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Hydrogen Binding Initiated Activation of O–H Bonds on a Nitrogen-Doped Surface for Catalytic Oxidation of Biomass Hydroxyl Compounds

Xin Liu,^{[a], [b]} Yang Luo,^[a] Hong Ma,^{*[a]} Shujing Zhang,^{[a], [b]} Penghua Che,^[a] Meiyun Zhang,^{[a], [b]} Jin Gao,^[a] and Jie Xu^{*[a]}

[a]	Xin Liu, Yang Luo, Hong Ma, Shujing Zhang, Penghua Che, Meiyun Zhang, Jin Gao,	Jie Xu
	State Key Laboratory of Catalysis	
	Dalian Institute of Chemical Physics, Chinese Academy of Sciences	
	Dalian National Laboratory for Clean Energy	
	457 Zhongshan Road, Dalian 116023 (P. R. China)	
	E-mail: xujie@dicp.ac.cn	
	mahong@dicp.ac.cn	
[b]	Xin Liu, Shujing Zhang, Meiyun Zhang	
	University of Chinese Academy of Sciences	
	Beijing 100049 (P. R. China)	
	Supporting information for this article is given via a link at the end of the document.	

Abstract: Hydrogen binding of molecules on specific solid surface is an attractive interaction that can be employed as driving force for chemical bond activation, material directed assembly, protein protection, etc. However, the lack of quantitative characterization methods for hydrogen bonds (HBs) on surface seriously limits its application. Herein, we measured the standard Gibbs free energy change (ΔG⁰) of surface HBs using NMR technique. HBs accepting ability of surface was investigated in term of comparing ΔG^0 values by employing model biomass platform 5-hydroxymethylfurfural on a series of Co-N-C-n catalysts with electron-rich doped-nitrogen contents adjusted. Reducing the ΔG^{0} effectively improves HBs accepting ability of the nitrogen-doped surface, and promotes the O-H bonds selectively initiated activation in the oxidation of 5hydroxymethylfurfural. As a result, the reaction kinetics is accelerated and the rate constant is significantly increased. In addition to excellent catalytic performance, the turnover frequency (TOF) value for this oxidation is extremely higher than the reported non-noble metal catalysts.

Introduction

The hydroxyl group (–OH) belongs to one of the essential building blocks in various types of chemicals, materials, protein, etc.^[1] In the chemical transformation of most hydroxyl groups, how to realize the highly efficient activation of O–H bonds becomes a critial point.^[2] Generally, the proton donating ability of hydroxyl groups contributes to hydrogen bonds (HBs) formed by themselves, which can usually lower their reactivity.^[3] Interestingly, however, this characteristic also endows HBs with the ability to facilitate activation of O–H bonds, through forming strengthened HBs with other proton acceptors such as electric-rich heteroatoms and halogen ions.^[4] The decreased electron cloud density near the proton nucleus might weaken O–H bonds, thus enhancing the reactivity of hydroxyl groups. Recently, some explorative studies have been performed in utilizing HBs for promoting the conversion of inert hydroxyl substrates and guiding

pathways in purpose. For example, the selective activation of the primary hydroxyl group in diol could be accomplished via forming O-H···O=S HBs with DMSO as a proton acceptor, which was in favor of the selective alkoxyl radical transformation, rather than occurring β-scission due to the unselective activation of both two hydroxyl groups.^[5] Han et al.^[6] presented that the HBs between the alcohol hydroxyl groups and ionic liquid [EMIM]OAc could accelerate the rate-determining step of hydroxyl groups activation, thus significantly promoting the oxidative esterification of inert aliphatic alcohols. In the case of heterogeneous catalysis, researchers also found that the surface-grafted nitrogencontaining ligands on EPy/Pt/Al₂O₃ catalyst could form HBs with specific hydroxyl groups.^[7] However, the research of HBs on heterogeneous surface mainly concentrated on the modification of catalyst surface, promotion of catalytic performance, and elimination of negative impacts via pre-converting -OH.^[8] There is lack of experimental methods beneficial for understanding the regularity of HBs on surface, which still remains in the stage of exploration.

