Non Noble-Metal Copper–Cobalt Bimetallic Catalyst for Efficient Catalysis of the Hydrogenolysis of 5-Hydroxymethylfurfural to 2,5-Dimethylfuran under Mild Conditions

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ABSTRACT: The efficient catalysis of the hydrogenation of 5-hydroxymethylfurfural (HMF) to 2,5-dimethylfuran (DMF) over non noble-metal catalysts has received great attention in recent years. However, the reaction usually requires harsh conditions, such as high reaction temperature and excessively long reaction time, which limits the application of the non noble-metal catalysts. In this work, a bimetallic Cox-Cu@C catalyst was prepared via the pyrolysis of MOFs, and an 85% DMF yield was achieved under a reaction temperature and time of 160 °C and 3 h, respectively. The results of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), energy-dispersive X-ray spectroscopy (EDX) mapping, and other characterization techniques showed that the synthesis method in this paper realized the in situ loading of cobalt into the copper catalyst. The reaction mechanism studies revealed that the cobalt doping effectively enhanced the hydrogenation activity of the copper-based catalyst on the C–O bond at a low temperature. Moreover, the bimetallic Cox-Cu@C catalyst exhibited superior reusability without any loss in the activity when subjected to five testing rounds.

INTRODUCTION

The demand for energy in modern society is rapidly increasing with economic and social developments. Problems such as limited fossil reserves and environmental pollution caused by fossil fuel combustion are becoming increasingly critical. Therefore, it is urgent to seek a renewable energy source to gradually replace fossil energy sources. Biomass, with abundant reserves, is easily converted into liquid fuel and is expected to gradually replace the use of commercial fuel, even faster than other renewable energy sources such as wind energy and solar energy. The popular biomass-derived platform compound 5-hydroxymethylfurfural (HMF), obtained from lignocellulose and other carbohydrates, can be transformed into a high-quality biofuel 2,5-dimethylfuran (DMF). This biofuel is regarded as an alternative to commercial gasoline owing to its many excellent physical and chemical properties, including high energy density, high octane number, and high stability.

However, the conversion of HMF into DMF requires the selective hydrogenolysis of aldehyde groups and hydroxymethyl on HMF while protecting other functional groups to achieve an efficient and highly selective conversion, and this presents certain challenges. Noble-metal catalysts such as Pd and Ru show good activity but have a high cost. Currently, the development of copper, a non noble-metal catalyst, for HMF hydrogenation has received attention, owing to its low cost and relatively high selectivity. Brzezinska et al. reported a CuZnO catalyst applied in HMF hydrogenation to produce DMF, and the catalyst could achieve a DMF selectivity of up to 94% at 220 °C reaction temperature. Esteves et al. used a variety of supports to prepare supported copper catalysts for the selective hydrogenation of HMF; the Cu/Al2O3 catalyst could achieve 90% DMF selectivity at a reaction temperature of 150 °C, but the required reaction time was 10 h. Sarkar et al. reported a Cu-Pd@C catalyst obtained from the pyrolysis of Cu-MOFs. The catalyst achieved 96% DMF selectivity under very mild reaction conditions (120 °C for 7 h) for HMF hydrogenation. In this reaction system, noble metals play an important role. For copper-based catalysts without noble metals, it is difficult to achieve the HMF conversion to DMF at a low temperature in a short time.

Numerous studies have shown that copper-based catalysts have high selectivity for HMF conversion to DMF. However, copper-based catalysts without noble metals exhibit low hydrogenation activity for the C–O bond; consequently,
the HMF hydrogenation requires higher reaction temperatures (usually above 180 °C) or excessively long reaction times (usually more than 8 h) for the intermediate products such as 2,5-dihydroxymethylfuran (DHMF) to convert to DMF.

In recent years, catalysts derived from pyrolysis of metal–organic frameworks (MOFs) have shown excellent catalytic activity. The MOF-derived catalysts have attracted considerable attention because of their excellent activity in catalytic hydrogenation. Herein, we report the development of a copper-based bimetallic catalyst derived from MOFs for the selective hydrogenation of 5-HMF to DMF under mild conditions. High-resolution transmission electron microscopy, energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) were utilized to study the physical and surface properties of the catalyst. The cobalt doping was found to effectively promote the catalyst hydrogenation activity on the C−O bond. Under the optimal conditions, the catalyst achieved 100% HMF conversion and over 85% DMF yield under a reaction temperature and time of 160 °C after 3 h, respectively, and exhibited excellent recyclability.

