Catalysis Science & Technology



View Article Online

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Cite this: Catal. Sci. Technol., 2021, 11, 1451

Received 9th October 2020, Accepted 2nd December 2020

DOI: 10.1039/d0cy01969k

rsc.li/catalysis

Introduction

Transformation of renewable biomass into high value-added chemicals and fuels has been recognized as an important approach to alleviate the current dependence on limited fossil fuels and cut the level of carbon dioxide emission. In this context, 5-hydroxymethylfurfural (HMF) dehydrated from lignocellulosic compounds (e.g., glucose and fructose) has been hailed as a 'sleeping giant' due to its rich chemistry and potential availability.^{1,2} Association with -C=O, furan ring and -OH groups make it more feasible for HMF to be used in downstream transformations.3-5 Both the oxidation and reduction of HMF can produce a variety of valuable building blocks. For example, oxidation of HMF could generate 2,5-furandicarboxylic acid (FDCA),^{6,7} hydrogenolysis of HMF results in 2,5-dimethylfuran (DMF) and 5-methyl-2-

Formic acid enabled selectivity boosting in transfer hydrogenation of 5-hydroxymethylfurfural to 2,5-furandimethanol on highly dispersed Co– N_x sites[†]

Ling Xu,^a Renfeng Nie, ¹⁰*^b Xujie Chen,^a Yanchen Li,^a Yuxi Jiang^a and Xiuyang Lu*^a

Catalytic transfer hydrogenation (CTH) reaction is considered as a potential route for upgrading bio-based carbonyl compounds to their corresponding alcohols. Herein, ordered mesoporous N-doped carbon confined Co-N_x (Co-NC) was adopted as a catalyst for converting cellulose-derived 5-hydroxymethylfurfural (HMF) to 2,5-furandimethanol (FDM) using formic acid (FA) as a hydrogen donor. Different catalysts and preparation methods were screened, by varying cobalt phases and template removal procedures. It is found that highly dispersed N-confined Co species (Co-N_x) other than naked Co NPs acted as catalytic species for the CTH of HMF with FA, which gave 86% yield of FDM at 100% HMF conversion. Kinetic experiments revealed that, compared with molecular hydrogen, Co-NC could effectively accelerate HMF hydrogenation and suppress as-formed FDM hydrogenolysis in the presence of FA, which is ascribed to its superior activity toward hydrogen transfer from FA and fast desorption toward FDM. Mechanism studies indicated that C-H dissociation of FA could be the rate-determining step in the CTH reaction, and the hydrogenation of HMF could proceed through an intermolecular hydride transfer route. This work shows that the bifunctional nature of the catalyst is critical in the efficient CTH of biomass-derived carbonyl compounds and provides insights toward the rational design of such catalysts.

furanmethanol (MFM),^{8,9} and selective hydrogenation of carbonyl groups produces 2,5-furandimethanol (FDM). In particular, FDM is a promising diol that can be used either directly for the synthesis of shape self-healing and memory polymers or for the production of 1,6-hexanediol, drugs and crown ethers.¹⁰

Selective hydrogenation of HMF to FDM is still challenging, because HMF is intrinsically unstable and can be transformed to many other undesirable byproducts when using traditional routes.^{11–14} For instance, FDM can be obtained *via* Cannizzaro reaction, but an equimolar amount of 5-hydroxymethylfuranoic acid (HMFA) by-products is also formed,^{15,16} leading to low atom economy and high cost for product separation. Moreover, catalytic hydrogenation of HMF to FDM catalyzed by Pt,¹⁷ Ru (ref. 18) and Au (ref. 19) catalysts is widely explored, however, high selectivity to FDM is hard to achieve since the as-formed FDM is easily hydrogenolyzed especially in the presence of high-pressure-H₂ and noble metal catalysts.

