PREPARATION OF A METAL COORDINATION POLYMER BASED ON A CARBOXYLIC ACID LIGAND AND ITS CATALYTIC PERFORMANCE RESEARCH

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This paper briefly presents metal coordination polymers based on carboxylic acid ligands. A cerium-ferrocene-based coordination polymer was prepared using 1, 1-ferrocenedicarboxylic acid and cerium nitrate. After characterization tests of the product, factors affecting photocatalytic reduction performance in CO2 photocatalytic reduction were tested using the product as catalysts. The results showed that the prepared product was a cerium-ferrocene-based coordination polymer with sufficient phase purity. The maximum yield of the photocatalytic reduction product CO was achieved when the temperature in the CO2 photocatalytic reduction reaction was 10 ° C, the dosage of the catalyst (preparation product) was 10 mg, the dosage of the sacrificial agent (triethanolamine vs. dimethylaniline: 1:9) was 5 mL, and the dosage of the photosensitizer (ruthenium bipyridine) was 32 mmol.

Keywords: Carboxylic acid, coordination polymer, photocatalytic reduction, metal

1. Introduction

Among all kinds of organic ligands, carboxylic acid ligands have become one of the most commonly used and successful ligand types for constructing coordination polymers due to their excellent coordination ability, structural diversity, and chemical stability [1,2,3]. Carboxylic acid groups can coordinate with metal centers through their monopentate, bicentate, and multidentate modes to form stable coordination bonds and construct rigid or flexible skeletons [4]. In addition, carboxylic acid ligands can also adjust the pore size and surface properties of polymer materials by introducing other functional groups. Catalysts are an important component of the chemical industry, involving key areas such as energy conversion, environmental protection, and fine chemical synthesis [5]. Conventional homogeneous catalysts have high activity but are difficult to separate after use, leave a lot of residue, and have a low reuse rate, while heterogeneous catalysts are easy to recover after use but have low catalytic activity. Metal-coordinated polymers based on carboxylic acid ligands have catalytic performance and ease of use between homogeneous and heterogeneous catalysts due to their

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structural advantages [6]. However, the catalytic performance of coordination polymers depends on their structure and synthesis method. Appropriate metal sources, carboxylic acid ligands, and topological structure can effectively enhance the performance of coordination polymers. Hu et al. [7] designed and synthesized non-noble metal coordinated hypercrosslinked polymers based on porphyrin, characterizing them, and then testing their performance as electrocatalysts for oxygen evolution reactions. Socha et al. [8] synthesized dinuclear two-dimensional metal-organic framework Ag(I) complex of 4-amino-N-pyridin-2yl-benzenesulfonamide (Ag-sprd) and characterized it using ^{1}H-NMR, FT-IR, and single-crystal X-ray diffraction analysis. Yao et al. [9] constructed a novel Ir-based single-metal-site catalyst for efficient hydroformylation of propylene with CO through coordination polymerization between zirconium and triphenylphosphine derivatives with carboxyl functional groups. In this article, a brief introduction to metal-coordination polymers based on carboxylic acid ligands was presented, followed by the preparation of the cerium-ferrocene-based coordination polymer using 1, 1-ferrocenediformic acid and cerium nitrate. The photocatalytic reduction performance of the product was tested after characterization tests.

2. Case analysis

2.1 Materials and equipment

Reagents used included 1, 1-ferrocenediformic acid (Sigma-Aldrich (Shanghai), China), cerium nitrate (Shanxi Jugong Chemical Co., Ltd., China), ethanol (Suzhou Qianlixing Chemical Co., Ltd., China), deionized water (Shenzhen Jianghui Environmental Protection Technology Co., Ltd., China), triethanolamine (Zibo Haijie Chemical Co., Ltd., China), dimethylaniline (DMA) (Sigma-Aldrich (Shanghai), China), and ruthenium bipyridine (Yunnan Hongsheng Platinum Industry New Material Technology Co., Ltd., China).