Nuclear magnetic resonance spectroscopy (NMR) is regarded as a quite appropriate technology to investigate the hydrogen binding interaction, since the proton chemical shift (δ) is extremely sensitive to the change of electron density around the hydrogen nucleus. It is widely accepted that the HBs between hydroxyl groups and high electron-rich acceptors can generate the depletion of electron density near the hydroxyl proton and deshielded nuclei, so that the hydrogen-bonded protons reveal a downfield shift in the resonance frequency in different degrees.^[9] Normally, researchers intuitively judge the formation of HBs directly in accordance with the chemical shift changes, or compare the relative strength of HBs by the relative size of downfield shift.^[10] For example, the chemical shift of the hydroxyl proton of benzyl alcohol presented a gradual downfield shift with the increase of [EMIM]OAc ILs content, which was mainly ascribed to the formation of O-H···OAc⁻ HBs between hydroxyl groups and the acetate anions.^[6] Researchers have been attempting to find out the relationship between the chemical shift change ($\Delta\delta$) and HBs energies, and the present studies still

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mainly depend on empirical equation derivations or DFT calculations.^[11] For example, Schaefer^[12] proposed a linear relationship between DFT-calculated HBs energy and the $\Delta\delta$ of hydrogen-bonded protons in some ortho-substituted phenol derivatives ($\Delta \delta = -0.4 \pm 0.2 + E_{HB}$). As a commonly accepted approach, the Benesi-Hildebrand equation was derived, for calculating association constants (Ka) of HBs between benzenethiol and nitrogen contained acceptors ($1/\Delta\delta$ = $1/(K_a\Delta\delta_{max}[A]_0) + 1/\Delta\delta_{max})$.^[13] Accordingly, the HBs energies could be reflected by K_a and the resulting Gibbs free energy change (ΔG) .^[14] Besides chemical shift, relaxation time is another NMR parameter that is suitable to reflect binding states of protons. Recently, D'Agostino et al.[15] demonstrated that the relative surface affinities could be exhibited by adsorbates of primary alcohols and cyclohexane within liquid-saturated mesoporous catalysts by measuring the ratio of NMR relaxation time constants T1:T2. Despite great efforts have been made for HBs in homogeneous and heterogeneous catalytic systems, it still lacks experimental methods for measuring the HBs energy on the catalyst surface.

Our laboratory has been investigating the catalytic conversion of biomass and its derivatives as well as trying to deepen the understanding of the role of HBs in hydroxyl groups and purposely make use of them.^[16] Quite recently, we determined the E_{HB} of HBs between donors and acceptors by conducting ¹H NMR experiments, and put forward for the first time a linear equation as a function of chemical shifts (δ) (In δ + σ_{δ} = -E_{HB}/RT + A).^[17] These bases make it feasible to determine whether an acceptor has sufficient capacity of forming new HBs with a donor by measuring E_{HB}. In the case of the heterogeneous catalyst, if catalyst surface was endowed with sufficient capacity in accepting protons, hydroxyl groups might form new O-H···X HBs on such surface. Thus, O-H bonds might be weakened and activated, aiming to enhance the reactivity of raw substrates and promote the catalytic conversions. Herein, an equation was proposed to determine the ΔG^0 and association constant (K_{HB}) for the formation of O-H···X HBs on surface. Through the comparison of ΔG^0 and K_{HB} , the proton acceptance ability of catalysts in forming HBs on surface can be directly compared. As a result, Co-N-C-9.6 catalyst with the most positive $\Delta G^0 = -11.53$ kcal/mol among Co-N-C-n catalysts exhibited unique ability in initiated activation of O-H bonds and afforded a turnover frequency (TOF) of 477 mol HMF mol⁻¹ Co h⁻¹, which was extremely higher than the reported nonnoble metal catalysts and even comparable to noble metal catalysts in probing the oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylicacid (FDCA).