Catalytic transfer hydrogenation (CTH) has emerged as a promising alternative for the upgrading of biomass-derived compounds without using high-pressure-H₂.^{20–23} Formic acid (FA), a co-product from biomass degradation processes,²⁴ has attracted much recent interest as a promising hydrogen

^a Key Laboratory of Biomass Chemical Engineering of Ministry of Education, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, P.R. China. E-mail: luxiuyang@zju.edu.cn

^b College of Chemical Engineering, Zhengzhou University, Zhengzhou, 450001, P.R. China. E-mail: refinenie@163.com

[†] Electronic supplementary information (ESI) available: Additional experimental results. See DOI: 10.1039/d0cy01969k

donor for hydrogenation reactions.^{25–28} As for CTH of HMF, rare examples using FA as a hydrogen donor and noble Pd or Ir catalysts were reported,^{29,30} although >90% yield of FDM was achieved successively. Considering their earth-abundant and low cost features, non-noble metals are more desirable for CTH of HMF with FA.³¹ However, selectively yielding FDM with non-noble metals and FA *via* a CTH route has not been reported until now.

Recently, N-doped carbon has been proved to be a very attractive catalytic material for Co-catalyzed CTH processes,³²⁻³⁸ but the nature of its active sites as well as reaction mechanism toward FA and reactants is still unclear. In this contribution, we fabricated ordered mesoporous N-doped carbon confined Co catalysts (Co-NC-A) by using a $Co(phen)_2(OAc)_2$ complex as a precursor and SBA-15 as a hard template. The resulting Co-NC-A catalyst exhibits a high surface area (883.5 m² g⁻¹) and highly dispersed Co-N_x species in carbon skeleton, which contributed to 88.2% HMF conversion along with 92.3% FDM selectivity at 160 °C for 5 h. By screening catalysts with different structured Co, the role of Co species as well as N species was explored. The influence of FA and H₂ on the CTH performance of Co-NC-A was studied. Wide controlled experiments, including deuterium labelling experiment, NMR analysis and in situ DRIFT, were employed for tracking the hydrogen transfer as well as substrate adsorption over the catalyst. Finally, with the above-mentioned studies, a possible reaction mechanism was proposed. This work would be helpful in providing the feasibility of CTH of HMF to DFM with biomass-derived FA in the presence of non-noble Co catalysts, which will advance the green preparation of DFM from biomass-based materials.

Results and discussion

Characterization of mesoporous Co-NCs

Co–NCs were synthesized by employing SBA-15 as a mesopore template through a carbonization procedure. In this process, $Co(phen)_2(OAc)_2$ was used as Co, C and N precursors and inserted into the ordered channels of SBA-15. After carbonization under a flow of nitrogen, HF was adopted to remove SBA-15 and exposed cobalt species, affording the catalyst denoted as Co–NC-A. For comparison, replacing HF with NaOH only got rid of SBA-15 but retained all Co species including both confined and exposed cobalt, which was denoted as Co–NC-B.

Firstly, the pore structure of Co–NCs was studied by smallangle X-ray diffraction (SAXRD) and is shown in Fig. S1.† Bare SBA-15 exhibits three well-resolved peaks below 2.5°, which are ascribed to the (100), (110) and (200) diffraction peaks derived from ordered mesopores.³⁹ The (110) diffraction is preserved but shifted to a higher 2θ value as shown in the pattern of Co–NC-A, suggesting the successful replication of mesopores with the aid of SBA-15. Comparatively, nearly no diffraction peaks are observed for Co–NC-B, revealing its low ordered meso-structure. N_2 adsorption/desorption isotherms (Fig. 1a) show that both Co–NC-A and Co–NC-B display a typical type IV curve with an H4-type hysteresis loop ($p/p_0 = 0.5-0.9$), along with which a clear steep at relative pressures of <0.05 could be observed, revealing the existence of both mesopores and micropores for the two catalysts. Pore size distributions (Fig. 1a and S2†) further confirm that Co–NC-A exhibits more distinct mesopores in the range of 2–10 nm. As shown in Table S1,† the BET surface area and pore volume of Co–NC-A are calculated to be 883.5 m² g⁻¹ and 0.3 cm³ g⁻¹, respectively, much higher than those of Co–NC-B (610.6 m² g⁻¹ and 0.2 cm³ g⁻¹). These results indicate that the meso-structure of Co–NC-A is replicated *via* the base-removal of SBA-15 and strengthened further *via* the acid-removal of unwrapped Co species.