## RESULTS AND DISCUSSION

**Catalyst Structure Characterization.** The XRD patterns of the Cu-MOFs and Co-Cu-MOFs (Figure S1) show Cu$_3$BTC$_2$ (BTC: 1,3,5-benzenetricarboxylic acid) crystal diffraction peaks (2θ = 11.6, 13.4, 17.5, 19.0°), indicating that Cu$_3$BTC$_2$ MOFs were successfully synthesized through this method. No new diffraction peak occurred in the XRD pattern of Co-Cu-MOFs compared with that of Cu-MOFs, and a new crystal structure was not formed, which was further confirmed via Fourier transform infrared spectroscopy analysis (Figure S2) of the precursor; the analysis results revealed that no new functional groups were formed on the Co-Cu$_3$BTC$_2$ precursor.

Furthermore, Cu-MOF catalysts derived under different pyrolysis temperatures were analyzed via XRD. Strong Cu diffraction peaks (2θ = 43.2°, 50.3°, 73.9°, ICSD: 70-3038) could be detected in all catalysts (Figure 1a), suggesting that most of the copper in the catalysts was reduced to Cu$_0$ after pyrolysis. However, weak CuO diffraction peaks (2θ = 35.6°, 38.8°, ICSD: 89-5899) were detected when the pyrolysis temperature was relatively low. As the pyrolysis temperature increased, CuO reduced to form Cu$_2$O, and the diffraction peak of Cu$_2$O (2θ = 36.4°, 42.3°, ICSD: 78-2076) increased. However, no diffraction peaks of Co or Co oxides occurred in the XRD patterns of the Co$_x$-Cu@C catalyst (Figure 1b) because the Co in the catalyst was highly dispersed and low in content, which accords with the inductively coupled plasma–atomic emission spectroscopy results (Table 1).

The nitrogen adsorption–desorption curves of the MOF-derived catalysts are of type IV with sharp adsorption in a relatively low pressure region (Figure S3), indicating the existence of micropores and mesoporous structures. The catalyst pore structure parameters are presented in Table S1. All of the catalysts showed a high specific surface area. When materials are highly porous, the diffusion rates of the substrates and the products are likely to be faster than the catalytic rate. As the pyrolysis temperature increased, the specific surface area
of the catalyst decreased, since the carbon structure of the catalyst collapsed at high temperatures. For the Co-doped catalysts, when the Co doping amount increased, both the catalyst surface area and pore size decreased, which is the result of the cobalt aggregation.

Figure 2 shows the electron microscopy analysis results of the MOF and MOF-derived catalysts. As shown in Figure 2a, the precursor has a typical octahedral structure, which agrees with relevant literature reports.27,28 The Cu$_3$BTC$_2$ synthesized via the static precipitation method had a smaller particle diameter, about 1–2 μm, than that synthesized via the traditional hydrothermal method.29 Also, there were no obvious differences in the shapes of the precursor before and after cobalt doping (Figure S5). After the pyrolysis treatment, the catalyst morphology significantly changed. The structure was transformed into an octahedral matrix embedded with spheres, and the diameter of the spheres was about 150 nm. The EDX mapping profiles (Figure 2d–f) of the catalyst showed strong copper signals around the sphere; the ball may be copper particles. Moreover, based on the signal distribution, the Co element was uniformly and highly dispersed on the catalyst.

The transmission electron microscopy image of the catalyst (Figure 2g–i) shows that the sphere was embedded in the octahedron. A significant contrast existed between the octahedral matrix and the spherical particles because the octahedral matrix mainly had a carbonaceous structure, and the spheres were metal particles. In addition, further magnification of the sphere revealed that the particles were covered with a carbonaceous shell; this finding is consistent with the results in the literature.30 Based on the above characterization analysis results, a schematic diagram of the structural changes during the catalyst synthesis process is presented in Scheme 1.

