



Excellent photo-Fenton catalysts of Fe–Co Prussian blue analogues and their reaction mechanism study



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ABSTRACT

Two kinds of Fe–Co Prussian blue analogues (Fe–Co PBAs) with different iron valence state, $\text{Fe}_3[\text{Co}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$ and $\text{Fe}[\text{Co}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$, were developed as the photo-Fenton catalysts for in-depth investigation of the heterogeneous Fenton reaction mechanism. These two catalysts showed exceptionally high efficiencies for the degradation of Rhodamine B. The efficient redox cycling of iron species in the Fe–Co PBAs photo-Fenton process was deeply explored by Mössbauer spectroscopy. The excellent photo-Fenton activities of these Fe–Co PBAs were ascribed to the existence of highly dispersed water coordinated iron sites and abundant vacancies in the metal-organic-frameworks. Singlet oxygen was identified by radical scavenger experiments and electron paramagnetic resonance spectroscopy, which plays a key role in the photo-Fenton process. Based on these comprehensive experimental results, a novel radical reaction mechanism was proposed. This work not only opens up a new avenue for the application of Fe–Co PBAs, but also gives a deeper insight into the mechanisms of heterogeneous Fenton reactions.

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1. Introduction

Nowadays, the scarcity of fresh water resources and the ever-growing environmental pollution have been attracting increased concern [1]. Toxic organic pollutants in the wastewater which adversely affect the health of human beings must be reduced to acceptable level [2–4]. Over the past few years, various wastewater treatment techniques have been developed, such as absorption and filtration processes [5], biological degradation [6], advanced oxidation processes (AOPs) [7], and so on. The heterogeneous Fenton process has been widely investigated due to its high efficiency in removing persistent organic contaminants with lower amounts of H_2O_2 consumption under a wide pH range [8–10]. Most of the recent researches concentrate on the modification of the iron minerals and design of heterogeneous Fenton-like catalysts with high activity and durability [11–13]. However, limited mechanism understanding hinders the breakthroughs in Fenton chemistry. In most cases, the relationship between the catalyst structure, the effi-

ciency of active radical (such as $\bullet\text{OH}$) generation, and the redox cycling process of iron species are still unclear [10,14–15]. For instance, Purceno et al. reported the oxidation of Fe^{II} after the Fenton process [16]. However, Yang et al. observed the opposite process, in which Fe^{III} was reduced after the Fenton reaction [14]. In order to understand the mechanisms of the heterogeneous Fenton reactions, it is vitally important to clarify the structure changes of the catalyst and the redox cycling of the iron species during the whole reaction process.

^{57}Fe Mössbauer spectroscopy is a unique method for determining the oxidation state and the coordination environment of iron species in solids [17]. In our previous study, the synergistic effects of TiO_2 photocatalyst and Prussian blue (PB, $\text{Fe}_3[\text{Fe}(\text{CN})_6]_4 \cdot 14\text{H}_2\text{O}$) Fenton-like system were demonstrated by Mössbauer technique [18]. Therefore, Mössbauer spectroscopy is a powerful technique for the study of the Fenton process. $\text{Fe}_3[\text{Co}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$ and $\text{Fe}[\text{Co}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ (Fe^{II} –Co and Fe^{III} –Co PBA) are Prussian blue analogues which exhibit some functional properties, such as striking photo-magnetic [19], hydrogen storage [20], zero thermal expansion [21], and catalytic properties [22,23]. Fe–Co PBAs are in a kind of metal-organic-framework (MOF) structure constructed by octahedral $[\text{Co}(\text{CN})_6]^{3-}$ anion groups bridged with iron ions to form