Results and Discussion

Design for surface HBs initiated-activation of O-H bonds. At first, a strategy of hydrogen binding initiated-activation of O-H bonds on the catalyst surface was proposed. Scheme 1a illustrated the thermodynamic model for the formation process of O-H…X HBs between -OH and the surface proton acceptor sites (X). X is expected to be electron-rich and capable of endowing the proton acceptance ability to the catalyst by introducing electron-rich atoms or species on surface. Due to the strong electrophilicity of X, the O-H bond strength of hydrogen bonded hydroxyl group is weakened, and it becomes easier to break in the process of hydroxyl group conversion, so as to realize its activation and

improve the reactivity of feedstock (Scheme 1c). For this purpose, the key point is to form O-H···X HBs on X sties with sufficient capacity in accepting protons, and find the corresponding criteria. Based on the theory in our previous research,^[17] we proposed the thermodynamic model for the HBs formation process on surface. Similarly, the formation of O-H···X HBs is a reversible process in equilibrium with its backward association reaction. The K_{HB} is the association constant of HBs donors and acceptors. The important physical parameter ΔG^0 for the formation process of HBs, is expected to determine the criteria of whether the -OH could form surface HBs. By performing concentration-variable experiments of proton acceptors, we studied the establishment of a quantitative measurement method for ΔG^0 . In addition, this study proposed a linear equation by determining the change of hydroxyl proton chemical shifts ($\Delta\delta$) with the variation of the concentration of proton acceptors (C), $1/\Delta\delta = a/C + b$, by which K_{HB} and ΔG^0 could be achieved based on the ratio of intercept to slope (K_{HB} = b/a. $\Delta G^0 = -RTln(b/a)$). The detailed derivation process can be observed in our previous work^[17] and the explanation of this formula is provided in the Supporting Information.

(a) Association and dissociation process for O-H…X HBs on surface.





Scheme 1 Schematic illustration for the thermodynamic model of the reversible association and dissociation process for $O-H\cdots X$ HBs on surface (a). Design for model catalysts as protons acceptors (b). A model oxidation reaction for HBs-initiated activation of O-H bonds using HMF as a donor (c).

As illustrated in Scheme 1b, Co-N-C, atomically dispersed cobalt on N-doped carbon, was selected as a model heterogeneous catalyst after the careful consideration. The reasons are presented as follows. Nitrogen is electron-rich that will pull the electron toward it and may play the role of protonacceptor owing to its basic lone pair of electrons. Cobalt exists in the form of single atom, which can guarantee that the catalytic performance is not affected by the distribution of particle size, but is mainly contributed by surface HBs. As illustrated in Scheme 1c, we took the important biomass platform HMF as the model hydroxyl compound, and its oxidation to produce FDCA as a model reaction in order to investigate the HBs-initiated activation of O-H bonds. Interestingly, the oxidation of hydroxyl group of HMF at the initial step is extremely crucial for the whole reaction,

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since its untimely consumption always lead to polymerization, thus inhibiting the whole process.^[18] Therefore, the initiated activation of O–H bonds by HBs could be probed by comparing the *K*_{HB} and ΔG^0 of the HBs on Co-N-C catalysts surface by employing the above established method, and observing the enhancement of TOF values, which is dramatically influenced by the improvement of the –OH reactivity, as well as the producibility to FDCA. Moreover, a high TOF value and productivity of FDCA can reflect the improvement of the activation effect of O–H bonds by HBs initiation.

Characterization of model catalysts. Co-N-C was designed and synthesized through annealing process by utilizing g-C₃N₄ as the nitrogen-rich precursor, as the model catalyst with the electron-rich nitrogen species modified the surface to introduce proton acceptance ability (Figure S1). The as-synthesized samples were denoted as Co-N-C-n (n is the molar ratio of nitrogen to cobalt in the catalyst). A series of characterizations have been conducted in detail to examine the structure and element states. On the representative Co-N-C-9.6, no metallic cobalt or cobalt oxide nanoparticles were detected as confirmed by TEM (Figures 1a-b) and XRD (Figure 1f). The XRD pattern only displayed two broad carbon peaks centered at 25 and 43 degrees. assigned to carbon with a higher degree of graphitization.^[19] The AC HAADF-STEM evidenced that the cobalt was predominantly in the form of atomically dispersed sites (Figure 1c). Furthermore, the EDX maps of Co-N-C-9.6 illustrated the highly homogeneous distribution of Co, N and O on the carbon matrix in the entire region (Figures 1d-e).