Figure 3 displays the XPS results of the catalyst. Figure 3a shows strong Cu 2p, C 1s, N 1s, and O 1s peaks and a weak Co peak. The high-resolution spectrum of Cu 2p (Figure 3c) shows a peak of Cu 2p$_{3/2}$ near 934 eV, which is decomposed into two peaks at 934.1 and 932.2 eV, corresponding to Cu$^{2+}$ and Cu$^0$/Cu$^+$, respectively.31−33 The ratio of the peaks of Cu$^+$/Cu$^0$ and Cu$^{2+}$ has been calculated and shown in Table S2. Similarly, in the Auger spectrum of Cu LMM (Figure 3d), peaks at 913.1, 917.1, and 920.8 eV correspond to Cu$^+$, Cu$^{2+}$, and Cu$^0$, respectively.34,35 The doublet separation between the 2p$_{3/2}$ and 2p$_{1/2}$ signals approaches 15.5 eV (Figure 3b), which agrees with the standard spectra of elemental cobalt, suggesting the existence of Co$^{3+}$ or Co$^{2+}$ species.36 The satellite peak at 789.6 eV corresponds to Co$^{2+}$, and the peaks at 785.2 and
780.5 eV correspond to the binding energies of Co$^{2+}$ and Co$^{3+}$, respectively, indicating that cobalt exists mainly in the form of oxides.37

Furthermore, the C 1s high-resolution XPS spectrum of the catalyst (Figure 3e) shows a sharp peak at 284.4 eV, caused by the hybridization of C sp$^2$ and C sp$^3$, which are mainly from the carbon structure of the catalyst. The wide peak near 289 eV corresponds to carbon nitride, indicating that the added PVP still retained a small amount of nitrogen in the catalyst after a high-temperature treatment.40,41 To further confirm the form of carbon in the catalyst, the catalyst was characterized via Raman spectroscopy. As shown in Figure S4, D and G bands were detected, and the $I_D/I_G$ ratio of the catalyst was less than 1, indicating that the carbon in the catalyst had a higher graphitization degree. From the N 1s high-resolution spectrum (Figure 3f), except for the nitrogen that formed carbon nitride, most of the nitrogen atoms remained in the catalyst as constituents of heterocyclic compounds.42

As shown in the Cu 2p high-resolution XPS spectrum and Auger spectrum, the undoped and doped catalysts had similar photoelectron binding energies and kinetic energies, and they also had similar atomic ratios, indicating that the Co doping had no significant effect on the chemical environment of copper. The C 1s and N 1s high-resolution XPS spectra of the catalyst were similar, which also shows that cobalt doping had little effect on the catalyst surface properties.

In summary, the above characterization results indicate that the precursor did not form new crystals or functional groups after cobalt doping; the cobalt was probably only loaded into the precursor. The XRD and XPS results indicate that the copper in the catalyst mainly existed as Cu$^+$ species and a small amount existed as Cu$^+$ species, and the cobalt mainly existed as CoO$_x$. According to the results of nitrogen adsorption–desorption and electron microscopy analysis, cobalt doping had no significant effect on the catalyst structure. Moreover, the XPS survey results show that cobalt doping did not significantly change the chemical environment of copper in the catalyst. Therefore, the Cu and CoO$_x$ nanoparticles may act as relatively independent active sites and play different roles in the catalytic process.

**Catalytic Performance in Selective Hydrogenation of HMF.** First, the effect of the pyrolysis temperature of the catalyst on the catalyst activity was studied. Different monometallic catalysts were prepared via precursor pyrolysis under different temperatures: 450, 550, 650, 750, and 850 °C. The results of the catalytic performance (Figure 4) depicted that almost all of the catalysts showed 100% HMF conversion. The catalyst prepared at 750 °C achieved the highest DMF yield of 92%. According to the above XRD analysis, this high DMF yield was due to the conversion of CuO to Cu$_2$O as the pyrolysis temperature increased. Previous studies have reported that Cu$^+$ species play an important role in the hydrogenation of HMF.29,43,44 Therefore, in this study on a bimetallic catalyst, the pyrolysis temperature of 750 °C was used for the catalyst preparation.

The monometallic catalyst achieved 100% HMF conversion and a 92% DMF yield, but the reaction required a temperature of 180 °C and a time of 4 h. However, our previous research has proved that the activity of the monometallic catalyst significantly decreases after a reaction.29 To enhance the catalyst stability and further reduce the requirements of the reaction conditions, metal doping is used to modulate the catalyst performance. The catalysts were separately doped with Co, Zn, and Ni. The corresponding catalysts were synthesized, and their activities were evaluated.

