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Nickel-catalyzed intelligent reductive transformation of aldehyde group with hydrogen

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The selective transformation of aldehyde group (-CHO) in multifunctional oxygenate is a key challenge in the upgrading of sustainable biomass feedstock. Herein, a smart Ni-MFC catalyst is developed from the 2D Ni-based metal-organic frameworks (MOFs), which can efficiently promote the transformation of -CHO with H<sub>2</sub> to methyl group (-CH<sub>3</sub>) via the reductive etherification and hydrogenloysis of C-O ether bond route in methanol. Moreover, the catalytic process can be controlled to directionally produce methyl ether (-CH2OR) using the reductive etherification protocol. For the catalytic reduction of vanillin, Ni-MFC-700 catalyst guarantees the full conversion of vanillin and 96.5% yield of desirable 2methoxy-4-methylphenol (MMP), while Ni-MFC-500 catalyst affords about 82.7% yield of 4-(methoxymethyl)-2methoxyphenol in methanol solvent. It is a novel and promising approach for valorization of multifunctional oxygenate and biomass-derived platform compound.

### Introduction

In recent years, developing the fuels and fine chemicals production process based on the renewable biomass resource has provoked great interests due to the continuous growth in energy demand and security.<sup>1-3</sup> As one of the most important components in the lignocellulosic biomass, lignin is the sole valuable rich in aromatic rings bio-resource that can be converted into the aromatic-based chemical and liquid fuels with high energy density.<sup>4, 5</sup> The aromatic aldehyde is the main ingredient of the crude bio-oil form pyrolysis of lignin. The selective transformation of aldehyde groups is one of the most attractive routes to improve the quality of liquid fuel and gain the bio-based fine chemicals. The process of selective hydrogenation aldehyde group (-CHO) to methyl group (-CH<sub>3</sub>) and methyl ether (-CH<sub>2</sub>-O-R) without destroying C=C in aromatic rings have attracted more and more attention, recently.6-9

The selective reductive transformation of -CHO to -CH<sub>3</sub> can afford us with the value-added methylated product, and minimize the hydrogen consumption and loss of carbon. Developing efficient and economical catalytic system and probing the mechanism of the transformation in different reaction systems are the key factors to successfully upgrade the bio-oils. Vanillin was often chosen as a model compound for investigation the selective transformation of -CHO to -CH<sub>3</sub>.

In the past decades, the precious metals such as Pd, Pt, Rh, Ru and Au supported catalysts have been applied for the transformation of vanillin into MMP.<sup>10-16</sup> But their widespread applications are limited by low earth-abundance and high cost. Moreover, the high hydrogenation activities of noble metal catalysts often result in the undesirable saturation of aromatic ring, in which the high hydrogen consumption is necessary. On basis of these, there is a pressing need for developing highly active, selective and steady non-noble metal-based catalysts with the prospects in practical application. Chen et al. used well-dispersed Mo<sub>2</sub>C nanoparticles supported on activated carbon to catalyse the transformation of vanillin hydrogenation and obtained the poor selectivity for methylated product.<sup>17</sup> In 2018, the highly dispersed copper nanoparticles supported on activated carbon was applied in the processes of vanillin hydrodeoxygenation toward MMP in aqueous-phase and the obtained 15wt%-Cu/AC-600 catalyst can promote the transformation of vanillin to MMP with 99.9% conversion and 93.2% selectivity of MMP under a moderate.<sup>15</sup> In the same period, Zhang et al and Xia et al. found nitrogendoped carbon supported cobalt or nickel nanoparticles displayed good activity in the process of vanillin hydrodeoxygenation.<sup>18-19</sup> With Co/nitrogen-doped carbon as catalyst, 98.8 % conversion of vanillin and 58.9 % selectivity of MMP were achieved in ethanol. However, the reduction of aldehydes, utilization of Ni catalysts mainly focused on the transformation of -CHO to -CH<sub>2</sub>OH. <sup>20-23</sup> Lee's group synthesized one caped Ni nanoparticles using a colloidal method to catalyze the selective hydrogenation of furanic aldehydes to generate furanic alcohols.<sup>24</sup> Recently, Stella's group reported NiO nanoparticles can effectively catalyze reduction of benzaldehydes to the correspondent benzylic alcohols.<sup>25</sup> There are very little reports on the catalytic