Equipment used included high-pressure reactor (Jiangsu Jiangnan Pharmaceutical Equipment Co. Ltd., China), electronic balance (Mettler-Toledo (China) Co., Ltd., China), magnetic stirrer (Mettler-Toledo (China) Co., Ltd., China), X-ray diffraction instrument (Mettler-Toledo (China) Co., Ltd., China), infrared spectrometer (Mettler-Toledo (China) Co., Ltd., China), gas chromatograph, and quartz reactor (Mettler-Toledo (China) Co., Ltd., China).

2.2 Preparation method

The metal coordination polymer was prepared by hydrothermal synthesis using ferrocenedicarboxylic acid and cerium nitrate. The preparation process is shown in Fig. 1.

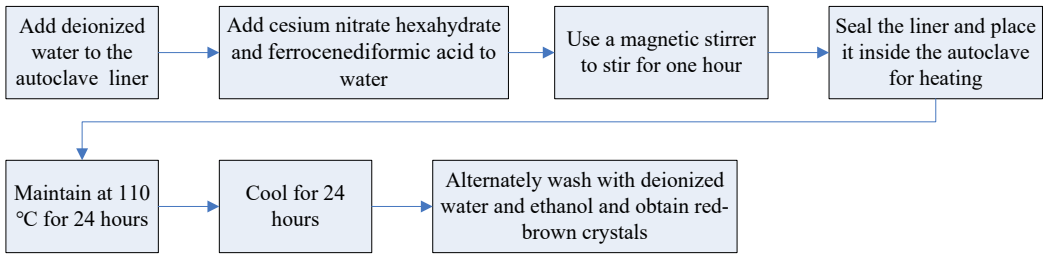

Fig. 1. Preparation process of the coordination polymer

① 10 mL of deionized water was taken and transferred into the autoclave liner [10].
② 0.4 mmol of cerium nitrate hexahydrate and 0.6 mmol of ferrocenediformic acid were taken and added to the deionized water in the liner.
③ A magnetic stirrer [11] was used to stir the mixed solution in the liner at a constant speed for one hour.
④ After stirring, the liner was sealed and placed in an autoclave for heating.
⑤ After heating the autoclave to 110 °C, it was kept for 24 hours.
⑥ The autoclave was depressurized, and the liner was left to cool for 24 hours.
⑦ Deionized water and ethanol were alternately used to wash the product in the liner, and finally reddish-brown crystals were obtained.

2.3 Test items

(1) Structural characterization test

Single-crystal X-ray diffraction, powder X-ray diffraction [12], and infrared spectroscopy [13] were used to perform structural characterization test on the product. In the single-crystal X-ray diffraction method, a single-crystal X-ray diffractometer was used to measure the crystal structure of the product. During the measurement, $Mo-K_\alpha$ ray and a graphite monochromator were employed, with a radiation wavelength of 0.71073 $\mathring{\mathbf{A}}$. The collected crystal data were restored and then the crystal structure was analyzed using Olex2 software. The X-ray diffraction signals, intensities, and infrared spectra of the product were simulated using the analyzed crystal structure.

In the powder X-ray diffraction method, the prepared crystal was first ground into fine powder, then the powder was spread evenly on the silicon wafer, and finally the silicon wafer was placed in the X-ray diffractometer according to the operating steps. The $Cu-K_\alpha$ target material was used. The range of 2θ was set as 5-50°. The rate of incident angle change was set at 5° per minute. The diffraction signal and intensity during the incident angle change of the ray were collected.

In the infrared spectroscopy method, the prepared crystals were first ground

into fine powder and then mixed with potassium bromide powder at a ratio of 1:100. The mixed powder was dried using an infrared lamp and then pressed into a transparent sheet using a mold. When using an infrared spectrometer for testing, the air background spectrum was tested. After excluding the air background spectrum, the thin sheet was placed in the instrument for measurement. The wavelength of the light wave directed at the sheet by the spectrometer was adjusted, and the change in light wave transmittance was recorded.

