Zhihao Bi, Zhihao Li and Lifeng Yan*

Catalytic oxidation of lignin to dicarboxylic acid over the CuFeS_2 nanoparticle catalyst

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Abstract: CuFeS_2 nanoparticles have been synthesized and used as catalyst for the degradation of lignin. Under mild condition of reaction at 60°C and 5 h in the presence of 2 ml hydrogen peroxide, lignin can be degraded completely and converted to dicarboxylic acids, such as oxalic acid (OA), fumaric acid, maleic acid, and succinic acid (SA), carbon oxides, and aromatic compounds. The major product is OA (up to 30% selectivity) and SA. On the basis of the chemicals detected, we proposed a logical mechanism similar to Fenton reaction. The results reveal that $\text{HO}^\cdot$ and $\text{HOO}^\cdot$, formed from the cleavage of hydrogen peroxide over the catalyst, play an essential role in the oxidation of lignin to destroy its aromatic structure and generate carboxylic or DCA. This is a potential method to convert native lignin as a renewable feedstock to produce valuable chemicals.

Keywords: catalysis; degradation; dicarboxylic acid; Fenton reaction; lignin.

1 Introduction

With the falling reserves of fossil fuels, biomass resource – as a kind of carbon renewable resource – has recently attracted a lot of attention to produce conventional fuels and other platform molecules. Lignin is a kind of natural amorphous organic polymer with a three-dimensional net structure; it constitutes the cell wall of plants with cellulose and hemicelluloses and is ubiquitous in biomass resource. It has a unique advantage in the preparation of high value-added chemicals, such as oxalic acid (OA), succinic acid (SA), and so on [1–6]. Generally, lignin contains three kinds of phenylpropane units, namely, guaiacyl (G), syringyl (S), and p-hydroxylphenyl (H), which are

connected by more than six different types of linkages to make a network structure. Some of the most common linkages are β -1 linkage (5%–15%), 5-5' linkage (10%–25%), and β -O-4 linkage (25%–50%) [3]. By breaking down these linkages, both the hydrogenation and oxidation of lignin can be used to obtain cyclohexane, phenolic, alkane derivatives, and other simple aromatic compounds, such as phenol [7–9]. However, the oxidation and fraction of lignin to form carboxylic acids [e.g. OA, formic acid (FoA), etc.], which are valuable raw chemicals and intermediates used in the pharmaceutical, chemical, and food additive industries, have not been fully investigated [8]. Current commercial carboxylic acids mainly come from oil, so it is essential to develop a mild, environmentally benign route to convert lignin into carboxylic acids; moreover, its unique aromatic structure provides a promising possibility [10]. With this in mind, lignin oxidation processes can potentially replace some route from petroleum. Unfortunately, converting lignin into value-added chemicals has proven to be difficult [7]. Dicarboxylic acids (DCAs), such as SA, maleic acid (MA), and OA have been widely used as essential platform reagents in the food and pharmaceutical industries. Aside from the aromatic compounds and their derivatives, DCAs have also been recognized from the oxidative cleavage of aromatic rings in lignin or its fragments, which has been overlooked for a long time until recently.

Zhang et al. [8] reported that lignin can be oxidized to produce DCAs, such as malonic acid and SA, over the catalyst of chalcopyrite, and the mechanism is assigned to the Fenton-like reaction [11–14]. The catalyst chalcopyrite they utilized was obtained commercially and then directly used in the reaction. Given the large particle size of the catalyst, investigating what would happen if nanoparticles of the chalcopyrite catalyst are employed, especially because nanoparticles work as a catalyst, has attracted great attention recently because of their efficiency and excellent performance. In addition, although DCAs are commonly observed as the main products, which are an attractive result for high added-value chemicals, there is a lack of fundamental description of how to control these oxidation reactions in order to selectively generate valuable chemicals from lignin.