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transformation of -CHO to -CH $_3$  or -CH $_2\text{OCH}_3$  using the Nibased catalysts.  $^{19}$ 

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For the selective hydrogenation reaction of vanillin, Xu's group suggested MMP could be produced via hydrogenation and further hydrogenolysis pathway, in which the hydrogenolysis of vanillyl alcohol occurred (path (i) in Scheme 1);<sup>8</sup> Also, several other investigations supported that MMP was obtained via the hydrogenation/hydrogenolysis pathway. <sup>15,25,26</sup> It is worth mentioning that Abu-Omar's group<sup>27</sup> and Jiang et al<sup>18</sup> performed the catalytic hydrodeoxygenation of vanillin in alcohol. They also thought of Route (i) as the reaction pathways and vanillyl alcohol as the reactive intermediate. In addition, they claimed 4-(methoxymethyl)-2-methoxyphenol (ether), which is the result of vanillyl alcohol reaction with the solvent MeOH can protect vanillin from hydrogenolysis.

In recent years, our group has employed the novel MOFsbased materials (MOFs: Metal-organic frameworks) to catalyze the transformation of biomass <sup>28,29</sup> Distinguishing from traditional supported catalysts, the active sites of MOFs-based catalysts can either originate from the immobilizing metal nanoparticles or from metal linkers, and sometimes from the functional groups on the organic ligands as well.<sup>30,31</sup> Furthermore, MOFs can be used as precursors of carbon matrix nanocomposites.<sup>32-35</sup> These composites not only remain two dimensional structure of the MOF precursor, but also have high specific surface area and uniformly dispersed active sites, which are essential in promoting catalytic activity. Most important of all, some heteroatoms such S, N, Si, B, active metal sites or some other functional groups may be incorporated into the nodes and linkers on the MOFs in advance resulting in co-doped porous carbon composites, which can endow the perfectly catalytic activity. 32,33,36

In this contribution, we performed the hydrogenation reaction of vanillin using novel Ni-based catalysts as potential heterogeneous catalysts, which were manufactured through calcining one 2D Ni-based MOFs ( $[Ni(tia)(H_2O)_2]_{\infty}$ ) (tia<sup>2-</sup> = 5-(1*H*-1,2,3-triazol-1-yl) isophthalate). With the higher calcination temperature at 700 °C, the derived active nanocomposites (designated as Ni-MFC-700 catalyst) show great performance in hydrodeoxygenation of vanillin into the desirable product MMP with 100% conversion and 96.5% selectivity. At the same time, 4-(methoxymethyl)-2methoxyphenol as the intermediate was detected and the high yield of it (82.7%) was obtained using the alternative Ni-MFC-500 catalyst under the mild conditions, where a more atomeconomic alternative reductive etherification protocol was proposed. Furthermore, a new possible reaction pathway of the reduction of -CHO to -CH<sub>3</sub>, especially for the hydrogenation of vanillin with hydrogen in methanol was explored. As shown in path (ii) of Scheme 1, the transformation of vanillin to MMP would proceed via the tandem reductive etherification and the ether C-O bond hydrogenolysis steps.





Path(ii):: the reductive etherification of -CHO/the ether C-O bond hydrogenolysis



The yeild of etherification and methylation products being controllable to 82.7% and 96.5%, respectively **Scheme 1** The possible pathways of the reductive transformation of aldehyde group under  $H_2$ .

