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99% yield of 2,5-dihydroxymethylfuran (DHMF) was achieved from biomass derived 5-hydroxymethylfurfural (HMF) with a novel CuNPs@ZIF-8 using a relative lower hydrogen pressure and shorter reaction time. The activation energy of transformation of HMF to DHMF is only 39 kJ/mol and TOF valve reached 21 h⁻¹. The coexistence of Cu¹ and Cu⁰ in Cu species is demonstrated to be high active for the hydrogenation of HMF to DHMF.

5-Hydroxymethylfurfural (HMF) is widely regarded as a key platform intermediate for the conversion of lignocellulosic biomass into valuable chemicals and fuels as the presence of – OH, -C=O and furan ring functional group.¹⁻³ In particular, the selective hydrogenation of HMF to 2, 5-dihydroxymethylfuran (DHMF) is highly desired for that DHMF is an essential precursor applied in the synthesis of resins, pharmaceuticals, artificial fibers and functional polymers.⁴ The conversion of HMF to DHMF can be regarded as the hydrogenation of a heteroaromatic aldehyde, thus a series of derivatives such as 5-



Scheme 1. Reaction path for the hydrogenation of HMF to DHMF

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Cu¹-Cu⁰ bicomponent CuNPs@ZIF-8 for high-selective hydrogenation of biomass derived 5-hydroxymethylfurfural

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methylfurfural (MF), 5-methylfurfuryl alcohol (MFA) and other chemicals could be formed as by-products (Scheme 1).

To achieve an efficient conversion of HMF to DHMF, considerable catalyst systems have been investigated with various hydrogen sources, for example, alcohols,⁵⁻⁷ formic acid,^{8, 9} silanes¹⁰ and molecular hydrogen (H₂).^{2, 11, 12} Among them, catalytic hydrogenation with H₂ obviously represents an attractive alternative with more atom-economic. So far effective catalysts for the selective hydrogenation of HMF to DHMF with H₂ are typically rare and high-cost noble metal ones (e.g., Au,^{13, 14} Pt,¹⁵ Pd,¹⁶ Ru^{17, 18} and Ir^{19, 20}. Unremitting efforts have been devoted to design and synthesis of high-performance noble metal free catalysts for DHMF production, among which copper-based materials show the highest activity and selectivity.²¹ However, high H₂ pressure (\geq 5Mpa) and long reaction time (\geq 5h) are required in most cases (Table S1). Thus, to develop high-efficiency Cu-based catalysts could improve the reaction rate via controlling the particle size and increasing the surface area of acquired catalysts such as Cu-nanoparticle (Cu-NP) catalysts, which does not rely on high H₂ pressure, is highly desirable.



Scheme 2. Schemetic illustration of the synthesis of CuNPs@ZIF-8

On the other hand, the small metal nanoparticles (NPs) are prone to aggregate and thermodynamically unstable during the

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reaction, resulting in the decline of activity.^{22, 23} The catalytic performance of metal was known to be significantly affected and/or eventually determined by the nature of supporters. In this context, metal organic frameworks (MOFs) could be a ideal candidate because (1) they posses large surface area and tunable pore sizes, which are desirable for hosting NPs and ensuring high NP dispersion; (2) their permanent pore structure allows the accessibility of substrates into the NP active sites; (3) stabilize NPs prevent their framework can and agglomeration/growth of NPs; and especially, (4) their unique property of H₂ adsorption is beneficial to the catalytic hydrogenation.²⁴ In view of the high chemical and thermal stability, ZIF-8, a zeolite-type MOF, has been widely studied as an effective matrix to encapsulate various metal NPs (e.g., Au, Pt, Pd,Ru, Ni) and improve their catalytic performance in recent years.²⁵⁻²⁹ In our recent work, effective catalysts have been applied for HMF production, achieving high HMF yields.^{3, 30-32} In this work, we report excellent ZIF-8 encapsulated Cu NPs (CuNPs@ZIF-8) catalysts for the conversion of HMF to DHMF (>99% conversion and 99% yield), which presents the first successful example of MOF-supported noble metal free catalysts for the hydrogenation of HMF.

The three-step synthesis of CuNPs@ZIF-8 was shown in Scheme 2 (also see Supporting Information for more details). Briefly, ZIF-67 was first synthesized using the modified room-temperature precipitation method.³³ Subsequently, Cu²⁺ were incorporated and dispersed in ZIF-8 framework. Finally, CuNPs@ZIF-8 was obtained by the fast reduction with NaBH₄.