In the current study, native lignin was extracted from wheat straw by our own unique method. Nanoscale

*Corresponding author: Lifeng Yan, Department of Chemical Physics, iCHEM, University of Science and Technology of China, Hefei 230026, P.R. China, e-mail: lfyan@ustc.edu.cn

Zhihao Bi and Zhihao Li: Department of Chemical Physics, iCHEM, University of Science and Technology of China, Hefei 230026, P.R. China

CuFeS₂ crystals were synthesized and their catalytic activity for lignin oxidation in the presence of hydrogen peroxide (H₂O₂) was examined. The CuFeS₂ nanoparticle is a composite metal catalyst that consists of two metal elements, which have great potential in selectively producing phenolic compounds through cleaving the β-O-4 linkages in lignin. The unique structure of CuFeS₂ nanoparticles with complex metal oxidation states includes Cu²⁺ and Fe²⁺, which can lead to a synergistic effect for oxidation reactions and allows for highly effective electron transfer on the surface of nanoparticles. Interestingly, an unexpectedly produced integral product is OA, which is different to Zhang's results [8]. Moreover, the effects of reaction conditions on the lignin degradation efficiency and the qualitative and quantitative analysis of products were studied. Based on the product distribution and the research results, a mechanism of catalytic oxidation reaction is been proposed, and quinones are considered to be a kind of essential intermediate reactants to promote the formation of DCAs.

2 Materials and methods

2.1 Materials

Industrial lignin was purchased from a local paper mill. Prior to use, it was washed with deionized water thrice, and fresh lignin was obtained in the laboratory via hydrolysis and biomass polysaccharide removal. Deionized water with resistivity of 18 MΩ·cm was produced by a Milli-Q (Millipore, USA) and was used for solution preparation. Iron chloride (FeCl₃, 99.95%, Sinopharm Chemical, China) and copper chloride (CuCl₂, 99.95%, Sinopharm Chemical, China) were used as the precursors of Fe and Cu ions, respectively. Other chemicals, including analytical grade FA, OA, acetic acid, sodium acetate, ethylenediamine, and thioacetamide, were purchased from Sinopharm Chemical Reagent Co. Ltd. (China). In addition, H₂SO₄ (98%), H₂O₂ (30%) aqueous solution, and hydrochloric acid (37%) aqueous solution were purchased from Shanghai Chemical Reagents Company, and were used directly without further purification. Chromatographic-grade methanol was purchased from Aladdin Chemical Reagent Co. Ltd.

2.2 Characterization of lignin and catalyst

The model compounds were characterized by means of ¹H-NMR, lignin was characterized by means of Fourier transform infrared spectroscopy (FT-IR), gel permeation chromatography (GPC), elemental analysis, and UV-Vis spectroscopy. The catalyst was characterized by means of X-ray powder diffraction (XRD), Raman spectroscopy, and transmission electron microscopy (TEM). Reaction products were analyzed using GPC (DMF), GC-FID, gas chromatography-mass spectrometry (GC-MS), and high performance liquid chromatography (HPLC).

2.3 Synthesis of the CuFeS₂ nanoparticle catalyst

The CuFeS₂ nanoparticle catalyst was prepared by using the sequential solvothermal and co-precipitation methods [15]. In brief, 0.01 mol FeCl₃ and 0.01 mol CuCl₂ were added into 100 ml ethanol, after which the solution was stirred for 1 h for the preparation of the CuFeS₂ sol-mixture. Then, thioacetamide (C₂H₅NS, 1.5 g, 0.02 mol), the sulfur source of the reaction, was added into the mixture. Thioacetamide, a kind of classical source of sulfide ions, has been widely used in inorganic qualitative analysis, and the addition of thioacetamide to a solution of different metal ions generates the corresponding metal sulfide:

Next, ethylenediamine (1.2 g, 0.02 mol) was added to reduce the Fe³⁺ ions to Fe²⁺ ions and the solution was stirred until it generated a homogeneous system. The ultimate liquor was poured into an autoclave and then heated at 200°C for 2 h in a Muffle furnace. After this step, the obtained black powder was cooled to room temperature, cleaned with ethanol, and dried at 80°C for 24 h. In the same way, we obtained several similar nanoparticles with sizes ranging from 10 to 30 nm by changing the reaction times and temperatures.