(2) Test the photocatalytic reduction performance of the coordination polymer for CO_2

The prepared cerium-ferrocene-based coordination polymer was used as the catalyst, DMA as the solvent, triethanolamine as the sacrificial agent, and ruthenium bipyridine as the photosensitizer for the reduction of CO_2. During the test, the catalyst, solvent, sacrificial agent, and photosensitizer were added according to a certain ratio to the quartz reactor [14] and then sealed and vacuumed. Then, CO_2 was introduced into the quartz reactor until the solution was saturated. The quartz reactor was then placed in a constant temperature environment and illuminated with light-emitting diode (LED) lights for the reaction [15]. Finally, the composition of the product was examined using a gas chromatograph. The benchmark reaction conditions in the above photocatalytic reduction experiment were a reaction temperature of 10 °C, 10 mg of catalyst, 5 mL of sacrificial agent (triethanolamine vs. DMA: 1:9), 32 mmol of photosensitizer, and four hours of reaction.

① Effect of reaction temperature: Based on the benchmark reaction conditions, the reaction temperatures were set at 0 °C, 5 °C, 10 °C, 15 °C, and 20 °C respectively to test the photocatalytic reduction performance of CO at different temperatures.

② Effects of catalyst dosage: Based on the benchmark reaction conditions, the catalyst dosage was set at 10 mg, 8 mg, 6 mg, 4 mg, and 2 mg respectively to test the photocatalytic reduction performance at different catalyst dosages.

③ Sacrificial agent dosage: When conducting comparative experiments, the volume of the solution must be constant. Therefore, on the basis of the benchmark reaction conditions, the volume of the sacrificial agent solution was kept at 5 mL, and the dosage of triethanolamine in the sacrificial agent was set at 0.1 mL, 0.2 mL, 0.3 mL, 0.4 mL, and 0.5 mL respectively to test the photocatalytic reduction performance.

④ Test the stability of the catalyst in the photocatalytic reduction: After the photocatalytic reduction reaction under the benchmark reaction conditions, the catalyst was separated by centrifugation, washed with water, and dried, followed by another round of photocatalytic reaction to test the photocatalytic performance. The process was cycled five times.

2.4 Test results

The composition of the prepared cerium-ferrocene-based coordination polymer was analyzed. The crystal structure data obtained using the single crystal X-ray diffraction method are shown in Table 1. The X-ray diffraction pattern and infrared spectrogram of the polymer are shown in Fig. 2. It can be seen that the X-ray diffraction and infrared spectrum of the product were almost consistent with the simulation results at the peak position, indicating that the prepared product was indeed cerium-ferrocene-based coordination polymer and has good phase purity.

Table 1.

The crystal structure data of the cerium-ferrocene-based coordination polymer

Crystal structure	Data
Chemical formula	$C_{36}H_{27}Ce_2Fe_3O_{13.5}$
Formula weight	1,123.36
Space group	P21/c
a (Å)	14.995
b (Å)	10.863
c (Å)	21.525
α (°)	90
β (°)	90.310
γ (°)	90
V (Å^3)	3,506
Z	4
μ (mm^{-1})	3.872
Goodness of fit	1.054
Rint	0.0337
R_1	0.0175
wR_2	0.0458

