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The Influence of the Cu/Fc Ratio in Cu-Fc MOF on Catalytic Performance

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Abstract: ***In this study, mesoporous amorphous bimetallic metal-organic framework materials (Cu-Fe-MOF) were synthesized through a ligand competition-mediated strategy for use as efficient catalysts. The synthesis involved adjusting the molar ratio between two precursors-1,1'-ferrocenedicarboxylic acid (Fc) and anhydrous copper chloride ($CuCl_2$)—followed by the addition of dimethylformamide (DMF) and acetic acid as modulators. Four distinct samples were prepared with Cu-to-Fe precursor molar ratios of 2:8, 6:5, 8:2, and 9:1 to systematically investigate the compositional effects on catalytic performance.***

Keywords: Metal-organic framework; Mesoporous; Photothermal; Reduction reaction; Organic pollutants.

1. INTRODUCTION

The catalytic reduction method is most widely used by virtue of its high efficiency and safety, but requires high catalyst performance. In this paper, using solvothermal, a facile synthesis method, we constructed a ligand competition-induced mesoporous amorphous bimetallic organoskeletal material (Cu-Fe-MOF) with photothermal synergism to enhance the separation and transfer of electron/hole pairs by using a certain molar ratio of 1,1-ferrocenecarboxylic acid and anhydrous copper chloride as the precursor [1], and then adding DMF and acetic acid as a high-efficiency catalyst for treating the carbonyl oxygen in DMF and the carboxyl oxygen in acetic acid have lone pair electrons that can be coordinated with metal ions [2]. When the concentration of copper ions increases, the ligand's coordination site is relatively sparse and intense ligand competition occurs [3].

To address the aforementioned issues, this study employed a ligand competition strategy by precisely regulating the iron-to-copper ratio, successfully developing a novel high-performance amorphous Cu-Fc MOF material. The research systematically investigated the catalytic performance of this MOF material under various experimental parameters, with particular emphasis on examining the enhancement effects of near-infrared light irradiation on catalytic efficiency. Current research on amorphous Cu-Fc MOF catalysts for organic pollutant treatment in wastewater remains in its nascent stage. Therefore, conducting in-depth investigations into the structural characteristics, functional properties, and underlying mechanisms of amorphous Cu-Fc MOF materials in water purification applications holds significant scientific merit and practical value for environmental remediation.

2. EXPERIMENTAL SECTION

2.1 Chemicals and Regents

Cu-Fc MOF was synthesized by a solvothermal method. Firstly, anhydrous copper chloride and 1,1-ferrocenecarboxylic acid were mixed according to four molar ratios of 9:1, 8:2, 6:5, 2:8 in a polytetrafluoroethylene liner, and 60 mL of N,N-dimethylformamide (99.5%) was added to the mixture, and stirred uniformly to form a solution. Then add 8 mL of glacial acetic acid to the above solution, sonicate for several minutes and put into the oven, react at 120 ℃ for 12 h [4]. The resulting solution was centrifuged at 8500 rpm for 10 min to obtain a black precipitate, which was then washed with deionized water and DMF for several times, respectively, and then dried in vacuum and prepared for use.

2.2 Characterization

The crystalline phase structure was determined by X-ray diffractometer (XRD, Rigaku MiniFlex 600) with Cu-Kα radiation (λ= 1.5406 Å). The specific surface area and pore structure were evaluated by Brunauer-Emmett-Teller (BET) analysis using N_2 adsorption-desorption isotherms (Micromeritics ASAP 2460). The microstructure and morphology of the sample were characterized using field-emission scanning electron microscopy (FE-SEM, TESCAN MIRA4, OXFORD XPLORE 30).

3. RESULTS AND DISCUSSION

Figure 1 (a-c) shows the SEM images of Cu/Fc MOF with Cu/Fc content ratios of 8:2, 6:5, and 2:8, respectively. Fc content ratio of 2:8, the morphology of the samples showed a large-sized lumpy morphology with a smooth surface and an average size of about 2 µm; the morphology of the samples with a Cu/Fc content ratio of 8:2 in the Cu-Fc MOF showed a homogeneous size and a large number of protrusions on the rough surface, with an average size of about 200 nm. Comparing with the morphology of the sample with a Cu/Fc content ratio of 9:1 in Cu-Fc MOF shown in Fig. 1b, the larger the difference between the Cu/Fc content ratio in Cu-Fc MOF, the size of the sample gradually becomes smaller and smaller, the surface roughness goes from smooth to rough, and the number of protrusions gradually increases [5].