Figure 1. (a) XRD patters for ZIF-8 and CuNPs@ZIF-8. (b) N_2 sorption isotherms for ZIF-8 and CuNPs@ZIF-8. (c) H_2 sorption isotherms for ZIF-8 and CuNPs@ZIF-8. (d) XPS spectra for CuNPs@ZIF-8. (e) Cu LMM Auger spectra of CuNPs@ZIF-8

The powder X-ray diffraction (XRD) pattern of synthetic ZIF-8 was consistent with a simulated analogue, proving the formation of pure phase of ZIF-8 (Figure S1). XRD pattern of

CuNPs@ZIF-8 (11.5wt% Cu as determined by ICP-QES), showed that the framework structure of ZIF-8 Was¹0 HCManged⁰ upon introduction of Cu NPs (Figure 1a, Figure S2). No visible diffraction peaks were detected for Cu NPs, which indicated that ZIF-8 encapsulated Cu NPs were small. N₂ sorption studies of CuNPs@ZIF-8 showed appreciable decreases in BET surface areas compared to parent supporters, revealing that Cu NPs were dispersed in ZIF-8 framework (Figure 1b, Table S2). H₂ sorption experiments evidently demonstrated the H₂ enrichment capability of CuNPs@ZIF-8, which favoured the catalytic hydrogenation (Figure 1c).



Figure 2. (a)TEM image of ZIF-8. (b,c)TEM image of CuNPs@ZIF-8. (d)HRTEM image of CuNPs@ZIF-8.

The chemical nature of the CuNPs@ZIF-8 was characterized by X-Ray photoelectron spectroscopy (XPS). Cu $2p_{3/2}$ peak around 932.4 could be assigned to Cu⁰/Cu¹ (indistinguishable), while no obvious shake up peak was observed, excluding the presence of CuO (Figure 1d).³⁴ Cu LMM Auger spectra corresponded to the typical Cu¹ (916.5) and Cu⁰ (918.4) peaks, demonstrating that Cu¹ and Cu⁰ coexisted in the Cu species (Figure 1e).³⁵

The size and distribution of ZIF-8 immobilized Cu NPs were characterized by transmission electron microscopy (TEM) subsequently. As shown clearly in the Figure 2a, synthetic ZIF-8 was composed of microcrystals with uniform morphology. After in-situ fast reduction of Cu²⁺, highly dispersed nano Cu species with size around 2~4nm were observed (Figure 2b, 2c). And obviously crystalline interplanar spacings in Cu NPs can be corresponded to Cu⁰/Cu¹ (Figure 2d).

The catalytic activity on the selectivity hydrogenation of HMF for the resulting composites was evaluated in ethanol. As shown in Figure 3a, around 99% DHMF yield was achieved at 140 °C for 3h with 2MPa H_2 , suggesting that CuNPs@ZIF-8 was enable to

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effectively catalyze HMF to DHMF. Detailed reaction condition inverstigations showed that the DHMF production rate can be improved by incresing H_2 pressure, reaction temperature and catalysts dosages without visible side reactions (Figure S3-S5), which further proved the high selectivity of CuNPs@ZIF in hydrogenation.

The kinetic studies HMF conversion to DHMF were investigated to further assess the catalytic activity of the Cu NPs@ZIF-8. Due to the high selectivity of DHMF, pseudo-firstorder kinetics is assumed in the investigated conditions using the equation of $\ln c_t/c_0 = -kt$, where c_t is the concentration of HMF after a reaction time of t, c_0 is the initial concentration of HMF, and k is the rate constant. As shown in figure 3b, the linear relationship between Inct and t supported the hypothesis of pseudo-first order for HMF to DHMF transformation. The rate constant (k) increased with the increase of reaction temperature, proving that higher reaction temperature can notably promote the conversion reaction. According to the Arrhenius equation of $\ln k = \ln A - Ea/RT$, The apparent activation energy (Ea) of the conversion of HMF over CuNPs@ZIF-8 is about 39 kJ/mol (Figure 3c), which is lower than that of 104.9 kJ/mol for Ru/C catalyst.³⁶



Figure 3. (a) Hydrogenation of HMF to DHMF by CuNPs@ZIF-8. (b) The kinetics profiles for the conversion of HMF to DHMF (fitted by first-order assumption) with CuNPs@ZIF-8 as catalyst. (c) Arrhenius plots for the conversion of HMF to DHMF. (d) The TOF values in various catalyst dosages. (e) The TOF values in various H₂ pressure. (f) Hydrogenation of HMF to DHMF in various catalyst.