Wide-angle X-ray powder diffraction patterns (XRD) of Co-NCs are shown in Fig. 1b. Apart from C(002) peak at 25.8° (PDF 01-0646), Co phases exist differently in Co-NC-A and Co-NC-B. The diffraction peaks of Co-NC-B that are located at 19.1°, 31.4°, 36.9°, 59.5° and 65.3° could be attributed to (111), (220), (311), (511), and (440) reflections of Co₃O₄ (PDF 43-1003), respectively.40 Meanwhile, CoO and metallic Co (Co⁰) are also observed in Co-NC-B. When etching with acid, neither Co_3O_4 nor CoO is observed. Although the Co^0 phase is preserved in Co-NC-A, the intensity relative to C(002) is weakened remarkably. ICP-OES (Table S1[†]) shows that the Co content of Co-NC-A is 2.8 wt%, which is much lower than that of Co-NC-B (21.5 wt%). These results indicate that those exposed Co species mainly include Co_3O_4 , CoO and Co^0 , and after etching with acid, almost all Co3O4 and CoO are removed, along with which only a small fraction of Co species $(Co-N_x)$ is preserved within Co-NC-A.

Surface composition of Co–NCs is detected by X-ray photoelectron spectroscopy (XPS). As shown in Fig. 1c, the Co 2p peak intensity of Co–NC-A is much weaker than that of Co–NC-B owing to the acid-removal of most Co species. The Co 2p spectra could be fitted into three characteristic peaks



Fig. 1 (a) N_2 adsorption/desorption isotherms, (b) XRD patterns, and (c) Co2p and (d) N1s spectra of Co-NC-A and Co-NC-B.



Fig. 2 (a and e) Bright field TEM and (b and f) HAADF-STEM images of Co-NC-A; (c, d, g and h) elemental mapping of Co-NC-A.

of Co^{0} , Co^{3+} and Co^{2+} with BEs at 778.7, 780.3 and 782.8 eV, respectively.³⁴ The fitting parameters (Table S2[†]) show that Co-NC-A exhibits higher Co^0 (7.6%) but lower Co^{3+} (42.6%) percentage than Co-NC-B, revealing the stabilization role of N-dopants for Co species. The N1s spectra were deconvoluted into peaks corresponding to pyridinic N (398.0 eV), pyrrolic N/pyridinic N-Co (399.6 eV), graphitic N (401.1 eV) and pyridine oxide (403.3 eV) for the two catalysts (Fig. 1d). The fitting parameters (Table S2[†]) show that Co-NC-B exhibits lower pyridinic N (31.7%) but higher pyrrolic N/pyridinic N-Co (52.3%) percentage than Co-NC-A, indicating that those unwrapped Co species in Co-NC-B also interact with N species. After etching with acid, the pyridinic N-Co species were partially recovered into pyridinic N. This speculation is also proved as shown in the C1s spectra (Fig. S3[†]), in which a relatively lower percentage of C-C/C=C species is observed for Co-NC-B.

The morphology of Co–NCs is disclosed using a transmission electron microscope (TEM) (Fig. 2 and S4†). TEM images show that the morphology of Co–NC-B and Co–NC-A is analogous to that of parent SBA-15. Base-etching resulted in more Co particles as well as wider particle size distribution in comparison to Co–NC-A. For instance, the mean particle sizes of Co NPs in Co–NC-B and Co–NC-A are 22.9 and 10.5 nm, respectively. After etching with acid, most exposed Co species were washed away, and the retained ones

could be confined by the N-dopants (Fig. S4d[†]). Apart from a few Co NPs observed in Co-NC-A, the signals of Co element are well overlapped with those of N element and spread all over the N-doped carbon (Fig. 2d and h). This observation indicates that, although a fraction of the Co species exist as NPs which are surrounded by N-doped carbon (Fig. S4d⁺), the rest of the Co species $(Co-N_x)$ could be highly dispersed within the N-doped carbon and interact intimately with the N dopants (especially for pyridinic N), since the $Co(phen)_2(OAc)_2$ complex was widely adopted as a precursor for fabricating single atom Co catalysts.⁴¹