### **Results and discussion**

Synthesis and characterizations of the catalysts. The precursors 2D Nickel-based MOFs ( $[Ni(tia)(H_2O)_2]_{\infty}$ ) has been method.28 synthesized using hydrothermal The crystallographic data and detail structural information was supplied in the Supporting information (Table S1). Single crystal X-ray diffraction analysis revealed an unusual infinite 2D-dimensional layer based on Ni3 rings formed in crystallographic ab plane and each Ni(II) ion has a slightly distorted octahedral coordination, formed by one nitrogen atoms and three oxygen atoms from the tia<sup>2-</sup> ligands, and two oxygen atoms from water molecules occupied on the apical positions (see Fig. 1a, 1b and 1c). In crystallographic bc plane, the 2D-dimensional layers was connected by hydrogen-bond interaction to form 3D supramolecular structure (Fig. 1(d)). Ni-MFC catalysts were manufactured by calcining this Ni-MOF under N<sub>2</sub> atmosphere at different temperature.

The purity of the bulk synthesized MOFs material was confirmed by PXRD (Supplementary Fig. S1 (a) and (b)). The derived catalysts (designated as Ni-MFC-300, 350, 400 500, 600, 700, and 800) were manufactured by calcining the Ni-based MOFs in the atmosphere of N<sub>2</sub> with different calcination temperature. The PXRD patterns of the derived catalysts showed the frameworks of MOFs were destroyed gradually with the calcination temperature increasing (Supplementary Fig. S1(c), (d), (e), (f), (g), (h) and (i)). At the same time, the diffraction intensity of Ni (111) and Ni (200) at  $2\theta = 44^{\circ}$  and 52°, respectively, increased greatly.<sup>37,38</sup>

The X-ray photoelectron spectroscopy (XPS) spectra of the fresh Ni-MFC-700, fresh Ni-MFC-500 and used Ni-MFC-700 were displayed in Fig. 2, Fig. S2 and S3 in Supporting Information, respectively. The photoelectron peaks at 853 eV (Ni2p3/2), 532 eV (O1s), 401 eV (N1s) and 285 eV (C1s) were assigned to the main elements of the catalyst. For the fresh Ni-MFC-700 catalyst, the best fitted peaks of Ni2p3/2 in Ni-MFC-700 at 852.1, 853.3, 855.1 and 859.8 eV, which were associated with the adsorption Ni(0), élément naturel, NiO and

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Ni<sub>2</sub>O<sub>3</sub>, respectively (Fig. 2(a)). The best fitted peaks of O1s at 529.7, 531.4, 532.3, and 533.1 eV could be attributed to the adsorption of NiO, Ni<sub>2</sub>O<sub>3</sub>, -C-O and -C=O, respectively (Fig. 2(b))<sup>39-42</sup>. The nicely fitted peak of N1s at 398.5eV was generally ascribed to pyridinic N atoms, which were bound to two C atoms at the edge of graphene layers. <sup>43</sup> Signals at 400.8 eV were usually attributed to N atoms, which was bound to O atoms (Fig. 2(c)). Peaks at 401.9 eV may originate from quaternary N, which substituted one C atom in the graphene layer forming three  $\sigma$ -bonds with C atoms. A very weak peak at 404.4 eV may be assigned to the coordination interaction between N and Ni. The best fitted peaks of C1s at 284.8, 285.5 and 289.1 eV are ascribed to the graphite C, -C-O and -C=O, respectively (Fig. 2(d)). The peak of Ni(0) in Ni-MFC-500 catalyst is much weaker than in Ni-MFC-700 (see Fig. 2(a) and Fig S2(a) in the Supporting Information). The best fitted peaks of Ni2p3/2 show the content of Ni(0) in Ni-MFC-700 and Ni-MFC-500 is 15.6% and 1.5 %, respectively. In addition, the best fitted peaks of Ni2p3/2 in Ni-MFC-500 at 857.1 and 861.9 eV may be assigned to the -Ni-O-, -Ni-N- of MOF's framework (see Fig. S2(a) in Supporting Information). At the same time, some best fitted peaks of C1s, N1s and O1s in Ni-MFC-500 are different from Ni-MFC-700, which indicated their existence form in the matrix carbon may be different. In addition, Fig S3 (a) in Supporting Information indicates the existence of Ni in Ni-MFC-700 keeps unchanged after being recycled for 5 times, which are responsible for the good recyclability.