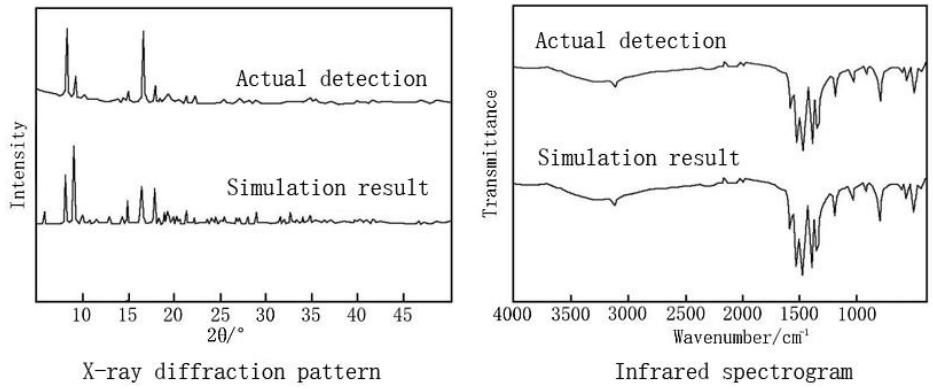

Fig. 2. Characterization test results of the prepared product

The effect of the reaction temperature on the photocatalytic reduction performance of the cerium-ferrocene-based coordination polymer was tested, and the results are shown in Fig. 3. It can be seen that as the temperature set for the photocatalytic reduction of CO_2 increased, the yield of the reduced product CO first increased and then decreased. The reason for this is that when the temperature rose, the molecular movement involved in the photocatalytic reduction increased, and the CO yield rose, but when the temperature exceeded a certain level, the overly active molecular movement increased the production of the more easily generated by-product H_2, resulting in a decrease in CO yield.

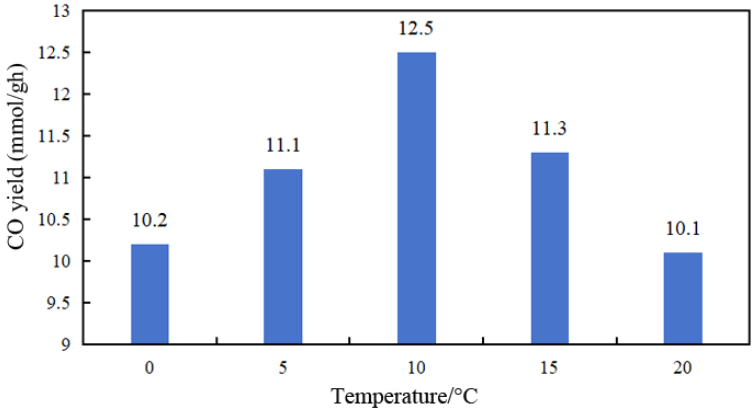

Fig. 3. Photocatalytic reduction performance of the coordination polymer at different reaction temperatures

The effect of catalyst dosage on the photocatalytic reduction performance of the cerium-ferrocene-based coordination polymer was tested, and the results are shown in Fig. 4. When the catalyst dosage was 2 mg, the CO yield of the photocatalytic reduction reaction was the highest. The reason is that when the

amount of photosensitizer was fixed, the increase in the amount of catalyst led to a decrease in the number of photoelectrons that can be obtained per unit amount of catalyst.

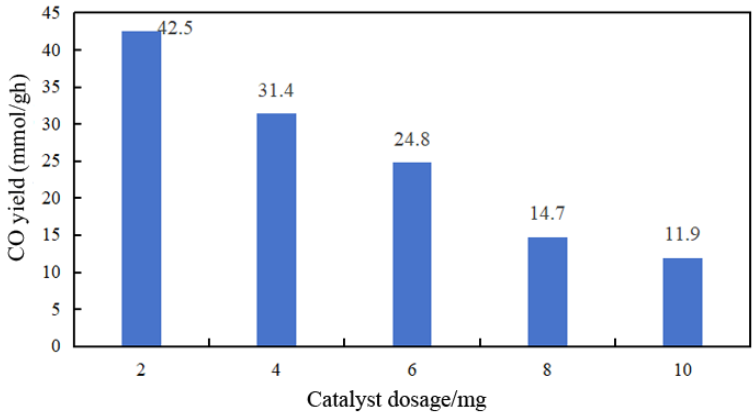

Fig. 4. Photocatalytic reduction performance of the coordination polymer at different catalyst dosages

The effect of sacrificial agent dosage on the photocatalytic reduction performance of the cerium-ferrocene-based coordination polymer was tested, and the results are shown in Fig. 5. The increase in sacrificial agent dosage led to an increase in CO yield, and when the sacrificial agent dosage was 0.5 mL, the CO yield of the photocatalytic reduction reaction was the highest.