CTH of HMF with FA

Initially, catalyst screening was carried out for CTH of HMF with FA at 160 °C for 5 h (Table 1). In the blank experiment, only 6.8% HMF conversion along with negligible FDM yield was obtained in the absence of a catalyst (entry 1). Among Fe-, Ni-, Cu- and Co-based catalysts (entries 2-5), Co-NC-A accounted for the highest HMF conversion (88.2%) and 92.3% FDM selectivity, exhibiting better performance than Fe-NC-A, Ni-NC-A and Cu-NC-A, in which 24.2, 31.7 and 15.8% HMF conversions were obtained, respectively. Compared with those reported catalysts in literature studies (Table S3[†]),^{18,19,29,30,43-46} Co-NC-A exhibited comparable catalytic performance for transfer hydrogenation of HMF. Other noble Ru/C, Pd/C and Pt/C catalysts only resulted in 41.7, 46.1 and 37.8% HMF conversions, respectively (entries 6-8), along with relatively low FDM selectivities (70.0-88.9%). It should be noted that high HMF conversion was commonly accompanied with high conversion of FA, indicating that efficient FA dehydrogenation should be a prerequisite for CTH of HMF.

In order to explore the active sites of Co–NC-A, several controlled catalysts were evaluated for CTH of HMF with FA (Fig. 3a). Co, Co_3O_4 and CoO accounted for similar HMF conversions (16.4–18.7%), but achieved 71.2, 39.7 and 36.7% FDM selectivities, respectively. As a precursor of Co–NC-A, $Co(phen)_2$ only resulted in 19.3% conversion which was higher than with phen (10.6%). These catalysts are much less

Table 1 Transfer hydrogenation of HMF with FA over different catalysts ^a							
	HMF FDM MFM LA						
	Catalysts	Molar ratio of HMF to Co		Selec./%			Copy of
Entry			Conv./%	FDM	MFM	LA	FA/%
1	No catalyst	_	6.8	0	0	14.7	1.6
2	Co-NC-Å	25.0	88.2	92.3	2.4	3.4	89.5
3	Fe-NC-A	22.8	24.2	90.1	2.1	5.0	16.7
4	Ni–NC-A	26.3	31.7	88.6	2.2	3.5	33.5
5	Cu-NC-A	35.3	15.8	84.8	0	1.9	23.1
6	5 wt% Ru/C	24.1	41.7	70.0	3.4	5.8	34.0
7	5 wt% Pd/C	25.3	46.1	88.9	2.4	5.6	40.7
8	5 wt% Pt/C	46.4	37.8	83.3	4.2	5.6	40.0

^a Reaction conditions: HMF (30 mg), catalyst (20 mg), n_{FA/HMF} = 7.5, 1,4-dioxane (3.5 mL), 0.5 MPa N₂, 160 °C, 5 h, 500 rpm.

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Fig. 3 (a) CTH of HMF over the controlled catalysts. (b) Effect of solvents and (c) FA usage on the CTH of HMF over Co-NC-A. (d) Recycling test of Co-NC-A for the CTH of HMF. Reaction conditions: HMF (30 mg), catalyst (20 mg), $n_{FA/HMF}$ =7.5, solvent (3.5 mL), 0.5 MPa N₂, 160 °C, 5 h, 500 rpm. Co-NC-A(H) catalyst was prepared *via* treatment of Co-NC-A with HNO₃ solution (3 M, 20 mL) under reflux at 100 °C for 5 h. Equivalent Co in the controlled catalysts was used in Fig. 3(a).

active than Co–NC-A, indicating the important role of N-doped carbon for promoting the CTH performance of Cobased catalysts, in which intimate interaction between cobalt and N-dopants (*e.g.* Co–N_x) could be existed.^{47,48}