2.4 Synthesis of model compounds

In order to further understand the catalytic activity and the reaction mechanism of lignin conversion, some model compounds with similar linkages as natural lignin were synthesized, including guaiacol, 1-phenyl-2-phenoxyethanol, and [2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-ol]. Among them, guaiacol is one of the three basic structural units of lignin and the two other model compounds represent the β-O-4 linked phenylpropane units, which are the predominant linkages in lignin. Our target was to verify the ability of CuFeS₂/H₂O₂ oxidation system to destroy the aromatic structure in lignin. The synthetic route of 2-phenoxy-1-phenylethanol has been provided in a previously reported process. In the current study, 2-phenoxy-1-phenylethanol was prepared in a two-step sequence from 2-bromoacetophenone and phenol. Here, in brief, phenol (2.26 g, 24.0 mmol), potassium carbonate (4.14 g, 30.0 mmol), and 2-bromoacetophenone (3.98 g, 20.0 mmol) were added into acetone (50 ml) under stirring. Then, the mixture was heated under reflux for 4 h under the protection of nitrogen gas. Finally, the mixture was cooled, filtered, and concentrated by a rotary evaporator. The eventual solid was re-crystallized with ethanol to obtain white crystals of 2-phenoxy-1-phenylethanol (3.70 g, 87%). ¹H-NMR (300 MHz, chloroform-d), 7.40–7.04 (m, 7H), 6.93–6.67 (m, 3H), 5.01 (dd, J=8.7, 3.3 Hz, 1H), 4.18–3.81 (m, 2H) (Figure 1A).

The white crystals of the as-prepared 2-phenoxy-1-phenylethanol (1.00 g, 4.1 mmol), were dissolved in a mixture of deionized water (5 ml) and THF (20 ml). Immediately, sodium borohydride (0.36 g, 9.5 mmol) was added dropwise into the mixture over three times in 20 min, after which the mixture was stirred at atmospheric temperature for 4 h. To quench the reaction, saturated NH₄Cl aqueous solution (30 ml) was added into the reaction mixture, after which it was diluted with distilled water (30 ml) and extracted with diethyl ether (3 × 50 ml). The extractive was washed thrice with saturated brine, and dried over Na₂SO₄, filtered and then concentrated under vacuum to achieve a white solid called 2-phenoxy-1-phenylethanol (0.75 g, 73%). Under the protection of

Figure 1: ¹H-NMR of the model compounds (A, 2-phenoxy-1-phenylethanol) and (B, 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-ol).

nitrogen gas, the mixture of 2-bromine-1-(4-methoxyphenyl)ethanol (11.04 g, 60.0 mmol), guaiacol (8.2 ml, 74.0 mmol), and potassium carbonate (12.42 g, 90.0 mmol) in acetone (250 ml) was stirred and then heated to reflux for 4 h. Then, the mixture was cooled and filtered, and the solution was concentrated by a rotary evaporator. The eventual solid was recrystallized with ethanol to obtain white crystals of 2-(2-methoxyphenyl)-1-(4-methoxyphenyl)phenylethanone (12.07 g, 74%).

The as-obtained white crystals, 2-(2-methoxyphenyl)-1-(4-methoxyphenyl) phenylethanone (1.00 g, 4.0 mmol), were dissolved in a mixture of deionized water (5 ml) and THF (20 ml). Immediately, sodium borohydride (0.36 g, 9.5 mmol) was added in batches into the above system over three times in 20 min, after which the mixture was stirred at room temperature for 4 h. To quench the reaction, the saturated NH₄Cl aqueous solution (30 ml) was prepared and added into the reaction mixture, after which it was diluted with distilled water (30 ml) and extracted with diethyl ether (3 × 50 ml). The extractive was washed thrice with saturated brine, and dried over Na₂SO₄, filtered and then concentrated under vacuum to achieve a white solid called 2-(4-methoxyphenyl)-2'-hydroxyl-ethoxyanisole (0.75 g, 73%). ¹H-NMR (300 MHz, DMSO-d₆) δ 7.40–7.31 (m, 2H), 6.90 (dddd, J = 15.8, 13.7, 7.2, 2.2 Hz, 6H), 5.48 (d, J = 4.7 Hz, 1H), 4.86 (dt, J = 6.9, 4.6 Hz, 1H), 4.01–3.86 (m, 2H) (Figure 1B).