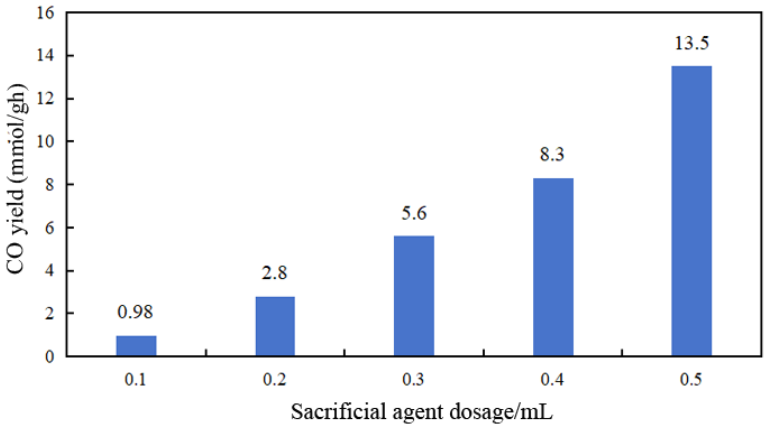

Fig. 5. Photocatalytic reduction performance of the coordination polymer at different sacrificial agent dosages

The reason is that during the photoelectron cycle assisted by the photosensitizer, the sacrificial agent loses electrons and acquires protons from the electrically neutral sacrificial agent to become a proton donor, and then the proton

donor reacts with CO_2 to generate CO and its by-products with the assistance of the photoelectron catalyst. Therefore, the more sacrificial agent is used, the more CO is generated.

The effect of the number of catalyst cycles on its photocatalytic reduction performance was tested, and the results are shown in Fig. 6. The number of catalyst cycles did not affect the CO yield, indicating that the catalytic performance of the prepared cerium-ferrocene-based coordination polymer was stable and could be reused multiple times.

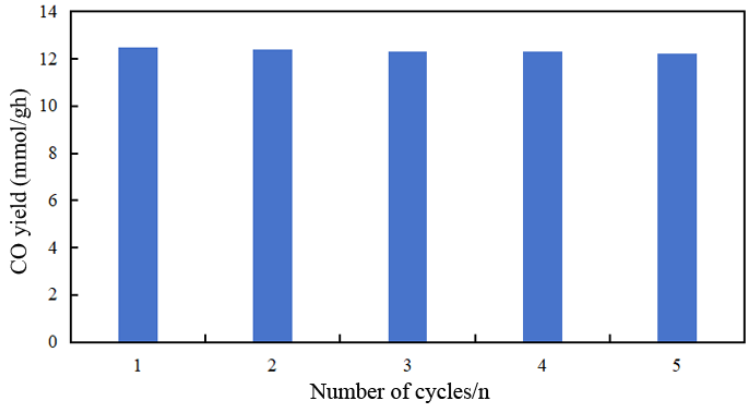

Fig. 6. Photocatalytic reduction performance of the catalyst at different cycles

3. Conclusions

This paper briefly presents metal-coordination polymers based on carboxylic acid ligands, followed by the preparation of the cerium-ferrocene-based coordination polymer using 1, 1-ferrocenedicarboxylic acid and cerium nitrate. After characterization tests of the product, the effects of temperature, catalyst dosage, sacrificial agent dosage, and the number of catalyst cycles on the photocatalytic reduction performance of the catalyst in CO_2 photocatalytic reduction were tested. The crystal structure data obtained using the crystal X-ray diffraction method, X-ray diffraction pattern, and infrared spectrogram showed that the prepared product was a cerium-ferrocene-based coordination polymer with good phase purity. It was found that with the increase of reaction temperature, the yield of the reduction product CO first increased and then decreased. As the amount of sacrificial agent increased, the yield of CO increased accordingly. As the amount of catalyst increased, the yield of CO decreased. As the number of cycles of the catalyst increased, the yield of CO produced by the photocatalytic reduction of CO_2 remained unchanged.

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