Figure 1 TEM images (a and b), AC HAADF-STEM image (c), HAADF STEM image (d), corresponding EDX maps for the overlapped Co, N, O and C (e), XRD pattern (f), normalized XANES spectra (g), EXAFS spectra (h), and N1s XPS spectrum (i) of Co-N-C-9.6.

XANES and EXAFS were used to investigate the detailed electronic structure of Co and the coordination environment of Co and N in Co-N-C-9.6 (Figures 1g-h). The valence state of the Co population in Co-N-C-9.6 was +2, as evidenced that Co-N-C-9.6 and CoO had almost the same E_0 value (the first inflection point) of 7720 eV (Table S1) in comparison with the cobalt foil and cobalt oxides in the reference.^[20] As shown in the EXAFS spectra (Figure

1h), Co-N-C-9.6 exhibited a main peak at 1.4 Å, corresponding to the Co-N first coordination shell. No obvious Co-Co peak (2.17 Å) and Co-O peak (2.57 Å) could be observed,^[20] suggesting that there was no metallic Co or CoO_x species in Co-N-C-9.6, which was in consistence with the AC HAADF-STEM and XRD results. The quantitative coordination of Co and N in the Co-N-C-9.6 is configured by EXAFS fitting (Figure S2 and Table S2), that is one Co atom coordinated with four N atoms (CoN₄ single site).

By performing N1s XPS analysis, the states of the doped nitrogen in Co-N-C-9.6 were explored (Figure 1i). Four overlapped peaks demonstrated the forms of nitrogen include pyridinic N/pyridinic N-Co (398.4 eV), pyrrolic N (399.9 eV), graphitic N (401.0 eV), and pyridine N-oxide (403.0 eV).^[21] Co-N-C-n catalysts have close distributions of the doped nitrogen species on surface (Figure S3 and Table S3), and achievement of specific nitrogen species sites alone on Co-N-C-n surface remains a challenge. Considering the high dispersion of nitrogen element on the Co-N-C-n surface according to the EDX analysis and extremely close distributions of doped nitrogen species, the total nitrogen content was used to represent the apparent concentration of HBs acceptors during the data fitting in calculation of the K_{HB} and ΔG^0 .

Measurement of the surface HBs energy. Afterwards, the HBs energy of O-H···X on the nitrogen-doped surface of the model catalyst were determined. The concentration-variation ¹H NMR measurements were performed in the poor HBs-accepting solvent CDCI₃, by taking HMF as a probe molecule with the concentration fixed at 0.41 mol·L⁻¹, and varying the concentrations of Co-N-C-n catalysts from 0 to 3.04 g-L-1. Tetramethylsilane (TMS) was employed as the internal standard. Typically, the suspension of uniform dispersed catalyst was mixed thoroughly and immediately determined within 4 minutes. All the ¹H NMR spectra displayed well resolved proton peaks, and a few partially overlapped that do not hinder the observation of the proton peak position. In the presence of Co-N-C-n, although the signals were broadened to a certain extent, the hydroxyl proton peaks could still be clearly distinguished. To guarantee the accuracy and repeatability of the NMR experiment, each sample was measured in succession for three times. The low standard deviation verified that the suspension could maintain a uniform dispersion state during the whole NMR measurement process, and the surface HBs formation process attained equilibrium.



Figure 2 Concentration-variation ¹H NMR spectra of HMF with different concentrations of Co-N-C-9.6 (a), the model of hydrogen bonded HMF with an acceptor of X (b), and locally amplified ¹H NMR spectra of HMF with different concentrations of pyridine (c) (400 MHz, CDCl₃).