2.5 Depolymerization of model compounds and lignin over the CuFeS₂ nanoparticles

Conversions of model compounds and lignin were performed in a 50 ml flask (THERMO SCI SUN-SRI). Typically, 100–200 mg substrates, 10 wt% catalyst, and 2 ml acetic acid/sodium acetate buffer (pH = 4.5) were stirred vigorously and dispersed homogeneously in 6 ml ultrapure water. Then the mixture was heated to a desired temperature for 0–6 h, and 2 ml hydrogen peroxide was added dropwise in 20 min; the reaction was carried out under vigorous stirring. After a desired period of time, the reaction was quickly terminated by cooling the reactor to room temperature. The resulting mixture was filtered through a 0.22 μm filter, diluted and analyzed by HPLC (LC-20AD, Shimadzu) on C18-column equipped with an UV-Vis detector. In addition, the qualitative analyses of degradation products were based on the results from GC and GC-MS. For GC or GC-MS analyses, the aqueous samples were evaporated by a rotary evaporator and the dried samples were dissolved in ethyl acetate. After passing the mixture through a 0.22 μm filter, it was then injected in GC-FID and GC-MS (Agilent 7890A/5975C) with a DB-5 capillary column.

3 Results and discussion

3.1 Analysis of lignin

The linkages between various aromatic units and the function groups in lignin depend on the species of biomass. To further understand the composition and structure of lignin used here, before degradation reaction, it was characterized by a wide variety of techniques, such as FT-IR, GPC, UV, TGA, the CHNOS elemental analysis, NMR, and ICP-OES (Figures S1 and S2). The results are listed in Tables 1 and 2.

Table 1: The context of lignin used in this study.

C ^a (wt%)	H ^a (wt%)	N ^a (wt%)	O ^a (wt%)	S ^a (wt%)	Ash ^b (wt%)
49.27	4.59	1.08	31.90	0.35	4.78
Fe ^c (mg)	Cu ^c (mg)	Ca ^c (mg)	Mg ^c (mg)	Zn ^c (mg)	Na ^c (mg)
0.183	0.089	2.318	0.162	0.003	0.078

^aCalculated by elemental analysis. ^bCalculated by TGA. ^cICP-OES for 1 g of lignin.

Table 2: Solid-state ¹³C NMR spectroscopy data.

¹³ C shift (ppm)	Probable assignment
174	C=O in aliphatic acid
146	C ₃ and C ₄ in etherified guaiacyl
114	C ₅ in guaiacyl and C ₃ and C ₅ in p-hydroxyphenyl
74	C ₂ in xylose internal unit and Cα in β-O-4-linked unit
55	Aromatic methoxy group

Figure 2: TGA curves of lignin in N₂ and air atmosphere.

The CHNOS elemental analysis indicates that the lignin used here is made up of 87.19% organic composition. In addition, the ICP-OES was utilized to determine the concentration of the presence of metal ions. Given that lignin is a kind of organic natural polymer, it could be destroyed into CO or CO₂ at a high temperature. In air atmosphere, lignin loses 95.22% of its weight in a thermogravimetric analyzer heated to 800°C, regardless of the heating rate. The rest of the un-burnt ash (4.78 wt%) contributed to the inorganic compounds in lignin (Table 1).

According to the thermogravimetric analysis, lignin eventually loses 50% of its weight when the temperature rises to 500°C in nitrogen atmosphere. Then, the weight of lignin continues to reduce slowly when the temperature rises from 500°C to 800°C. Analogously, when the temperature reaches 450°C under air atmosphere, lignin loses its mass bluffly until the pyrolysis is almost completed. By the TGA measurement, we can conclude that some of the lignin still remains stable as a solid even at high temperatures (Figure 2).