Typical morphologies of the fresh Ni-MFC-700, Ni-MFC-500, used Ni-MFC-700, used Ni-MFC-500 and Ni/activated carbon were displayed in Fig. 3 and Fig. S8 in the supporting information. Ni-MFC-700 maintained the cuboid block shape of the synthesized 2D Ni-based MOFs (see Fig. 3(a) in Supporting Information). Meanwhile, the images of the catalyst highlight the lamellar structure (see Fig. 3(b)). High magnification HRSEM images revealed that the compact morphology converted to porosity after calcination. There are spherical nanoparticles distributed uniformly on some cottonshaped matrix, whose sizes fell within the range of 0~10 nm (shown in Fig.3(c)). Fig. 3(d), 3(e) and 3(f) exhibit the morphology of the used Ni-MFC-700 remained unchanged after five cycles. It was found in Fig. 3(g), 3(h) and 3(i), the shapes of Ni-MFC-500 are similar to those of Ni-MFC-700. Different from the latter, no lamellar structure was found. Comparison Fig. 3(c) with Fig. 3(i), it is found a large quantity of Ni nanoparticles with uniform particle size are uniformly dispersed in the lamellar in Ni-MFC-700. While in Ni-MFC-500,

### Ni nanoparticles are not fully grown. After being reused for 5 times, the morphologies of Ni-MFC-500 Changed greatly (Ffg. 3(j), 3(k) and 3(l)). In addition, the HRSEM images of Ni/activated showed the particle sizes are in the range of 30-100 nm. These non-uniform particles are distributed on the surface of the support (see Fig. S8 in Supporting Information).

To get a clear vision of the elemental distribution of Ni, N, O and C on the fresh Ni-MFC-700, used Ni-MFC-700, fresh Ni-MFC-500 and used Ni-MFC-500 catalyst, one representative region was subjected to EDX mapping (see Fig. S4-S7 in Supporting Information). It was found Ni and N elements were uniformly distributed on each catalyst. Obviously, the dispersion effect of the active Ni species using MOFs as templates is better than the conventional supported catalyst

The Brunauer-Emmett-Teller (BET) results of the derived Ni-MFC catalysts were shown in supplementary Table S2 and Fig. S9. Their isotherm presented a type IV isotherm according to BDDT classification. There are hysteresis loops of type H2 in Ni-MFC-700 and Ni-MFC-800 catalysts according to IUPAC classification.44 While the adsorption and desorption hysteresis loop of Ni-MFC-500 belonged to H3. The hysteresis loop H2 is attributed to the presence of relatively uniform pores in the form of channels. Hysteresis loop H3 in Ni-MFC-500 may be ascribed to the presence of mesopores surrounded by a matrix of smaller pores, which is associated to the incomplete degradation of organic skeletons. It was worth mentioning that the pore feature of Ni-MFC-700 almost kept unchanged after 5 cycles. However, the pore size of Ni-MFC-500 became smaller after being recycled for 5 times. The isotherm curves of them also changed (see Fig. S10 and S11 in Supporting Information).

The ammonia desorption profile of Ni-MFC-500, 700, 800 were investigated in a normalized mode (initial coverage of NH<sub>3</sub> = 1) at a heating rate of 10 °C/min and the results were shown in supplementary Fig. S12. The first broad peak of Ni-MFC-500 may be ascribed to the two contributions: (i) decomposition of the remnant MOFs' framework and (ii) weak Brønsted acidic sites. As far as the TPD profiles of Ni-MFC-500, 700, 800 were concerned, a narrow desorption peak was observed around 375 °C referred to Bronsted acid sites in the catalysts. After being recycled for 5 times, the acidity of Ni-FMC-700 became stronger. However, the number of weak acidic sites increased (see Fig. S13 and S14 in Supporting Information).