With the optimal Co-NC-A in hand, the influence of solvents on the CTH of HMF was studied and is shown in Fig. 3b. Four polar protic solvents, e.g. methanol, ethanol, water and isopropanol, resulted in moderate to good HMF conversions (40.2-92.5%) but low FDM selectivities (6.5-30.4%). It is reported that strong proton solvent would favor the generation of H⁺ ions from FA, thus aggravating the polymerization or condensation of HMF.⁴⁹ Other four aprotic solvents, e.g. ethyl acetate, dichloromethane, DMF and cyclohexane, exhibited 31.6-92.3% HMF conversions but better FDM selectivities (55-64%). Comparatively, 1,4-dioxane is the best solvent for achieving both high conversion and FDM selectivity. Moreover, catalyst loading has a profound influence on the CTH performance (Fig. S5[†]). Increasing the catalyst loading from 5 to 20 mg resulted in a remarkable increase of HMF conversion from 47.3 to 88.2%, while the FDM selectivity remained almost constant at above 80%. However, excess catalyst loading led to a drop of FDM selectivity, probably due to its over-hydrogenation or degradation of HMF.

Considering that FA acts as a hydrogen source, the mole ratio of FA/HMF could affect the CTH performance of Co–NC-A (Fig. 3c). It can be found that no FDM was formed without adding of FA. Increasing the mole ratio of FA/HMF from 1 to 9 led to a significant increase of HMF conversion from 11.7 to 92.5% but a slight drop of FA conversion from 100 to 85.8%. FDM selectivity was increased dramatically from 31.4 to 92.9% with the increase of the mole ratio of FA/HMF from 1 to 7.5. However, further increasing this value to 9 decreased the FDM selectivity to 87.8%, ascribing to over-hydrogenation of FDM in the presence of excess FA.

As shown in Fig. S6,† reaction temperature had a remarkable effect on the catalyst performance in CTH of HMF. Increasing the temperature from 120 to 180 °C resulted in an increase of the reaction rate but a decrease of FDM selectivity at a high HMF conversion. It is found that $\ln(c/c_0)$ followed a linear relationship with the initial reaction time. On the basis of the Arrhenius plot, the apparent activation energies (E_a) for the transformation of HMF was calculated to be 27.5 kJ mol⁻¹. Meanwhile, a gram-scale experiment was performed using one gram of HMF as a reactant at 180 °C (Fig. S7†). After 10 h, 92.1% HMF was converted, accompanied with 76.3% FDM yield.

Catalyst recycling shows that Co–NC-A is highly stable and could be recycled five times without a significant loss in the efficiency (Fig. 3d). ICP-OES analysis for the reaction liquid shows that the Co concentration was below the detection limits, but 28.8% Co leached into solution for Co–NC-B. Fig. 1b shows that Co_3O_4 , CoO and metallic Co are observed in the XRD pattern of fresh Co–NC-B. However, after being used, neither Co_3O_4 nor CoO is observed (Fig. S8b†). By contrast, XRD, TEM and XPS characterization techniques (Fig. S8–S10†) show that the morphology or crystalline phase of the recycled Co–NC-A did not change too much, confirming the stable physicochemical properties of Co–NC-A in acidic media.

Mechanism of CTH of HMF with FA

NH₃-TPD analyses for Co-NC-A and Co-NC-B were performed and are shown in Fig. S11.† It is found that nearly no desorption peaks could be observed for the two samples, revealing that negligible acid sites exist in the two catalysts. This result indicates that Lewis acid might not be an active center for the CTH reactions with FA. Detailed studies of the CTH performance of Co-NC-A and base-treated counterpart (Co-NC-B) were carried out and are shown in Table S4.† It is found that Co-NC-B exhibited 58.1 and 95.2% HMF conversions at 2 h and 5 h, respectively, which are slightly higher than those obtained on Co-NC-A (54.9 and 88.2%). Co-NC-B contains nearly an equivalent amount of acidinsoluble cobalt species (existing as $Co-N_x$) as Co-NC-A, but a much higher amount of acid-soluble cobalt species (existing as Co or CoO_x) than Co–NC-A, indicating that the Co– N_x species could be the active sites that are responsible for CTH of HMF with FA. In order to verify this assumption, Co-NC-A was treated with 3 M HNO3 (denoted as Co-NC-A(H)) so as to destroy the Co-N_x species (Fig. 3a). It is found that HNO₃ treatment led to \sim 13% Co removal as well as a 9.4% drop of HMF conversion, although FDM selectivity remained nearly constant. This result indicates that those Co– N_x species are relatively stable in acid and could be acted as main active centers.