The results of catalytic performance are illustrated in Figure 5, compared with the performances of monometallic catalysts. The activity of the metal-doped catalysts was significantly improved. Cobalt doping had the most significant effect on the catalyst activity, with the DMF yield higher than that of the monometallic catalyst by 29.4%.

Subsequently, the cobalt doping amount was optimized, and catalysts with cobalt doping amounts of 5, 10, 20, 30, and 40% were synthesized. The catalytic performance results are illustrated in Figure 6. When the cobalt doping amount increased, the DMF yield first increased and then decreased. When the Co doping amount is too low, the rare CoO$_x$ sites
cannot effectively activate the C−O bond. However, excessive amounts of cobalt may accumulate and block the pores of the catalyst. When the doping amount was 20%, the maximum yield was obtained.

To research the effect of cobalt doping on catalyst activity, the catalytic performances of Co$_{20}$-Cu@C and Cu@C-N750 catalysts in the selective hydrogenation of HMF at different temperatures were investigated. As shown in Figure 7, at low temperatures, the Co$_{20}$-Cu@C catalyst showed higher yields of DMF and 2,5-dimethyltetrahydrofuran (DMTHF) than Cu@C-N750. At 180 °C, both catalysts showed similar activity results. This finding indicates that the cobalt doping modulated the low-temperature catalytic activity of the catalyst.

In addition, we optimized the reaction time (Table S4). After 3 h of reaction, an 85% yield of DMF could be obtained. The reaction time was further extended to 4−6 h, and the DMF yield did not significantly increase.

In summary, the research on the reaction conditions of catalytic hydrogenation shows that the Co$_{20}$-Cu@C catalyst could achieve the best activity results under 160 °C and 3 h reaction time, which were 100% HMF conversion rate and 85% DMF yield. Also, to compare the catalyst activity with those in the literature, recent reports on the use of copper-based catalysts for the hydrogenation of HMF to DMF are summarized in Table S3.17,18,33,45−50 As shown in Table S3, the catalyst synthesized in this study achieved an excellent DMF yield after a short reaction time at a relatively low temperature. The Co$_{20}$-Cu@C catalyst prepared by pyrolysis of MOF has a highly porous structure, and the active components of the catalyst are highly dispersed. When materials are highly porous, the diffusion rates of the substrates and the products are likely to be faster than the catalytic rate.

Role of Cobalt in the Selective Hydrogenation of HMF. The process of HMF hydrogenation to DMF can be simplified in the following two steps: (1) the hydrogenation of aldehyde groups on HMF (C=O bond) and (2) the hydrogenation of hydroxymethyl groups on intermediate products such as DHMF (C−O bond of the hydroxyl...
group). In previous studies, the hydrogenation of the C–O bond (hydroxyl group) was found to be the rate-determining step for the hydrogenation of HMF to DMF.\(^{19,51,52}\)

In the current study, the achieved catalytic performance was 100% HMF conversion for almost all catalysts, and the DMF yield was relatively large. The different DMF yields obtained by the catalyst were mainly for the different activities in catalyzing the hydrogenation of the C–O bond (hydroxyl group). Therefore, we assume that the cobalt doping may mainly increase the catalyst activity for the hydrogenation of the C–O bond (hydroxyl group), thereby increasing the DMF yield. To verify this assumption, an experiment was designed for research, as described below.

Furthermore, the catalysts before and after cobalt doping were used to evaluate the hydrogenation activities of 5-methylfurfural (MF) and 5-methylfurfuryl alcohol (MFA). The conversion rates of MF and MFA were determined by the hydrogenation activities of the catalyst for the C–O bond and the C–O bond (hydroxyl group), respectively. The catalytic performance results are illustrated in Figure 8. In the MF hydrogenation activity test, the difference between the results of the two catalysts was small, while in the MFA hydrogenation activity test, the cobalt-doped catalyst showed a higher conversion rate. The experimental results confirm the above assumption that the difference in catalyst activity before and after cobalt doping is mainly reflected in the hydrogenation of the C–O bond (hydroxyl group), and the cobalt doping successfully modulates the hydrogenation activity of the catalyst for the C–O bond (hydroxyl group).