In addition, the Ni content of all as-obtained catalysts were determined by quantitatively by ICP-OES technique (ICP-OES: Inductively Coupled Plasma Optical Emission Spectrometry) and the results were shown Table S3 in the Supporting Information.

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Fig. 3. HRSEM images of the catalysts at different magnification: (a), (b) and (c) for the fresh Ni-MFC-700; (d), (e) and (f) for the used Ni-MFC-700; (g), (h) and (i) for the fresh Ni-MFC-500; (j), (k) and (l) for the used Ni-MFC-500.

**Catalysts screening.** In view of the uniformly dispersed active sites originated from the MOFs-based derived materials, we have synthesized 2D Ni-based metal-organic frameworks (MOFs:  $[Ni(tia)(H_2O)_2]_{\infty}$ ) as the precursors for fabricating the

excellent hydrogenolysis catalysts. Here, the different derivative catalytic materials (designated as Ni-MFC, Ni-MFC-300, Ni-MFC-350, etc.) were generated through the calcination process of  $[Ni(tia)(H_2O)_2]_{\infty}$  in the N<sub>2</sub> atmosphere with different

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temperature. We conducted the hydrogenation of vanillin reaction in methanol over these derivative catalysts under the condition of 2 MPa  $H_2$ , 160 °C and the results were shown in Scheme 2 and Table 1. MMP (1), 2-methoxy-4-(methoxymethyl)phenol (2) and 4-(dimethoxymethyl)-2methoxyphenol (3) were detected in our reaction systems, but the vanillyl alcohol (4) and deep hydrogenation (saturation of C=C) product were not observed. The calcination temperature of Ni-MFC catalysts shows great influence on the distribution of products. As shown in Table 1, the conversion of vanillin increased with the calcination temperature increasing before 500 °C (Entries 3~7 in Table 1). The as-synthesized 2D Ni-based MOF showed no activity for hydrogenation of vanillin (Entry 3 in Table 1). Selectivity towards reductive etherification product 2 increased and 3 decreased with the calcination temperature increasing. Ni-MFC-400 catalyst can promote the selectivity of reductive etherification product to 88.9% (Entry 6 in Table 1). For further increasing the calcination temperature of MOFs,

the derived catalysts Ni-MFC-500~700 exhibited strong promotion effect in producing 1 via Daydoddeoxygenation process (Entries 7~9 in Table 1). With Ni-MFC-700 catalyst, the conversion of vanillin and selectivity of the desirable product 1 can be up to 100% and 26.4%, respectively. However, the higher calcination temperature at 800°C, the catalytic active towards 1 decreased (Entry 10 in Table 1). So Ni-MFC-700 was screened as the best HDO catalyst for up-grading vanillin (Entry 9 in Table 1). If we calcined 2D Ni-based MOFs in  $O_2$ atmosphere and the derived Ni-MFC-700 showed no catalytic on the hydrodeoxygenation and reductive activitv etherification process of vanillin (Entry 11 in Table 1). The full conversion of vanillin and 96.5% selectivity of 1 were obtained using Ni-MFC-700 as the catalyst under the condition of 2 MPa H<sub>2</sub>, at 200°C for 10 h (Entry 12 in Table 1). The higher yield of 2 was up to 82.7% with Ni-MFC-500 as the catalyst under the condition of 2 MPa H<sub>2</sub>, at 160°C for 4 h (Entry 7 in Table 1).