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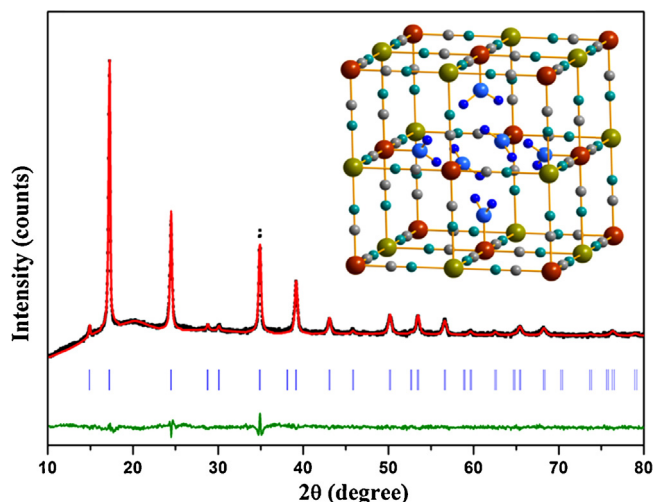


Fig. 1. Results of the Rietveld refinement for $\text{Fe}_3[\text{Co}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$ ($a = 10.282 \text{ \AA}$, space group $\text{Fm}\bar{3}\text{m}$, $R_{\text{wp}} = 12.5\%$, $R_{\text{exp}} = 8.62\%$). The tic marks display the reflection positions, and the lower solid line displays the difference profile. (Inset: Cubic MOFs structure of $\text{Fe}_3[\text{Co}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$ with vacancies and water coordinated iron sites.)

simple cubic lattice structure [24]. The charge balance in the crystal structure is achieved by random distribution of the $[\text{Co}(\text{CN})_6]^{3-}$ vacancies, leading to the coordination of Fe^{II} or Fe^{III} centers with one or several water molecules as shown in the inset picture of Fig. 1 [25]. The existence of abundant vacancies and water coordinated iron sites in the MOFs structure may be beneficial for the Fe–Co PBAs in the Fenton process. However, there is no report on the application of Fe–Co PBAs in Fenton chemistry to date.

In this work, we studied the catalytic properties of the Fe–Co PBAs (Fe^{II} –Co and Fe^{III} –Co) in heterogeneous Fenton reactions with particular emphasis on the underlying reaction mechanism. Extensive investigations have been carried out on the Fenton activities of Fe–Co PBAs, including the degradation of model pollutant Rhodamine B (RhB) under various conditions, the stability of the Fe–Co PBAs in the photo-Fenton process, the redox cycling of iron species and the photo-Fenton mechanisms of Fe–Co PBAs explored by ^{57}Fe Mössbauer spectroscopy. Singlet oxygen was identified by radical scavenger experiments and electron paramagnetic resonance (EPR) spectroscopy, which plays a key role in the photo-Fenton process. Relevant radical reaction pathways in photo-Fenton process were proposed.

2. Experimental

2.1. Materials and chemicals

Potassium hexacyanocobaltate(III) (98%) was purchased from Beijing J&K Co., Ltd., China. Sodium azide, p-benzoquinone (BQ), 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) and iron oxide (II,III) (99.5%, ~20 nm) were purchased from Aladdin Co., China and RhB was acquired from Sigma–Aldrich. Ferric chloride, ferrous chloride, cobaltous chloride, copper chloride, potassium ferrocyanide, *t*-butanol (TBA) and 30% hydrogen peroxide aqueous solution were purchased from Tianjin Kermel Chemical Reagent Co., Ltd., China. All chemical reagents were used without further purification.

2.2. Preparation of Fe–Co PBAs

$\text{Fe}_3[\text{Co}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$ (Fe^{II} –Co PBA) and $\text{Fe}[\text{Co}(\text{CN})_6]_2 \cdot 2\text{H}_2\text{O}$ (Fe^{III} –Co PBA) were prepared by reaction of aqueous solutions of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ or $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{K}_3[\text{Co}(\text{CN})_6]$. The preparation process was similar to previous reports [21,26] but with slight mod-