Typical ¹H NMR spectra of HMF and Co-N-C-9.6 in CDCl₃ are displayed in Figure 2a. After adding Co-N-C-9.6 into HMF in CDCl₃, an obvious change in proton chemical shift value was observed for the hydroxyl proton (H1). For example, the hydroxyl

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proton chemical shift appeared 0.1138 ppm downfield at 3.04 g·L⁻ ¹ concentration of Co-N-C-9.6 in CDCl₃, implying that a formation of O-H···X HBs resulted in the proton deshielded (Figure 2b). The $\Delta \delta$ values increased with the increase of catalyst concentration, which is similar to our previously reported studies concerning homogeneous donor-acceptor systems.^[17] In contrast, there is no change in the rest of proton chemical shifts in C-H of hydroxymethyl group (H2), the furan ring (H3 and H4), and formyl group (H5), because carbons in such groups are not sufficiently electron-rich in the formation of C-H···X HBs, as well as the new formed O-H...X bonds have negligible influence on them. Considering that besides HBs, the decrease in HMF concentration may also generate a change of chemical shift of hydroxyl protons, verification experiments were performed to confirm that the change of chemical shift caused by addition of catalysts into the solution of HMF could be ignored (Table S4). Therefore, the change in proton chemical shifts is closely associated with the hydrogen binding state of hydroxyl protons of HMF.

Then, Co-N-C-n catalysts was compared with pyridine, which was well recognized as a HBs acceptor, in term of the proton acceptance ability. The concentration-variation ¹H NMR spectra of HMF-pyridine couple were recorded in CDCl₃ at the same concentration of HMF (Figure 2c). As expected, the downfield shift of the hydroxyl proton in HMF exhibited after the addition of pyridine, implying the formation of HBs between HMF and pyridine. When the concentration of pyridine was 0.0180 M, the chemical shift change of the hydroxyl proton in HMF was 0.1064 ppm. Additionally, Co-N-C-9.6 catalyst could also lead to a close chemical shift change (0.1138 ppm) at 3.04 g·L⁻¹ (nitrogen concentration is 0.0220 M). Therefore, it is reasonable to attribute the change of chemical shift to the contribution of hydrogen binding. After the data fitting of $1/\Delta\delta$ and 1/C for HMF-pyridine couple, a linear equation based on $1/\Delta \delta = a/C + b$ (a = 0.1615, b = 0.5205, R^2 = 0.994) was obtained (Figure S7), with the determined K_{HB} and ΔG^0 being 3.22 L/mol and -2.90 kcal/mol, respectively, far smaller than those of Co-N-C-n catalysts.



Figure 3 Locally amplified ¹H NMR spectra of HMF with different concentrations of Co-N-C-9.6 (a), Co-N-C-8.5 (b), Co-N-C-6.3 (c), Co-N-C-4.1 (d), N-C (e), and Co/CB (f) (400 MHz, CDCl₃).

After confirming the reliability of the NMR measurements, we carefully checked the change of the chemical shifts by increasing the concentration of Co-N-C-9.6, Co-N-C-8.5, Co-N-C-6.3, and Co-N-C-4.1, respectively. As shown in Figures 3a-d, for all these four catalysts, the hydroxyl proton chemical shifts in HMF moved





Figure 4 The change of chemical shift ($\Delta\delta$) of hydroxyl proton in HMF with different concentrations of catalysts (a). Plots of 1/C versus 1/ $\Delta\delta$ with HMF as donors and catalysts as acceptors (b).

All the HMF-Co-N-C-n couples satisfy the linear quantitative equation $(1/\Delta\delta = a/C + b)$. Figure 4b shows five linear plots between the reciprocal of the proton chemical shift changes $(1/\Delta\delta)$ and the reciprocal of the concentrations (1/C, calculated according to the nitrogen content of the catalysts) for Co-N-C-9.6, -8.5, -6.3, -4.1, and N-C with satisfied correlation coefficient R² of 0.990, 0.980, 0.972, 0.997, and 0.985, respectively. Based on the above discussion, the overall K_{HB} for the formation and dissociation of surface HBs is the ratio of intercept to slope of the fitting curves ($K_{HB} = b/a$) and ΔG^0 could be obtained by $\Delta G^0 =$ -RTInKHB. Considering the real surface possesses multiple states of the doped nitrogen and the chemical shift change represents the overall contribution of the catalyst surface, the average across the catalyst surface was regarded as the proton acceptor. Both K_{HB} and ΔG^0 indicate the apparent proton accepting ability. Table 1 listed ΔG^0 of the surface HBs between HMF and the catalysts. The negative values of ΔG^0 suggested that the hydroxyl proton of HMF could form HBs on all these catalyst surface. The ΔG^0 values increase in the order of Co-N-C-9.6 < Co-N-C-8.5 < Co-N-C-6.3 < Co-N-C-4.1, which is consistent with the decrease order of nitrogen content in Co-N-C-n, indicating that increase in the