Based on the above structural characterization and catalytic test results, a possible reaction mechanism for the hydrogenolysis process of HMF to produce DMF is proposed (Scheme 2). For the dissociation of hydrogen, first, the hydrogen molecule may interact with the Cu\(^0\) site on the catalyst, and then, the hydrogen molecule can be dissociated to form active hydrogen species. Subsequently, the carbonyl oxygen of HMF that has lone-pair electrons first adsorbs on the electrophilic Cu\(^0\) site, which will promote the activation of the C=O bond. Then, the hydrogenation of the carbonyl group is induced by Cu particles in combination with the active hydrogen species, leading to the formation of DHMF. The electrophilic Cu\(^+\) and CoO\(_x\) species, serving as Lewis acid sites,
can facilitate the polarization and activation of the C–O bond (hydroxyl group) in DHMF and MFA, leading to DMF production.\textsuperscript{53,54} In the case of reaction route 1, Cu\textsuperscript+ species play a key role in the activation. However, according to our previous research,\textsuperscript{29} Cu\textsuperscript+ is unstable during the reaction and is likely to be reduced. Therefore, the CoO\textsubscript{x} species in reaction route 2 play an important role in maintaining a stable and high activity of the catalyst, especially in the C–O bond (hydroxyl group) hydrogenation.

**Catalyst Recyclability.** To study the reusability of the Co\textsubscript{20}-Cu@C catalyst, the catalyst was subjected to multiple cycles. The cyclic performance results are shown in Figure 9a. The catalyst was subjected to five testing rounds, but the HMF conversion and DMF yield did not significantly reduce; this indicates that the catalyst has high stability and reusability. Interestingly, in the second round of reaction, the DMF yield increased slightly, which may be due to the weakening of the deep hydrogenation capacity of the recycled catalyst, preventing the deep hydrogenation of the target product DMF.

As shown in Figure 9b–d, the characterized results of the used catalyst had proven that the catalyst maintained a stable structure after the reaction. Compared with the characterized results of the fresh catalyst (Figures 1b, 2g,h, and 3c), the used one shows the same micromorphology and XRD results, indicating that the catalyst has high stability. In the high-resolution spectrum of Cu 2p, the peak weakening of Cu\textsuperscript{2+} might be on account of the reduction of Cu\textsuperscript{2+} during the reaction.

**CONCLUSIONS**

In this study, a copper–cobalt bimetallic catalyst derived from MOFs was synthesized and applied in the catalytic transfer hydrogenolysis of HMF to produce DMF. The catalyst showed excellent catalytic activity and selectivity under relatively mild reaction conditions without the participation of any precious metal. The cobalt doping did not significantly affect the chemical and physical environments of copper in the catalyst, suggesting that the cobalt was in situ loaded into the copper catalyst during the synthesis. The results of characterization tests indicated that the doped cobalt mainly existed as CoO\textsubscript{x}. The results of the catalyst activity test showed that the CoO\textsubscript{x} in the catalyst could effectively activate the C–O bond and

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**Figure 8.** Reaction behaviors of (a) 5-methylfurfural (MF) and (b) 5-methylfurfuryl alcohol (MFA) over Co\textsubscript{20}-Cu@C and Cu@C-750 catalysts. Reaction conditions: MF or MFA loading, 0.5 g; catalyst loading, 0.1 g; IPA loading, 30 mL; hydrogen partial pressure, 2.5 MPa; T, 140 °C; time, 2 h; and agitation speed, 400 rpm.

**Scheme 2.** Possible Mechanism of the Hydrogenolysis Process of HMF to Produce DMF through Two Reaction Routes
improve the hydrogenation activity of the catalyst. The remarkable catalytic activity of Co$_{20}$-Cu@C for the hydrogenation of HMF is attributed to the synergistic catalytic effect between Cu and CoO. Furthermore, the Co$_{20}$-Cu@C catalyst was used in the reaction under optimized reaction conditions, i.e., a reaction temperature of 160 °C, a hydrogen partial pressure of 2.5 MPa, and a reaction time of 3 h to obtain 100% HMF conversion and 85% DMF yield. More importantly, the catalyst activity did not decrease significantly after five rounds of testing, indicating that the catalyst has high stability. The presented copper−cobalt bimetallic catalyst provides a guiding principle and a reference value for the design of future non-noble catalysts in the field of HMF conversion.