ification. Typically, 25 mL $\text{K}_3[\text{Co}(\text{CN})_6]$ aqueous solution (0.10 M) was slowly added into 25 mL $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ or $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ aqueous solution (0.10 M) under magnetic stirring. The mixed solution was further stirred for another 30 min and aged for 1 day. Finally, the resulting precipitates were centrifuged and washed for at least three times with deionized water, followed by drying in an oven at 333 K for 12 h. For comparison, the insoluble PB sample was synthesized by the same process as that of Fe^{III} –Co PBA, except the replacement of $\text{K}_3[\text{Co}(\text{CN})_6]$ (0.10 M) using $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ (0.15 M). The $\text{Cu}_3[\text{Co}(\text{CN})_6]_2$ (Cu^{II} –Co PBA) and $\text{Co}_3[\text{Co}(\text{CN})_6]_2$ (Co^{II} –Co PBA) were also synthesized by the similar process but with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ as the metal precursors, respectively.

2.3. Characterization of Fe–Co PBAs

The X-ray diffraction (XRD) patterns were measured on a PANalytical X'Pert-Pro X-ray diffractometer equipped with Ni-filtered $\text{Cu K}\alpha$ ($\lambda = 0.15406 \text{ nm}$) radiation source in an angular range of 2θ from 10° to 80° . The structural refinements were conducted by the Rietveld method using the FULLPROF software based on the XRD data. The surface morphologies were studied using a Tecnai G^2 Spirit transmission electron microscopy (TEM) with an accelerating voltage of 120 kV. The specific surface areas were analyzed by the Brunauer–Emmett–Teller (BET) N_2 adsorption–desorption method on a Micromeritics ASAP 2010 instrument at 77 K, and the pore size distributions were analyzed using the Barrett–Joyner–Halenda (BJH) method from the desorption branch of the N_2 adsorption–desorption isotherms. Fourier transform infrared spectra (FT-IR) were recorded on a Bruker spectrometer equipped with a MCT detector in the region of $400\text{--}4000 \text{ cm}^{-1}$ at a resolution of 4 cm^{-1} . The thermo-gravimetric and differential scanning calorimetry (TG–DSC) analyses were carried out using a Setaram Setsys 16/18 thermo-analyzer at a heating rate of $2^\circ \text{C min}^{-1}$ in N_2 flow. The X-ray photoelectron spectra (XPS) were measured on an ESCALAB 250 X-ray photoelectron spectrometer equipped with monochromated $\text{Al K}\alpha$ source. All binding energies were calibrated by a standard sample of contaminated carbon ($\text{C } 1s = 284.6 \text{ eV}$). The spectra were fitted by the XPSPEAK41 software using Shirley-type background.

The room temperature ^{57}Fe Mössbauer spectra were recorded using a proportional counter and a Topologic 500A spectrometer with ^{57}Co (Rh) as a γ -ray radioactive source. The EPR spectra carried out in the Fenton process were obtained using a Bruker ESR I200 spectrometer with the sweep width of 100 G and a center field at 3320 G at room temperature. The detailed procedures of Mössbauer and EPR measurements can be found in our previous work [18].

2.4. Catalytic activity measurements of Fe–Co PBAs

The Fenton performance of Fe–Co PBAs was tested by the degradation of RhB dye (12 mg L^{-1}) with H_2O_2 (4 mM) at pH 4.8 (initial pH of RhB aqueous solution) in a dark box. If necessary, the pH value was adjusted by either 0.1 M HNO_3 or NaOH aqueous solution and recorded with an Orion pH meter (model PHSJ-3F). The temperature was kept at 308 K using a water bath. The concentrations of leached iron and cobalt in solution were measured by Thermo IRIS Intrepid II inductively coupled with plasma-optical emission spectroscopy (ICP-OES).

In all experiments, 10 mg Fe–Co PBAs were added into a 50 mL RhB solution (12 mg L^{-1}) and stirred for 30 min to establish the adsorption-desorption equilibrium. The reaction was initiated by adding certain amounts of H_2O_2 aqueous solution and simultaneously turning on the Xenon lamp (MAX-303, Asahi Spectra Co., Ltd.) equipped with a 400 nm long-pass filter (light intensity: $\sim 13.3 \text{ mW cm}^{-2}$, the photo emission spectrum of the lamp can be found in our previous work [18]). During the reaction, 2 mL

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