On the other hand, there is a large rise in the TOF value from 8 to 16 and 21 upon increasing the H₂ pressure and Cu dosages, respectively (Figure 3d and 3e). Besides the ultrasmall size of Cu NPs and H₂ enrichment capability of ZIF-8, these high TOF values may be determined by the coexistence of Cu¹ and Cu⁰ in Cu species. To remove the supporter effect of ZIF-8, Cu⁰, Cu⁰/Cu¹,

Cu⁰@MCM-41, Cu⁰/Cu¹@MCM-41, Cu⁰@/C and reCu⁰/Cu¹@C were prepared to understand if the synergistic leffect between Cu¹ and Cu⁰ exists without or with other common supports (see supporting information for preparation details, see Figure S6-S7 for XRD pattren). As shown in figure 3f, the TOF values of Cu¹/Cu⁰ with/without supports were much higher than that of

Cu⁰, directly proving that the doping of Cu¹ in Cu⁰ species can

promote the hydrogenation of HMF.

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Figure 4. (a) leaching experiment of CuNPs@ZIF-8. (b) catalyst recycling studies for CuNPs@ZIF-8. (c) XRD patters of CuNPs@ZIF-8 before and after 4 catalytic runs. And (d) TEM images of CuNPs@ZIF-8 after 4 runs.

The heterogeneous nature of the CuNPs@ZIF-8 was checked by removing catalysts from the solution after 1h of reaction, and heating the filtrate for another 2 hours (Figure 4a). ICP-OES analysis of the reaction solution conformed that the content of Cu was below the detection limit, suggesting no obvious Cu leaching during the reaction. The reusability/stability of the nanocatalyst CuNPs@ZIF-8 is important for further practical applications. Our prepared Cu-NPs could be recycled and reused for up to four runs without significant loss of catalytic activity and selectivity (Figure 4b), suggesting that the highly dispersed Cu-NPs have been effectively immobilized by the frameworks of ZIF-8.

The crystallinity of CuNPs@ZIF-8 was well maintained after the reaction as demonstrated by XRD (Figure 4c), and two obvious peaks of 36.5° (Cu₂O, PDF# 77-0199) and 43.3° (Cu, PDF#85-1326) were observed, which should be due to (1) the increase of Cu-NP size or (2) the shifting of Cu-NP from the framework of ZIF-8 into the surface of ZIF-8. As shown in TEM images (Figure 4d), only ignorable Cu species existed in the outline of ZIF-8, while a slight aggregation was observed, which was consistent with the XRD analysis. Thus, the slight decrease in the activity is ascribed to the increase of CuNP size as evienced by TEM. For comparison, NiNPs@ZIF-8 and CoNPs@ZIF-8 were also prepared, and exhibited lower

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selectivity than CuNPs@ZIF-8 (Figure S8), further demonstrating the key role of the Cu particles in hydrogenation.

Selective hydrogenation of various unsaturated aldehydes over CuNPs@ZIF-8 were also investigated subsequently (Table 1). Biomass-derived furanic aldehydes such as furfural and 5methylfurfural, which are also very important platform chemicals, gave high yields to the correponding alcohol products. With unsaturated aromatic aldehydes and pyridine aldehydes as substrates, the desired products were also obtained in satisfying yields, indicating that CuNPs@ZIF-8 has high selectivities and activities for the transformation of unsaturated aldehydes to alcohols.

 Table 1. Selective hydrogenation of various unsaturated aldehydes

 over CuNPs@ZIF-8



Conditions: HMF(0.5mmol), CuNPs@ZIF-8 (7.2mol% Cu), ethanol (5mL), H_2 (2Mpa), 3h, 140°C.



Scheme 3. Plausible mechanism for the conversion HMF to DHMF by CuNPs@ZIF-8

According to the above study, a possible reaction mechanism was proposed in Scheme 3. Firstly, an aldehyde group was attracted by Cu¹ species via the interaction between the lone pair electrons of oxygen and the strong electron-deficient Cu center. Meanwhile, hydrogen molecules dissociate at the Cu⁰ site and move to ZIF-8 supporter via so-called 'hydrogen spillover' effect.³⁷ Then, the absorbed aldehyde reacts with the dissociated hydrogen to produce alcohol.

In conclusion, highly dispersed Cu NPs with small size have been successfully prepared using ZIF-8 as template, which shows very high selectivity and activity for hydrogenation of HMF to DHMF. Compared to other Cu-based catalysts, this wok has advantages of higher selectivity, lower H₂ pressure and shorter reaction time. The low activation energy and high TOF value are also achieved. This is also the first example of MOF- encapsulated Cu NPs for the selective hydrogenation of unsaturated aldehydes to alcohols POF utther hore, 013 He coexistence of Cu¹ and Cu⁰ in Cu species is demonstrated to be high active for the hydrogenation of HMF to DHMF.

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Conflicts of interest

There are no conflicts to declare.

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