Fig. 4 shows the hydrogenations of HMF/FDM with FA or $\rm H_2$ over Co–NC-A. Using FA as a hydrogen donor resulted in



Fig. 4 Using (a and c) FA or (b and d) H₂ as hydrogen donors for the CTH of HMF and FDM. Reaction conditions: HMF or FDM (30 mg), Co-NC-A (20 mg), $n_{FA/HMF}$ = 7.5, 1,4-dioxane (3.5 mL), 0.5 MPa N₂ or 0.5 MPa H₂, 160 °C, 500 rpm.

FDM as the main product and no formation of DMF (Fig. 4a). Comparatively, H_2 led to much a slower reaction rate and lower FDM selectivity (Fig. 4b). For instance, prolonging the reaction time from 0.5 to 8 h, HMF conversion increased slowly from 14.8 to 48.1%, while FDM selectivity decreased from 80.3 to 39.5%, which was accompanied with an increase of DMF selectivity from 18.3 to 55.3%. When replacing 0.5 MPa N_2 with H_2 , allowing both FA and H_2 as hydrogen donors (Fig. 5a), although the reaction rate was comparable with FA alone, significant DMF formation could still be observed. This result indicates that, compared with FA, although molecular H_2 is hard to be activated, it facilitates hydrogenolysis of FDM over Co–NC-A. To further demonstrate the different catalyst performances of Co–NC-A



Fig. 5 (a) The effect of hydrogen donor to the CTH of HMF: reaction conditions: HMF (30 mg), Co-NC-A (20 mg), $n_{FA/HMF}$ = 7.5, 1,4-dioxane (3.5 mL), 0.5 MPa H₂/N₂, 160 °C, 500 rpm, 3 h; (b) H₂-TPD spectra of Co-NC-A and Co-NC-B; (c) reactant absorption over Co-NC-A; (d) deuterium-labelling studies of FAL using FA.

in the presence of FA and H_2 , selective hydrogenation of FDM was investigated as shown in Fig. 4c and d. It is found that FDM was not stable and easy to polymerize, and the main detected product was MFM when using FA as a hydrogen donor. Meanwhile, the as-formed MFM could be quickly hydrogenolyzed into DMF in the presence of H_2 , further revealing the strong hydrogenolysis capacity of Co-NC-A with the aid of H_2 .

In order to figure out the reason, H₂-TPD studies were conducted and are shown in Fig. 5b. It is found that Co–NC-B exhibited three large peaks at 147 °C, 265 °C and 317 °C, attributing to chemically adsorbed hydrogen on the exposed metallic cobalt.^{50,51} Meanwhile, Co–NC-A showed a weak desorption peak at 288 °C and exhibited 13.3 times lower H₂ adsorption capacity (0.14 mmol g⁻¹) than Co–NC-B (1.84 mmol g⁻¹), revealing its weak capacity for activating H₂. Meanwhile, the adsorption capacity of HMF over Co-NC-A is 0.86 μ g g⁻¹ (Fig. 5c and S12†), much higher than that of FDM (0.23 μ g g⁻¹), indicating that Co–NC-A could facilitate HMF conversion but restrain over-hydrogenation of FDM due to its easy desorption.

In order to study the hydrogenation mechanism of HMF with FA over Co-NC-A, furfural was used as a model reactant for the in situ DRIFT studies (Fig. 6). As for FA adsorption at room temperature (Fig. 6a), the absorption bands at 2946, 1795, 1735 and 1214 cm^{-1} can be ascribed to C-H, C=O (gaseous FA), C=O (absorbed FA) and C-O vibrations of FA, respectively. Increasing temperature to 135 °C led to significant weakening of C=O (gaseous FA) and C-O vibrations, indicating enhanced interaction between FA and Co-NC-A, in which the protons of FA could be scrambled by N-dopants while the as-formed HCOO* was stabilized by adjacent cobalt. With prolonged reaction time, C=O (absorbed FA) and C-H vibrations weakened gradually, which followed with the appearance of CO_2 stretching at 2324 cm⁻¹. During the whole reaction time, no signals of CO and water were observed, indicating that FA decomposition was dominated by dehydrogenation other than dehydration.⁵²⁻⁵⁴ Fig. 6b shows the FTIR spectra with introducing both furfural and FA. The weakening of characteristic vibrations of FA was accelerated compared with FA alone, indicating that the introduced furfural facilitated its interaction with FA, which decelerated the FA dehydrogenation. Meanwhile, new peaks at ~3200 and 1061 cm⁻¹ were strengthened with prolonged reaction time, which could be ascribed to the -OH and C-O