3.2 Characterization of the CuFeS₂ nanoparticle

Wide-angle X-ray diffraction (XRD) analyses were carried out on a X-ray diffractometer (D/MAX-1200, Rigaku Denki Co. Ltd., Japan). As can be seen in Figure 3A, CuFeS₂ shows several peaks at 2θ values of 29.45°(112), 34.19°(200), 48.93°(220), 57.95°(321), 71.40°(400), 79.56°(332), and 90.99°(415), thus indicating a tetragonal crystal. According to Debye-Scherrer's equation, $t = 0.9\lambda / \beta \cos\theta$ (where λ is the wavelength of incident X-rays, β is the full width at half maximum height in radians, and the θ is the

Figure 3: XRD (A) and Raman spectra (B) of the CuFeS₂ nanoparticles.

Figure 4: Typical TEM image of the CuFeS₂ nanoparticles.

diffraction angle). The size of the crystalline representing 112 planes of CuFeS₂ is about 20 nm. Moreover, we used Raman analyses to verify the crystalline structure of CuFeS₂ at the range of 100–1800 nm on RAMANLOG 6 (Spex, USA) under the condition of 50 times objective and

Figure 5: Distribution of products of the degradation of the three model compounds of lignin over CuFeS₂ nanocatalysts. (A) guaiacol, (B) 1-phenyl-2-phenoxylethanol, (C) 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-ol.

Figure 6: GPC curves of lignin and degraded products.

Scheme 1: Degradation of model compounds to oxalic acid.

514.5 nm wavelength excitation. Three main peaks could be observed at 211 cm⁻¹, 275 cm⁻¹, and 470 cm⁻¹ (Figure 3B), indicating the successful synthesis of the CuFeS₂ nanoparticles. In addition, TEM was used to measure the size and morphologies of the CuFeS₂ nanoparticles. As shown in Figure 4, plenty of nanoparticles were obtained with sizes ranging from 20 to 30 nm, consistent with the result of the XRD measurement.

3.3 Depolymerization of the model compounds

To better explore the activity of CuFeS₂ and the mechanism of lignin oxidation reaction, guaiacol, 1-phenyl-2-phenoxylethanol, and 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-ol were selected as the model compounds to react in the CuFeS₂/H₂O₂ oxidation system. As shown in Figures 5, S3 and S4, all the model compounds not only have high conversion yield over the oxidation reaction (over 85%), but also achieved selectivities of 21.70%–58.70% towards OA. These results demonstrate that the aromatic ring could be decomposed into OA, thus proving the feasibility of this oxidation system for use in the degradation of lignin (Scheme 1). In addition, for 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-ol the major product is glycolic acid (42.37%), whereas the yield of OA is only 21.7%, indicating the insufficient oxidation of the model compound under such reactive condition.

3.4 Depolymerization of lignin

The activity of the CuFeS₂ catalyst was evaluated in the depolymerization of lignin; this was dissolved in DMF and analyzed by means of GPC (Figure 6). In the case of lignin, a strong peak was observed, implying that this peak must be arising from the presence of high-molecular-weight lignin. On the contrary, after reaction at both 60°C and 100°C, the peak disappeared, and a new weak peak appeared for low-molecular-weight products, implying that the lignin has been converted into small molecular products. These contrasting analyses indicate that lignin is almost completely degraded.

3.5 Product separation and analysis

After reaction, the mixture was filtered first and the solid fraction was washed with deionized water thrice. Then the filtrate was collected and divided into three parts, while the residue was dried at 80°C constantly. The first one was diluted by deionized water for the qualitative and quantitative analyses of the deliquescent product by means of LC-MS and HPLC. The second part was extracted by ethyl acetate, and then identified and measured by means of gas chromatogram (GC) and gas chromatography-mass

spectrometry (GC-MS) with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The conversion of lignin was calculated through the weight losing ratio of lignin [Eq. (1)]. Yields of MA, propanedio acid (PA), fumaric acid (FA), and FoA as well as other unknown products were evaluated according to the similar method based on the HPLC results. Therefore, the selectivity of DCAs was evaluated in terms of yield and conversion. These are calculated respectively as shown in Eq. (3).

$$C_L(\%) = \text{Conversion of lignin} = (W_L - W_R) / W_L \times 100\% \quad (1)$$

$$Y_o(\%) = \text{Yield of OA} = W_o / W_L \times 100\% = (c_o \times V / W_L) \times 100\% \quad (2)$$

$$S_A(\%) = \text{Selectivity of different acids} = Y_A(\%) / C_L \quad (3)$$

where W_L , W_R , and W_o represent the weight of lignin, residues, and OA, respectively; V is the volume of the diluted filtrate; and c_o is the concentration of OA, which could be calculated by standard curve.

