SEM photos of Cu-Fe-Pd-La/γ-Al$_2$O$_3$ catalyst before and after reaction

![TEM photos of Cu-Fe-Pd-La/γ-Al$_2$O$_3$ catalyst before and after reaction](image2)

Figure 5. TEM photos of Cu-Fe-Pd-La/γ-Al$_2$O$_3$ catalyst before and after reaction

As can be seen from Figure 4 above, the reduction in catalyst activity is not very obvious before and after calcination. From the SEM photos of the catalyst before and after use, the morphology of the catalyst do not change much, which also showed that the optimally prepared Cu-Fe-Pd-La/γ-Al$_2$O$_3$ catalyst had good stability.

According to Figure 5, the size of catalyst particles ranged from 10 to 20 nm by zooming in the TEM image of 20 000 times, and the concentration of catalyst nanoparticles existed before use, and the particle distribution of catalyst was relatively uniform after reaction. However, there was no
significant difference in TEM photographs of the catalyst before and after the reaction, which indicated that the catalyst was highly stable.

3.4. XRD analysis of catalyst
The XRD patterns of the Cu-Fe-Pd-La/γ-Al₂O₃ catalyst before and after the reaction are showed in Figure 6 below.

![Figure 6. XRD patterns of Cu-Fe-Pd-La/γ-Al₂O₃ catalyst before and after reaction.](image)

Each peak in Figure 6 has its corresponding crystal phase structure, and from this, the composition of the substance can be inferred. It has been reported that the 2θ of the three strongest diffraction lines of the standard CuO is located at 35.6°, 38.8°, and 48.7°, and the 2θ of the two strongest diffraction lines of the standard CuAl₂O₄ are located at 31.4° and 36.9°. The above can be used as evidence for the existence of CuO and CuAl₂O₄ phases in the sample. The diffraction peak of CuO in the figure is clear; and the catalyst generally exists in the form of γ-Al₂O₃. As can be seen in the figure, the catalyst Cu-Fe-Pd-La/γ-Al₂O₃ has a peak at about 27° after use. The corresponding substance of the peak is Fe₂O₃, indicating that Fe is unstable, while the rest of the peak positions are basically the same, indicating that the catalyst has strong stability.

4. Conclusion
The experiment investigated the stable performance of supported catalyst Cu-Fe-Pd-La/γ-Al₂O₃ (ratio 1:1:1:3) in the treatment of printing and dyeing waste-water by CWAO method. The results showed that in the first and second use of the catalyst, the decolorization rates of the waste-water were 97.92% and 97.85%, and the COD removal rates were 84.72% and 84.16%, respectively. The morphology and structure of the catalyst did not change significantly. It can be seen that Pd-catalyst has better stability.

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