Fig. 6 In situ DRIFT of (a) FA and (b) FA + FAL adsorption over Co-NC-A.



Fig. 7 Possible reaction mechanism of CTH of HMF over Co-NC-A.

vibrations of the newly generated furfuryl alcohol, respectively. 55

The deuterium-labelling studies (Fig. 5d and S13†) reveal that, replacing HCOOH with DCOOH resulted in a much lower reaction rate for both furfural and FA. As for furfural conversion, the reaction rate constant ratio $(k_{\rm H}/k_{\rm D})$ with HCOOH and HCOOD was calculated to be 2.03, while this value was 2.53 for FA dehydrogenation. The relatively low reaction rate along with high $k_{\rm H}/k_{\rm D}$ of FA confirm that the dissociation of the C–H bond in FA could be the rate determining step in the CTH reaction.⁴² Moreover, using DCOOH as a hydrogen donor resulted in 61% conversion as determined by ¹H-NMR (Fig. S14†), in which 88% deuterium was incorporated into the α -carbon of furfural.

In light of the above observations, a possible mechanism for CTH of HMF with FA was illustrated in Fig. 7. Firstly, the electron-rich N species in Co-NC-A capture H^{*} from FA to form N-H*, and cobalt-formate (Co-HCOO*) species are generated due to the coordination between electronegative formate anions and the empty d orbitals of adjacent Co species.42,56 Then, carbonyl oxygen in HMF is adsorbed on Co owing to its oxophilic nature^{57,58} and coordinates with the Co-HCOO* species. The hydrogen is transferred from formate to the carbonyl group via an intermolecular hydride transfer mechanism with a six-membered-ring intermediate, similar to the Meerwein-Ponndorf-Verley (MPV) mechanism. Finally, FDM is formed and desorbed from the catalyst, accompanied with the release of CO₂. The proposed mechanism reveals that the transfer of hydrogen in formate species should be the ratedetermining step in the CTH of HMF with FA.

Conclusion

Ordered mesoporous N-doped carbon confined $Co-N_x$ catalysts (Co–NCs) were synthesized by facile carbonization using SBA-15 as a hard template with $Co(phen)_2(OAc)_2$ as Co, C and N sources. As revealed by catalyst screening, different catalyst preparations and cobalt phases remarkably affected the catalyst performance in CTH of HMF with FA as a hydrogen donor. It is found that Co–N_x species other than naked Co species are responsible for FA dehydrogenation and carbonyl group hydrogenation. With Co–NC-A as the optimal catalyst, 86.0% FDM yield could be obtained,

exhibiting better performance than other frequently-used cobalt-based catalysts and commercial noble Pd-, Pt- and Rubased catalysts. Control experiments suggest that FA facilitated HMF hydrogenation but restrained FDM hydrogenolysis in comparison to molecular hydrogen. Mechanism studies reveal that FA dehydrogenation could be rate-limiting for CTH of HMF, in which hydrogen was transferred directionally from formate to the α -carbon of carbonyl group *via* an intermolecular hydride transfer process. Additionally, Co–NC-A was acid-resistant and could catalyze scalable CTH of HMF without an obvious loss of its activity. The atom-level understanding gained regarding the reaction pathway lays the foundation for the development of efficient catalytic process for biomass upgrading, showing potential applications in sustainable chemical industry.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 21676243, 22078290), and the Fundamental Research Funds for the Central Universities (No. 2020BCE002).

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