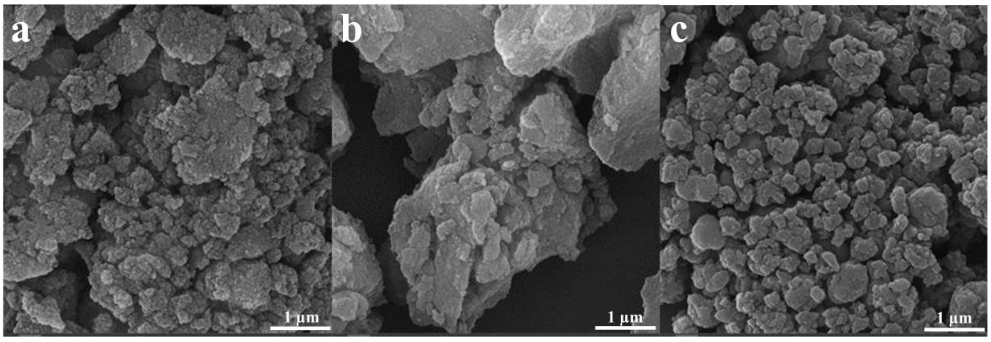

Figure 1: Analysis of UV-Vis absorption spectra and kinetic profiles for 4-NP catalytic reduction using Cu-Fc MOFs synthesized with varying Cu/Fe ratios:(a) Original UV-Vis absorption spectra for Cu/Fe = 8:2;(b) Original UV-Vis absorption spectra for Cu/Fe = 6:5;(c) Original UV-Vis absorption spectra for Cu/Fe = 2:8;(d) First-order kinetic curves for the four Cu/Fe ratios;(e) Apparent rate constant curves for the four Cu/Fe ratios;(f) XRD patterns of Cu-Fc MOFs with the four Cu/Fe ratios.

N_2 adsorption measurements were performed to reveal the porosity of Cu-Fe-MOF with a Cu/Fe ratio of 6:5. Figs. 2 a show the N_2 adsorption-desorption isotherms and pore size distributions of Cu-Fe-MOF, which exhibit a type III isotherm up-concave shape, with the heat of adsorption in the first layer being much smaller than the heat of gas coalescence. The low adsorption amount in the low-pressure region and the absence of B-points indicate that the force between the adsorbent and the adsorbate is rather weak. The higher the relative pressure, the more adsorbed amount shows pore filling. As for the rapid rise in the second half of the curve, capillary polymerization occurs. Since the adsorbent has a pore size that increases from small to large until there is no end, the sharp increase in adsorption caused by capillary coalescence also has no end, and the adsorption isotherm is upwardly curved without showing saturation. It indicates that the surface of the sample with this Cu/Fe ratio presents a smoother surface with less porosity [6]. Figure 2 b shows the pore size distribution of the sample with a Cu/Fe content of 6:5, which shows that there are pore sizes in the sample mainly concentrated in 2-6 nm, while there are also a small number of pore sizes ranging from 7 nm and above, and the BET results indicate that the specific surface area of the Cu-Fe-MOF material reaches 14.281 m2/g, with an average pore size of 11.71 nm. However, from the Fig. 10b shown in the reduction rates for different Cu/Fe ratios, it can be concluded that the decisive factor for the good or bad reduction performance of the catalyst is related to the content of Cu in the pressed samples, whereas the porosity in the samples has less influence on the catalyst performance [7].

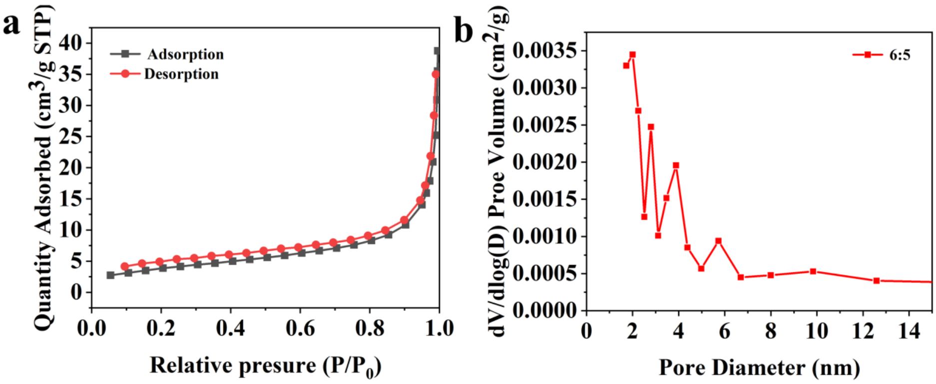

Figure 2: N_2 adsorption-desorption isotherm and pore size distribution of Cu/Fc MOF with a Cu/Fc ratio of 6:5

The degradation paths of four different ratios of samples (0.27 mg), in the presence of 0.132 M NaBH4 for five minutes on 90 mg/L of 4-NP can be seen in Fig. 3 (a-c). As shown in Fig. 3 d, the reduction rate constant k value of the catalyst increased from 0.75 min-1 to 7.67 min-1 as the percentage of Cu content in the Cu to Fc ratio of the samples increased (Fig. 3 e), and the rate constant of the samples with a ratio of Cu and Fe of 9:1 was 10.23 times higher than that of 2:8. As shown in Fig. 3f, the XRD curves observed that the peak widths of all four ratios of the samples ranged from from 12.7° to 29.08°, with no species-specific characteristic peaks for the elements Fe and Cu, indicating that the four different ratios of the samples are similar to the amorphous structure of carbon nanomaterials [4, 8-10].