Table 1. Parameters of hydrogen bonds determined by ¹H NMR

Catalyata	Ν		h	Кнв	ΔG^0
Calalysis	(wt%)	a	U	(L/mol)	(kcal/mol)
Co-N-C-9.6	10.1	0.0585	6.1303	104.79	-11.53
Co-N-C-8.5	8.4	0.0643	5.7357	89.20	-11.13
Co-N-C-6.3	7.1	0.0742	5.7167	77.04	-10.76
Co-N-C-4.1	5.9	0.0755	4.7843	63.37	-10.28
N-C	5.5	0.1056	5.0298	47.63	-9.57

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nitrogen content for the Co-N-C-n catalysts led to decreasing energy of the formed surface HBs, as well as the improvement in the ability of the Co-N-C-n catalysts to construct surface HBs.

It is acknowledged that there are multiple states of the doped nitrogen on the Co-N-C-n surface, which could be distinguished by performing N1s XPS analysis (Figures 1i and S3). Based on our previous work,^[16d] the protonation energy of pyridinic N was negative value ($E_P = -0.26 \text{ eV}$), while the protonation energy of other nitrogen species (pyrrolic N, graphitic N and pyridine Noxide) were all positive values, suggesting that the pyridinic N might play the role of proton acceptor just liking pyridine which has been evidenced to form HBs with HMF as discussed above. However, the K_{HB} and $-\Delta G^0$ of pyridine-HMF couple were far smaller than those of Co-N-C-n catalysts. This obvious difference may come from the strong proton accepting ability of Co-N-C-n surface. Owing to that the pyridinic N contents on the Co-N-C-n surfaces determined by N1s XPS analysis were all higher than 50% (Table S3), the nitrogen-doped surface possessing stronger ability to accept protons may be due to the increasing electron donating ability of doped nitrogen through conjugation with surface carbon species.^[22]

Surface Hydrogen binding initiated activation of O-H bonds for oxidations. Subsequently, we probed the surface HBs induced activation of O-H bonds in term of catalytic performances and TOF values in the oxidation of HMF to FDCA. The oxidation of HMF was performed over five different heterogeneous catalysts with well-defined compositions and structures containing the Co-N-C-n catalysts with varied nitrogen content (Co-N-C-4.1, -6.3, -8.5, and 9.6), Co NPs supported on active carbon (Co/AC), and nitrogen-doped carbon (N-C) (Table 2). As demonstrated above, Co-N-C-n catalysts were predicted to have the ability in initiated activation of O-H bonds due to their negative ΔG^0 value. As expected, all of them achieved rapid conversions of HMF under 1.0 MPa O₂ at 120 °C for 1 h. The yields to FDCA are in order of Co-N-C-9.6 > Co-N-C-8.5 > Co-N-C-6.3 > Co-N-C-

4.1, consistent with the increase order of nitrogen contents, and Co-N-C-9.6 catalyst with the highest nitrogen content and the strongest ability to form surface HBs (the lowest ΔG^0 value) afforded the best catalytic performance for HMF oxidation to FDCA (Table 2, entry 4). As a result, Co-N-C-9.6 catalyst afforded an excellent catalytic performance (> 99% conversion of HMF, 94.3% yield of FDCA) with a high TOF value (477 mol HMF mol⁻¹ Co h-1). In the case of nitrogen-free Co/AC and metal-free N-C, the results are close to that of blank experiment. The distinct difference in catalytic performance verified the indispensable role of doped nitrogen in carbon, and revealed a strong correlation with the K_{HB} and ΔG^0 (discussed below).