Scheme 2. Hydrodeoxygenation and reductive etherification of vanillin in methanol with the Ni-based catalysts

Entry		Conv. (%) <sup>b</sup> –	Sel. (%) <sup>b</sup>				TON <sup>h</sup>	TOF <sup>i</sup>	
	Catalyst		1	2	3	Others		(1/h)	
1	No	62.0	0.0	12.1	87.9	0.0	/	/	
2	Cd-MFC-700 <sup>j</sup>	58.9	0.0	7.8	88.2	4.0	/	/	
3	Ni-MFC	62.5	0.0	11.1	88.9	0.0	/	/	
4	Ni-MFC-300 <sup>c</sup>	82.9	5.2	43.9	50.9	0.0	574.8	143.7	
5	Ni-MFC-350 <sup>c</sup>	81.4	5.3	61.2	30.9	2.6	595.1	148.8	
6	Ni-MFC-400 <sup>c</sup>	62.4	7.4	88.9	3.7	0	577.2	144.3	
7	Ni-MFC-500 <sup>c</sup>	100	13.1	82.7	3.8	0.4	1343.6	335.9	
8	Ni-MFC-600 <sup>c</sup>	100	17.2	80.2	1.0	1.6	1859.5	464.9	
9	Ni-MFC-700 <sup>c</sup>	100	26.4	72.5	0.4	0.7	2640.0	660.0	
10	Ni-MFC-800 <sup>c</sup>	100	20.6	59.3	19.3	0.8	1961.9	490.5	
11	Ni-MFC-700 <sup>f</sup>	71.5	0.0	7.1	92.9	0.0	/	/	
12	Ni-MFC-700 <sup>d</sup>	100	96.5	3.1	0.4	0.0	8772.7	877.3	
13	Ni/Activated Carbon <sup>e</sup>	71.3	20.0	30.5	49.5	0.0	4074.3	1018.6	
14	Ni/γ-Al <sub>2</sub> O <sub>3</sub> -700 <sup>e</sup>	70.1	0.0	29.9	70.1	0.0	0	0	
15	Ni/nano graphite-700 <sup>e</sup>	71.5	1.5	23.3	73.9	1.3	286.0	71.5	
16	Ni/TiO <sub>2</sub> -700 <sup>e</sup>	64.0	1.1	31.6	66.2	1.1	234.7	58.7	
17	Ni/ZrO <sub>2</sub> -700 <sup>e</sup>	60.5	0	19.3	79.2	1.5	0	0	
18	Ni/nano MgO-700 <sup>e</sup>	74.9	1.5	46.0	48.0	4.5	374.5	93.6	
19	Ni/Activated Carbon used <sup>g</sup>	65.5	0	10.2	89.7	0.0	/	/	

Table 1. Hydrogenolysis of vanillin using Ni-MFC catalysts and the conventional supported catalysts<sup>a</sup>.

<sup>*a*</sup> Reaction conditions: 0.1 g vanillin, 0.025 g catalyst, in 15 mL methanol, under 2 MPa of H<sub>2</sub>, at 160 °C for 4 h.

<sup>b</sup> The results were obtained by GC analysis with the internal standard technique, 1,3-dichlorobenzene as internal standard.

<sup>c</sup> The catalyst was obtained by calcination 2D Nickel-based MOFs ([Ni(tia)(H<sub>2</sub>O)<sub>2</sub>]<sub>∞</sub>) in N<sub>2</sub> flow at 300~800 °C.

<sup>d</sup> Reaction conditions: 0.1 g vanillin, 0.025 g catalyst, in 15 mL methanol, under 2 MPa of H<sub>2</sub>, at 200 °C for 10 h.

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<sup>e</sup>Catalysts preparation: support (0.1 g) and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.04 g), and 2 mL H<sub>2</sub>O were mixed together, and the mixture was treated under ultrasonic irradiation for 6 h, then the mixture was placed in an oven and dried at 80 °C for 12 holder because powder was grinded and calcined under N<sub>2</sub> flow at 700 °C for 4 h.

<sup>f</sup>The catalyst was obtained by calcination 2D Nickel-based MOFs ( $[Ni(tia)(H_2O)_2]_{\infty}$ ) in O<sub>2</sub> flow at 700 °C.

<sup>g</sup> The Ni/Activated Carbon was reused for one time.

