A general route of using lignite depolymerized derivatives for catalyst construction: insights into the effects of the derivative structures and solvents

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S1 Studies of the preparation conditions of Cu-DM catalyst

In the preparation of Cu-DM, Cu (CH$_3$COO)$_2$·H$_2$O and DM catalysts with mass ratios of 1:4, 1:2, 1:1, 2:1 and 4:1 were prepared in order to determine the appropriate ratio of copper precursor to DM. The phenomenon of centrifugation for each proportion of samples was shown in Figure S1. It could be seen from the figure that DM presented a brown solution in water without copper. When the ratios of the two were 2:1 and 4:1, the centrifugal supernatant was dominated by the green color of copper ions, and the brown color of DM disappeared. It was believed that the coordination combination of carboxylic acids and copper precursor in DM was sufficient at this time, forming a large amount of precipitation, and Cu$^{2+}$ was in an excessive state. In order to further screen out the most suitable ratio, the catalytic oxidation of benzyl alcohol to benzaldehyde was used as a model reaction to investigate the activity of the two catalysts, as shown in Table S1. The results showed that the conversion and selectivity of 2:1 were higher than those of the ratio of 4:1, and thus the ratio of copper to DM was ultimately chosen as 2:1.
Figure S1  Optical images of Cu-DM catalysts prepared at different mass ratios of 

$\text{Cu(CH}_3\text{COO)_2 \cdot 8H}_2\text{O}$ to DM

Preparation condition: 30°C, 3h.

Table S1. Comparison of the catalytic activities of Cu-DM catalysts prepared under different conditions.

| Sample     | Conv.% | Yield% | Sel.% |
|------------|--------|--------|-------|
| Cu-DM (2:1)| 46.5   | 43     | 92.6  |
| Cu-DM (4:1)| 35.9   | 34.3   | 95.4  |

Reaction conditions: 80 °C, 1.5 h; alcohol (1 mmol), Catalyst(40mg), Na$_2$CO$_3$ (1 mmol), TEMPO (0.5 mmol), DMF (5 mL), O$_2$ (0.1 MPa).

S2. Characterization results of Cu-DM catalyst
Figure S2. Characterization of the as-prepared Cu-DM catalyst by SEM (a), EDS (b), XRD spectra (c), FTIR pattern (d), XPS spectrum (e) and N$_2$ adsorption-desorption isotherms (f, inserted figure, pore size distributions).

SEM analysis was used to study the morphology of Cu-DM, as shown in Figure S2a, Cu-DM presented as small aggregates composed of irregular particles. EDS characterization of Cu-DM showed that there were signal peaks of Cu and I elements. The crystal structure of Cu-DM was characterized by powder XRD, as shown in Figure S2c. The results showed that Cu-DM had an amorphous structure, but it had the diffraction peak of CuI crystal, indicating that CuI and Cu-DM co-existed in the amorphous Cu-DM structure$^1$. Compared with the FTIR spectrum of DM, the Cu-DM
sample presented C=O stretching vibration peak at 1589 cm\(^{-1}\) and C-O symmetric stretching vibration peak at 1374 cm\(^{-1}\). Meanwhile, the Cu-O specific stretching vibration peak at 474 cm\(^{-1}\) and 1094 cm\(^{-1}\), which proved the successful combination of some copper and oxygen-containing functional groups in DM (Figure S2d).

In order to reveal the chemical state of copper in Cu-DM, the local environment of Cu species in catalyst was detected by XPS (Figure S2e). In Cu2p core level photoelectron spectra, the two peaks between 950.0 and 965.0 eV are Cu 2P 1/2 electron energy combining center peak and satellite peak. The main Cu 2p3/2 signal was composed of two contributions at 932.7 and 934.7 eV, where the former was assigned to Cu\(^{+}/0\) and the latter to Cu\(^{2+}\). Cu\(^{+}\) and Cu\(^{0}\) are hard to discriminate because they only have a difference of ~0.3 eV difference in binding energy, whereas Cu\(^{+}/0\) and Cu\(^{2+}\) have a difference of more than 2 eV. The appearance of satellite peaks between 937.0 and 947.0 eV also confirmed the existence of divalent copper. Therefore, the prepared Cu-DM catalyst contained both Cu\(^{+}/0\) and Cu\(^{2+}\). Characterized by SEM-EDS and XRD, Cu\(^{+}/0\) and Cu\(^{2+}\) correspond to CuI and Cu-DM respectively, and they existed together.

The nitrogen adsorption-desorption isotherms showed that the Cu-DM catalyst was type IV isotherm, with hysteresis loops characteristic of mesoporous materials centered around 12 nm (Figure S2f) and the specific surface area 242.8m\(^2\) g\(^{-1}\).