It is worthwhile pointing out that the FDCA productivity, to the best of our knowledge, achieved the highest value in comparison with previously report non-noble metal heterogeneous catalysts (Table 2, entries 12-13). Generally, non-noble metals have the disadvantages of large amount loading and low efficiency in the synthesis of FDCA from HMF, such as manganese catalyst, requiring the MnO₂ and HMF molar ratio of 0.4 even high to 5.7.^[23] Such a high loading amount of non-noble metal catalyst needed is mainly due to that HMF is extremely unstable and easy to polymerize on the catalyst surface in the harsh oxidation system when it is not converted timely, poisoning the catalyst and stopping the conversion.^[18] In contrast, the surface HBs-initiated activation of O-H bonds efficiently promoted the TOF values, with the Co-N-C-n catalyst dosage being significantly reduced. The lowest molar ratio of Co and HMF can reach 0.007. In addition, the gram scale oxidation of HMF was also carried out and obtained 82.1% yield of isolated FDCA (Figure S12). The stability and reusability of Co-N-C-9.6 was investigated by recycling the used catalyst for successive reuse. There was only a slight attenuation of activity of Co-N-C-9.6 catalyst after five cycles (Figure S13), suggesting that the Co-N-C-9.6 catalyst remained highly stable and reusable.

Та	Table 2. The oxidation of furan hydroxyl compounds to carboxylic acids over various heterogeneous catalysts ^[a]									
Entry	Catalyst	O ₂ (MPa)	Т (°С)	t (h)	Conv. (%)	Yield of target acid (%)	Productivity of target acid (h ⁻¹)	Ref.		
1 ^[b]	Co-N-C-4.1	1.0	120	1	> 99	59.2	16.1			
2 ^[b]	Co-N-C-6.3	1.0	120	1	> 99	81.2	23.7			
3 ^[b]	Co-N-C-8.5	1.0	120	1	> 99	88.4	25.5			
4 ^[b]	Co-N-C-9.6	1.0	120	1	> 99	94.3	30.2			
5 ^[b]	Co/AC	1.0	120	1	23.9	0.3	n.d.	This		
6 ^[b]	N-C	1.0	120	1	26.5	0.2	n.d.	WORK		
7 ^[b]	Blank	1.0	120	1	21.9	0.4	n.d.			
8 ^[c]	Co-N-C-9.6	1.0	120	1	> 99	96.5	20.2			
9 ^{[d] [e]}	Co-N-C-9.6	1.0	120	1	> 99	96.7	20.3			
10 ^[b]	Au-Ce	1.0	70	4	100	92	23.0	[24]		
11 ^[b]	Au/HY	0.3	60	6	> 99	> 99	27.5	[16e]		
12 ^[b]	CoO _x -MC	0.5	80	3	98.3	95.3	2.2	[25]		
13 ^[b]	Co-Mn-0 25	1.0	120	5	<u>_ 99</u>	95.2	0.1	[26]		

^[a] Reaction condotions: 0.5 mmol furan hydroxyl compounds, 0.024 mmol Co in Co-N-C-n catalysts, 2.0 mmol NaHCO₃, 5 mL of H₂O. ^[b] The substrate: HMF, the target acid: FDCA. [c] The substrate: HMFCA, the target acid: FDCA. [d] The substrate: furfuryl alcohol, the target acid: 2-furancarboxylic acid. [e] 1.0 mmol NaHCO3.

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Figure 5 The time courses of HMF conversion over Co-N-C-n catalysts (a). The linear fitting of ln([HMF]₀/[HMF]₀) against the reaction time of the HMF oxidation over Co-N-C-n catalysts (b). Linear relationships between the apparent rate constants *k* (c, left) and TOF values (c, middle) of HMF oxidation over Co-N-C-n catalysts, together with the $-\Delta G^0$ for HMF and Co-N-C-n catalysts (c, right) with nitrogen contents of catalysts (c). Reaction condition: for the time courses and fitting of *k*, 1.0 mmol HMF, 0.024 mmol Co in Co-N-C-n catalysts, 4.0 mmol NaHCO₃, 10 mL of H₂O, 100 °C, 0.5 MPa O₂; for calculating of TOF, 0.5 mmol HMF, 0.0035 mmol Co in Co-N-C-n catalysts, 2.0 mmol NaHCO₃, 10 mL of H₂O, 120 °C, 1.0 MPa O₂, 10 min.