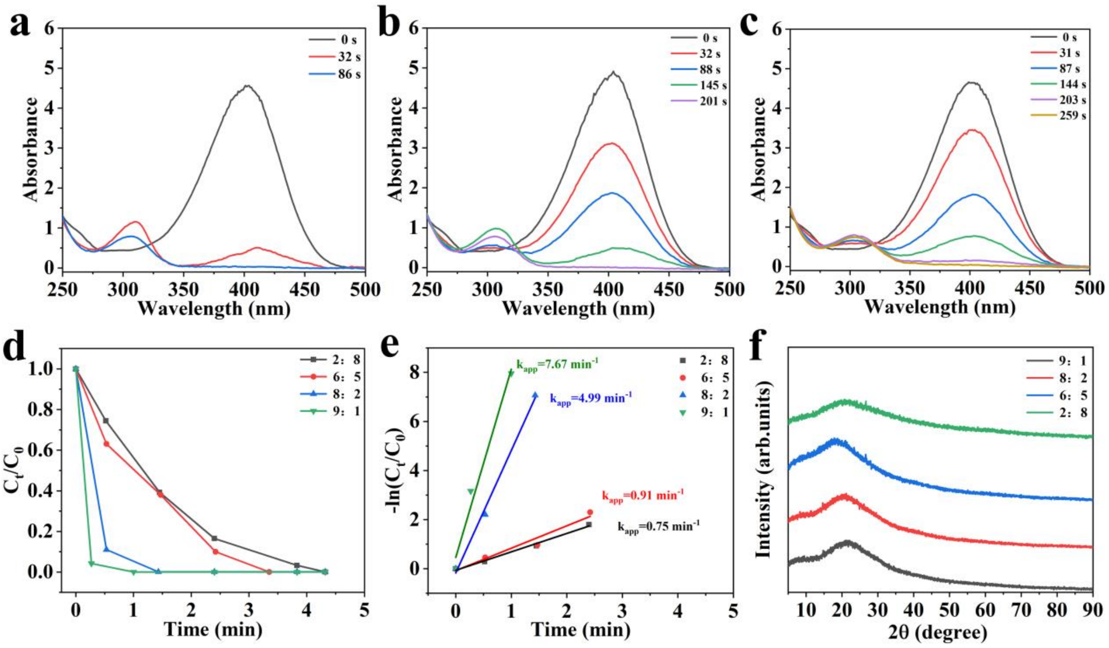

Figure 3: Proto-Uv-vis raw UV interpretation curves of the catalytic reduction process of 4-NP by Cu-Fc MOF synthesized with different Cu and Fe ratios: (a) 8:2 (b) 6:5 (c) 2:8 (d) first-order kinetic curves of the four ratios; (e) curves of the apparent rate constants of the four ratios; and (f) XRD curves of the Cu-Fc MOF of the four ratios

4. CONCLUSIONS

In this study, an amorphous bimetallic organoskeletal material (Cu-Fe-MOF) with a mesoporous structure resulting from ligand competition was prepared as an efficient catalyst at the sample synthesis stage by modulating the molar ratios of 1,1-ferrocenecarboxylic acid and anhydrous copper chloride as the precursors, followed by the addition of DMF and acetic acid. The carbonyl oxygen in the DMF and the carboxyl oxygen in the acetic acid have lone-pair electrons, and both the divalent iron ions and divalent copper ions have empty orbitals and can accept the lone pair of electrons provided by the ligand. Copper ions have a smaller ionic radius than ferrous ions, which results in a greater charge density and an electronic configuration of $3d^9$, with the d orbitals incompletely filled, which can be utilized in the formation of ligand bonds by using the d orbitals to form a feedback π-bond with the lone pair of electrons of the ligand, which strengthens the ligand bond and thus makes it easier to coordinate with the ligand. When the concentration of Cu^{2+} in the metal precursor gradually increases, the coordination sites are relatively sparse, and the carbonyl oxygen and acetic acid of DMF compete for these limited coordination sites. At the same time, there is a synergistic effect between the two metal ions, which can regulate the electronic structure of the MOF and optimize its adsorption and activation ability of the reactants. When the laser irradiates the surface of the amorphous bimetallic MOF, a localized high temperature is generated, which causes the temperature of the reaction system to rise rapidly and accelerates the reaction rate. The laser can also induce the generation of plasma, so that the decomposition of sodium borohydride produces more highly reactive hydroxyl radicals, which can reduce p-nitrophenol more effectively. In addition, the action of laser can enhance the electromagnetic field on the surface of the MOF catalyst, promote the transfer and excitation of electrons, improve the stability of the structure of the MOF material, and further improve the catalytic activity.

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