**EXPERIMENTAL SECTION**

**Catalyst Synthesis Method.** The Cu monometallic catalyst was synthesized by the static precipitation method. Typically, 10 mmol of BTC (1,3,5-benzenetricarboxylic acid) was dissolved in 100 mL of methanol, while 20 mmol of copper nitrate and 2 g of poly(vinyl pyrrolidone) (PVP) were dissolved in 100 mL of methanol. Then, BTC−methanol solution was slowly dropped into the metal nitrate solution with stirring. Subsequently, the blue mixed liquid was transferred to a round-bottom flask and kept at a constant temperature of 60 °C for 24 h in an oil bath. The blue precipitate was separated by filtration, washed with 100 mL of methanol three times, and dried in a vacuum oven to obtain the precursor powder. One gram of the precursor powder was measured and heated in a tube furnace under the protection of nitrogen, and the temperature was increased to the required temperature and kept constant for 4 h. Based on the pyrolysis temperature, the obtained catalyst is named Cu@C-X (X = 450, 550, 650, 750, and 850).

The method for synthesizing the precursor of the copper-based bimetallic catalyst is the same as above, except that the second metal nitrate (cobalt nitrate, zinc nitrate, or nickel nitrate) is additionally added, and all precursors of the bimetallic catalyst are pyrolyzed at 750 °C. The amount of second metal nitrate added is based on the molar ratio of copper nitrate. Based on the element and amount of doped metals, the catalyst is named M$_x$-Cu@C (M = doped metal element, x = second metal molar ratio).

**Activity Test and Product Analysis.** The catalytic performances in selective hydrogenation of the catalyst were carried out in a high-pressure autoclave. In a typical experiment, 0.5 g of the reaction substrates (HMF) and 0.1 g of the internal standard (toluene) were dissolved in 30 mL of isopropanol (IPA), the mixture was transferred to a stainless steel autoclave (100 mL) equipped with a mechanical agitator, and then 0.1 g of the catalyst was added. After sealing the
autoclave, H2 was purged at least eight times to remove the air. Then, the autoclave was aerated with H2 to the required pressure, and the temperature was increased according to the demand, while the mechanical agitation speed was modulated to 400 rpm. After a period of reaction, the autoclave was cooled to room temperature quickly. Finally, the solid catalyst and liquid product were separated using a centrifuge for the next experiment.

The qualitative and quantitative determination of liquid products is done by gas chromatography (Agilent 6820). The internal standard curve method was used for the quantification of the substrates and main products. In all cases, we have calculated that the respective carbon balances were above 90%.

To study the stability of the catalyst, the catalyst was subjected to multiple rounds of reaction. After the reaction, the catalyst was centrifuged, washed with ethanol three times, dried at 80 °C in vacuum for 2 h, and finally used for the next round of reaction without any additional treatment.

**Catalyst Characterization.** The inductively coupled plasma-optical emission spectroscopy (ICP-OES) was carried out on an Agilent 720ES. The Fourier transform infrared spectra of the samples were recorded on a PerkinElmer Spectrum 100 instrument (wave number 400−4000 cm⁻¹). X-ray diffraction (XRD) patterns of the prepared materials were recorded on a PANalytical PW3040/60 X-ray diffractometer. The N2 adsorption−desorption isotherms at 77 K were measured using a Micrometrics ASAP2460 instrument and calculated using the multipoint Brunauer−Emmett−Teller (BET) method. The high-resolution transmission electron microscopy (HRTEM) image was obtained using an instrument JEOL JEM-2100F. X-ray photoelectron spectroscopy (XPS) spectra of the samples were recorded on a Thermo XPS ESCALAB 250Xi spectrometer equipped with a monochromatic Al Kα (1486.8 eV) X-ray source. Raman spectra were recorded on a PANalytical PW3040/60 X-ray diffractometer.

**ASSOCIATED CONTENT**

-supporting information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c00676.

X-ray diffraction patterns; infrared spectroscopy and electron microscopy characterizations of precursors; N2 adsorption−desorption curve and textural parameters of catalysts; Raman spectra; effect of reaction time on the reaction; and comparison of the catalytic activity with other works (PDF)

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**Notes**

The authors declare no competing financial interest.

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