The third part of the filtrate was dried via rotary evaporation and then dissolved in D₂O for the detection of ¹³C NMR spectra. As shown in Figure 7, the peak at $\delta = 170$, 176 ppm indicates the presence of C=O groups, which belong to aldehydes, carboxylic acids, or aroxyacetic structures. In terms of carboxylic acids, they are products

Figure 7: ¹³C NMR spectra of lignin solid and the liquid degradation product catalyzed by the CuFeS₂ nanoparticles.

of burning aromatic units. Obviously, compared with the substrate, methoxyl groups are not detected after the reaction, which illustrates that the aromatic methoxyl groups and β -O-4 bonds have been broken. As for the signal at δ =129 and 134 ppm, these correspond to the C₂ and C₆ and C₃ and C₅ in aromatic units, respectively. We also attribute the signal at δ =28 to the CH₂ groups. Hence, the results showed that the CuFeS₂ nanoparticle is an alternate catalyst for catalytic upgrading lignin.

3.6 Effect of reaction conditions

After reaction, the diluted filtrate was analyzed by means of HPLC. Figure 8 shows the typical HPLC trace of the degraded product. The HPLC trace of the product liquid delivers the message that OA is the predominant product. In addition, there are some weak peaks representing different DCAs respectively: although its peak is so weak, SA is the secondary chemical followed by SA and acetic

acid (AA), which comes from the buffer solution. As for the other peaks, including MA, PA, FA, and FoA, unfortunately, HPLC is unable to detect all the compounds from lignin. Based on the LC-MS and GC-MS analyses of the degradation products, we cannot identify whether other chemicals are oligomers with low-weight-molecular characteristics or are mixtures of aromatic compounds. Hydrogen peroxide is the critical parameter for lignin degradation in water using the CuFeS₂ nanoparticle as a catalyst. The dosage of H₂O₂ is thus decided by the amounts of lignin added. As shown in Figure 9A and B, with the increased dosage of hydrogen peroxide, the amount of DCAs arise gradually, whereas the yield of DCAs reaches its maximum when the H₂O₂ dosage reaches 2.0 ml. Meanwhile, the selectivity of OA could surpass 30%. In our catalytic oxidation system, the CuFeS₂ nanoparticle plays another important role. The formation of HO[•], the reactive species that disrupt the lignin linkages, is generated by the Cu²⁺ and Fe²⁺ redox reactions on the surface of the CuFeS₂ nanoparticle. According to the previous discussion, the range of nanoparticle size is similar. We could eliminate the influence of nanoparticle size on the product distribution. However, the role of the nanoparticle dosage should not be ignored. As shown in Figure 10, when the dosage of the catalyst reaches 10 wt% and 15 wt%, although their DCAs yields are approximate, the former has higher oxalate selectivity than the latter. Hence, the stability of hydrogen peroxide in the reaction system is a key factor affecting reaction efficiency. A superfluous catalyst may accelerate hydrogen peroxide decomposition into O₂. Moreover, reaction time affects the yields of DCAs during the lignin depolymerization process when the temperature reaches 60°C with 10 wt% catalyst for 5 h (Figure 11). Obviously, the yield of DCAs is at its maximum when the time reaches 5 h. After 5 h, the content of carboxylic acids, especially OA, declines sharply, and this may be ascribed to the breakdown of OA to FoA or CO₂. Thus, we selected the optimum conditions for the reaction time as 5 h. Meanwhile, temperature is another key factor in the reaction, as shown in Figure 12, the yield of DCAs was curved with an upward trend from 20°C to 60°C. This can be attributed to the formation of HO[•], which we explored via the heterolytic cleavage of the peroxy bond (O-O) in H₂O₂. When the temperatures reached 80°C and 100°C, it exhibited a downward trend because the H₂O₂ has been broken down to O₂.