As illustrated in Figure 5 and Table 1, the obtained parameters were linearly corrected with doped nitrogen contents of the catalysts. The apparent rate constants (k) and TOF are the most commonly used quantities describing the catalytic activity, while ΔG^0 represents the proton acceptable ability on catalyst surface. Interestingly, the k, TOF, and $-\Delta G^0$ were linearly correlated with the Co-N-C-n catalysts in term of the nitrogen contents with high R^2 of 0.981, 0.966, and 0.985, respectively. All the trends in k, TOF, and $-\Delta G^0$ are in the same order as that of the doped nitrogen contents (Co-N-C-9.6 > Co-N-C-8.5 > Co-N-C-6.3 > Co-N-C-4.1). These indicate that the higher nitrogen content in the catalysts could contribute to higher proton accepting capacity on catalyst surface (lower ΔG^0), thus enhancing the abilities in initiated activation of O-H bonds and promoting the oxidation of HMF to FDCA. Regarding the oxidation of other furan hydroxyl compounds such as 5-(methoxymethyl)-2-furoicacid (HMFCA) and furfuryl alcohol, the high TOF values and yields of corresponding acids may also be attributed to such hydrogen binding initiated activation on the Co-N-C-9.6 catalyst (Table 2, entries 8-9). All the results indicated that the ΔG^0 values from NMR measurements are in complete consistence with the experimental results in the hydrogen binding initiated activation of O-H bonds and oxidation of biomass-derived hydroxyl compounds.

Conclusion

In this paper, we reported the initiated activation of O-H bonds with hydrogen binding on nitrogen-doped surface as driving force for catalytic oxidation. The formation trend of surface hydrogen bonds is reflected by hydrogen binding standard Gibbs free energy change (ΔG^0) based on model 5-hydroxymethylfurfural on a series of Co-N-C-n catalysts with electron-rich doped nitrogen contents adjusted. We developed a method to determine the ΔG^0 as well as the association constant (KHB) on catalyst surface via NMR experiments by a linear equation as a function of the hydroxyl proton chemical shift changes ($1/\Delta \delta = a/C + b$, $K_{HB} = b/a$, ΔG^0 = -RTIn(b/a)). The proposed method is of significance in demonstrating the high ability of Co-N-C-9.6 catalyst surface to form O-H…X HBs with ΔG^0 value of -11.53 kcal/mol, which is much more negative than that of pyridine. Remarkably, in probing the oxidation of HMF to FDCA, the obtained parameters of k and TOF describing the catalytic activity, together with ΔG^0 presenting the proton acceptable ability, are linearly correlated with the doped nitrogen contents with high correlation coefficients, suggesting that hydrogen binding interaction could drive the initiated activation of O-H bonds. The stronger the HBs formation ability is, the better the capability of HBs initiated activation of O-H bonds on the catalyst is. Excellent catalytic performance (> 99% conversion of HMF and 94.3% yield of FDCA in 1 h) and high TOF value (477 mol HMF mol⁻¹ Co h⁻¹) were achieved by Co-N-C-9.6 catalyst with high metal utilization and high stability. This study provides an experimental method for the determination of solid surface HBs energy, and provides the guidance for promoting the activation O-H bonds in biomass-derived hydroxyl compounds by the HBs interactions as well as the design of oxidation catalysts.

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Keywords: surface hydrogen binding • O-H bond • initiated activation • selective oxidation • biomass hydroxyl compound

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The ΔG^0 of hydrogen binding on surface was obtained by linear fitting of the chemical shifts change of surface hydrogen bonded protons and the variation of acceptor concentrations via NMR techniques, which reflected to the abilities of catalyst surface to form HBs with hydroxyl groups. And the surface hydrogen binding was successfully employed to drive the initiated activation of O–H bonds in probing the oxidation of HMF with Co-N-C catalysts.