**S3. Activity comparison of Cu-DM with other benzyl alcohol oxidation catalysts**

The performance of the prepared Cu-DM catalyst was compared with other commonly reported catalysts for aerobic oxidation of benzyl alcohol (Table S2). It
was found that the Cu-DM catalyst prepared in this work showed similar or even better performance than other catalysts (Entries 2-11) under mild conditions. Only 1.5 h was needed to reach a yield of higher than 90% at 120 ºC and the amount of catalyst was lower than other catalysts. Compared with the catalysts reported in other literatures, the Cu-DM catalyst constructed in this work had some obvious advantages. On one hand, the raw materials for the preparation of the catalyst are the DM obtained by RICO of lignite, which are more common, low-cost, and naturally available. On the other hand, the preparation process of the catalysts is simpler than other catalysts (e.g. Cu$_3$(BTC)$_2$ MOFs) because DM can be used directly with no need of complex purification in water. These advantages combining with the excellent activity and selectivity of the catalyst, made the catalyst competitive among the analogues reported in the literatures.

**Table S2** Activity comparison of Cu-DM with other benzyl alcohol oxidation catalysts

| Entry | Catalyst | T (ºC) | t (h) | Yield (%) | Conv. (%) | Sel. (%) | Ref. |
|-------|----------|--------|-------|-----------|-----------|---------|------|
| 1     | Cu-DM    | 120    | 1.5   | 90.5      | 92.7      | 97.6    | This work |
| 2$^b$ | Cu(OAc)$_2$$\cdot$H$_2$O | 80     | 1.5   | 94.3      | 96.0      | 98.2    | 9    |
| 3$^c$ | Cu-Dpps  | 100    | 2.0   | 90.0      | 90.6      | 99.4    | 9    |
| 4$^d$ | Cu$_3$(BTC)$_2$ | 75     | 22.0  | 91        | -         | -       | 10   |
| 5$^e$ | Cu$_3$(BTC)$_2$ | 75     | 3.0   | 96        | 97       | >99     | 11   |
| 6$^f$ | Cu$_3$(BTC)$_2$ | 75     | 3.0   | 97        | >99      | >98     | 8    |
| 7$^g$ | SPS-Cu (II)@Cu$_3$(BTC)$_2$ | 75     | 8.0   | >99       | -        | -       | 12   |
| 8$^b$ | Cu(I)/NMI | 25     | 24.0  | 44        | -        | -       | 13   |
| 9$^i$ | (bpy)Cu(I) | 27     | 3.0   | 95        | -        | -       | 14   |
Typical reaction conditions were as follows except for otherwise stated in the table: benzyl alcohol 1 mmol, catalyst 160 mg, TEMPO 0.5 mmol, Na$_2$CO$_3$ 1 mmol, DMF 5 mL, O$_2$ 0.1Mpa.

The homogeneous property, difficult to recycle.

Dpps: depolymerized products of lignite by alkali-oxygen oxidation; benzyl alcohol 1 mmol, catalyst 200 mg, TEMPO 0.5 mmol, Na2CO3 1 mmol, DMF 5 mL, O2 0.1Mpa.

BTC: Trimesic acid. Benzyl alcohol 0.925 mmol, catalyst 150 mg, TEMPO 288 mg, Na$_2$CO$_3$ 85 mg, acetonitrile 5 mL, oxygen atmosphere.

The Cu$_3$(BTC)$_2$ MOFs synthesized in CO$_2$-expanded DMF, benzyl alcohol 0.185 mmol, catalyst 30 mg, TEMPO 0.5 equiv, Na$_2$CO$_3$ 1 equiv, DMF 1 mL, O$_2$ 0.1 MPa.

The Cu$_3$(BTC)$_2$ MOFs synthesized in P104/PEG solution (P104=EO$_{27}$PO$_{61}$EO$_{27}$, PEG=Poly(ethylene glycol)), benzyl alcohol 0.185 mmol, catalyst 30 mg, TEMPO 5 mg, acetonitrile 1 mL, O$_2$ 0.1 MPa.

SPS-Cu(II)@Cu$_3$(BTC)$_2$ catalyst consisted of a functional sulfonated-polystyrene (SPS) core, a porous Cu$_3$(BTC)$_2$ shell and an active Cu(II) interface between the core and shell. Benzyl alcohol 1 mmol, catalyst 2 mol%, TEMPO 0.09 mmol, acetonitrile 5 mL, O$_2$ 0.1 MPa and 1 mmol nitrobenzene.

Homogeneous Cu(I)/NMI/TEMPO. Benzyl alcohol 5 mmol, NMI 0.5 mmol, CuI 0.25 mmol, TEMPO 0.25 mmol, CH$_3$CN 5 mL, air.

Pyridine(bpy) as a ligand, Cu(OTf) 5 mol %, bpy 5 mol %, TEMPO 5 mol %, and NMI 10 mol % in MeCN 0.2 M.