Figure 8: Typical HPLC curve of the product (A), and the enlargement curve of indicated part (B).

3.7 Mechanisms

According to the trend of product distribution, the content of OA increases with the reduction of the four-carbon

Figure 9: Effect of oxidation reaction: (A: large, B: small) the dosage of H₂O₂.

Figure 10: Effect of the amount of CuFeS₂ on the oxidation reaction.

Figure 12: Effect of reaction temperature on the oxidation reaction.

Figure 11: Effect of reaction time on the oxidation reaction.

acids. Identically, the change in the yields of FoA and OA is the opposite. The suggested reaction hypothetical mechanisms are shown in Scheme 2. The presence of

transition metal catalysts (e.g. Fe, Cu, Mn) can help generate the reactive free-radical species from hydrogen peroxide to accelerate the degradation of lignin into o- and p-quinone structures [8, 16]. HO[•] and HOO[•] formed from the cleavage of the hydrogen peroxide play an essential role in oxidation of lignin to destroy its aromatic structure and generate carboxylic or DCA. The oxidation processes could be mainly divided into four steps. The transition metal could facilitate hydrogen peroxide decomposition into free-radical (HO[•]) and molecular oxygen [17]. Hence, these ions have the potential positive ability to substantially enhance the yields of lignin oxidation by hydrogen peroxide in order to generate DCAs.

In addition, a radical pathway for the oxidation catalytic processes has been illustrated (Scheme 2B). The CuFeS₂/H₂O₂ catalyst system increases the content of HO[•] and surface molecular oxygen so that the yield and selectivity of aromatic aldehydes are improved. These phenolic units of lignin can be converted to quinones, including o-quinone and p-quinone, and this conversion has already

Scheme 2: Possible degradation mechanism of lignin over the CuFeS₂ nanoparticles.

been proven through the Dakin-like oxidation reaction. It is noteworthy that H₂O₂ could more efficiently generate free-radicals in the presence of the CuFeS₂ nanocatalyst. The free-radical accelerates the oxidation of lignin being converted to quinone structure, which could be attacked by hydroperoxide anions to yield aromatic ring cleavage products (Scheme 2C). Then, o-quinone structures have been oxidized to muconic acids, whereas p-quinone structures could generate four-carbon acids (malic acid, MA, FA, etc.) and OA. Finally, lignin being oxidized completely by hydrogen peroxide has led to the generation of OA, FoA, and CO₂ as the final products (Scheme 2D) [16, 18, 19].

4 Conclusion

First, the CuFeS₂ nanoscale crystals have been synthesized to increase the contact-surface area of the metal ions and hydrogen peroxide in deionized water; this process facilitated the formation of HO• and HOO•. Then, the as-prepared catalyst was used to successfully degrade native lignin into carboxylic acid under the mild reaction condition. The procedure yielded excellent catalysis activity in terms of the oxidation of lignin. The conversion of native lignin to small fragments is over 85% based on the CuFeS₂/H₂O₂ reaction system. Meanwhile, the presence of

HO[•] contributes to the high selectivity (more than 30%) of OA. Both yield and selectivity have significant potential in the use of native lignin as a renewable feedstock to produce valuable chemicals. In addition, developing a mild-condition catalytic system is a key point in establishing a competitive lignin conversion process. The application of nanosized metal catalysts for use in lignin degradation is an untapped area with significant potential for the production of value-added chemicals in the future.

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Conflict of interest statement: The authors declare no conflicts of interest.

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Bionotes

Zhihao Bi

Zhihao Bi obtained his BS degree in 2014 from Anhui University. Currently, he is a PhD candidate at the University of Science and Technology of China. His study focuses on biomass conversion.

Zhihao Li

Zhihao Li obtained his BS degree in 2014 from South China University of Technology. Currently, he is a student at the University of Science and Technology of China. His study focuses on biomass conversion.

Lifeng Yan

Lifeng Yan obtained his PhD degree in Physical Chemistry from University of Science and Technology of China (USTC) in 2001. He is now a full professor in the School of Chemistry and Material Sciences, USTC. His studies focus on biomass conversion, degradable polymers for nanomedicine, and green catalysis.