P-toluenesulfonic acid (OTs) was used to construct the catalyst, catalyst 0.1 mmol, BnOH 10
mmol, Chloroform 10 g, $n(H_2O):n(BnOH) = 6:1$.

$^k$ (Co$_9$(btc)$_6$(tpt)$_2$(H$_2$O)$_{15}$)-solvent (tpt = 2,4,6-tris(4-pyridyl)-1,3,5-triazine) was selected as the MOF precursor to construct Co/C-N700 catalyst. Benzyl alcohol 0.5 mmol, Co/C-N700 (10 mol% Co), H$_2$O 0.5 mL, air.

S4. Heterogeneity and reusability of Metal-DM catalysts

The cyclic usability and heterogeneity of the prepared Cu-DM catalyst were investigated, and the experimental results were shown in Figure S3. The reaction conditions were controlled so that the conversion rate of benzyl alcohol and the yield of benzyl formaldehyde reached about 50%, and the cyclic stability of the catalyst was investigated under these conditions. After the first reaction, the catalyst solids were separated by centrifugation, washed three times with DMF solvent, and transferred to the new reaction system for the second use. The following reaction conditions and treatment methods were the same as the first time. It can be seen from the Figure S3a that the reaction results were basically the same in the subsequent reactions, indicating that the catalytic activity remained basically stable after 5 cycles of cyclic use of the catalyst, and the catalyst had a good cycling usability.

The heterogeneity of catalyst was investigated in a similar way to that of Zr-DM in the main text. When the reaction was stopped after 30 min, the catalyst in the reaction system was removed by centrifugal separation, and the centrifugal supernatant continued to react under the original conditions, as shown in Figure S3b. As can be seen from the figure, after the catalyst was removed, the reaction time continued to be prolonged, and the yield of benzaldehyde was basically the same as that at 30 min,
which was significantly different from the reaction results with the catalyst, indicating that the reaction stopped immediately after the catalyst was separated by centrifugation. Therefore, the Cu-DM catalyst prepared were considered to be the heterogeneous catalyst.

Figure S3 Reusability(a) and heterogeneity(b) of the Cu-DM catalyst.

Reaction conditions: benzyl alcohol 1 mmol, catalyst 160 mg, TEMPO 0.5 mmol, Na₂CO₃ 1 mmol, DMF 5 mL, O₂ 0.1 MPa, (a) 60ºC, 90 min (b) 120 ºC.

Figure S4 Comparison of the freshly prepared and recycled Cu-DM catalysts after five reuses.

SEM of the fresh (a) and recycled catalyst (b), FTIR spectra (c), and XRD patterns (d).

The Cu-DM catalyst was characterized by SEM, XRD and FT-IR, and compared
with the Cu-DM catalyst. It can be seen that, compared with the newly prepared catalyst, the catalyst after recycling still exists in the form of particles (Figure S4a, b), with little change in the morphology and structure of the main body. As shown in Figure S4c, d, it can be seen from the FTIR spectrum that the main infrared characteristic peak of the catalyst still exists after cycling, and there is no significant change compared with the fresh catalyst. The characteristic peak of sodium carbonate in the XRD pattern is caused by the fact that the sodium carbonate added in the oxidation reaction is not separated out. Meanwhile, the new peak (1444 cm\(^{-1}\),879 cm\(^{-1}\)) in FTIR is also caused by sodium carbonate residue. The analysis of catalyst structure showed that Cu-DM had no obvious structural changes before and after cyclic use, and the catalyst had good structural stability.

**S1.5 Analysis of catalytic mechanism**

According to literature reports, the oxidation mechanism of alcohols catalyzed by copper catalysts varies greatly with the composition of the catalyst system and the reaction conditions. Under the condition of the participation of TEMPO, the reaction mechanism mainly includes two kinds. One kind thinks that TEMPO\(^+\) is a real oxidant. TEMPO is first oxidized to TEMPO\(^+\), and then oxidized to alcohols by TEMPO\(^+\), making the system acidic. The other is the direct oxidation of alcohols by the TEMPO radical, with the help of copper ions, which requires the presence of a base. According to the experimental results of Cu-DM catalyst, the system in this paper requires the presence of alkali to play a good catalytic effect. Therefore, the mechanism of Cu-DM catalytic oxidation of alcohols is more in line with the second
one. The specific mechanism is as follows: the substrate benzyl alcohol first forms an intermediate with the copper active center of Cu-DM catalyst, and TEMPO is then combined with the copper active center of the intermediate. In this process, benzyl alcohol is oxidized into benzaldehyde by Cu-DM and TEMPO. Meanwhile, divalent copper and TEMPO in Cu-DM catalyst were reduced to monovalent copper and TEMPOH, respectively. Subsequently, monovalent copper and TEMPOH were oxidized into divalent copper and TEMPO by oxygen, and continued to participate in the reaction until the substrate was completely consumed and converted into benzaldehyde \(^{21,23,24}\).

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