<sup>*h*</sup> TON = mole of product (MMP) /mole of Ni species.

<sup>*i*</sup> TOF = TON/time.

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<sup>1</sup>The Cd-MFC-700 catalyst was prepared by calcination 2D Cadmium-based MOFs ([Cd(tia)(H<sub>2</sub>O)<sub>2</sub>]<sub>∞</sub>) in N<sub>2</sub> flow at 700 °C.

In addition, the conventional Ni-based solid catalysts were also investigated and the experimental results were summarized in Table 1 (Entries 13-18). Therein, in the presence of Ni/activated carbon, a 71.3% conversion of vanillin and 20.0% selectivity of **1** were obtained under the same conditions. The turnover number (TON) and turnover frequency (TOF) of it is higher than Ni-MFC-700 (see the last two columns in Table 1).<sup>45, 46</sup> However, when we tested the stability of the catalysts, we found the activity of Ni/activated carbon is lost after one cycle (Entry 19 in Table 1). Furthermore, the other supported Ni-based catalysts nearly showed no selective conversion toward the generation of **1**. Meanwhile, the yield of reductive etherification product was not desirable.

Here, the great performance of Ni-MFC-700 was obtained by comparison with other Ni-based catalysts supported on the conventional porous materials. The metal-organic frameworks are compounds consisting of metal ions or clusters coordinated to organic ligands to form one-, two-, or threedimensional structures, so pyrolysis metal-organic frameworks (MOFs:  $[Ni(tia)(H_2O)_2]_{\infty}$ ) afforded us Ni-based carbon composites, so in order to determine the active species is Ni rather than other ingredients of the derived materials, one isostructural Cd-based MOFs  $[Cd(tia)(H_2O)_2]_{\infty}$  has been synthesized and used as the precursors for fabricating Cd-MFC-700 catalyst under the same condition as Ni-MFC-700 (Entry 2 in Table 1). Cd-MFC-700 showed no activity for hydrogenolysis vanillin to 1 or 2. So we are ascertained Nickel is the active species for catalyzing the transformation of vanillin into 1 or 2. Furthermore, a significant change in the catalytic activity depending on the calcination conditions was observed (see Entries 4-8 in Table 1), which may be ascribed to the different existence form of Nickel under the different calcination conditions. The Ni(II) centers in the as-synthesized 2D MOFs  $([Ni(tia)(H_2O)_2]_{\infty})$  are coordinated by the donor atom (N and O) show no catalytic activity. With the calcination temperature increased, the organic component decomposed and the Ni centers were exposed little by little. In addition, the existence form of Ni and the morphology of the as-obtained Ni-MFC-X also changed. The evidence for these is from XPS spectra, XRD patterns and HRSEM images of Ni-MFC-500 and Ni-MFC-700. The correlation between structural properties and catalytic activity is as follows. (i) The lamellar structure and the uniform particles are uniformly dispersed in the lamellar in Ni-MFC-700, while in Ni-MFC-500, Ni nanoparticles are not fully grown. This explains a significant change in the catalytic activity depending on the calcination conditions. (ii) The XRD patterns of Ni-MFC-X show the intensity of Ni(0) diffraction peaks in Ni-MFC-700 is

stronger than other Ni-MFC-X catalysts. Another evidence from the analysis results of XPS data. The best fitted peaks of Ni2p3/2 show the content of Ni(0) in Ni-MFC-700 and Ni-MFC-500 is 15.6% and 1.5%, respectively. So we speculated that Ni(0) is the active species for hydrogenation vanillin to product **1**, While the nickel in oxidation state may be responsible for producing **2**, because the Ni(0) content of Ni-MFC-700 is much higher than Ni-MFC-500.

Optimization of reaction conditions. In order to improve the yield of 1, the reaction conditions were further optimized and the results were displayed in Supplementary Fig. S15 and S16. It is found that the conversion of vanillin and selectivity of 1 was increased with the increase of temperature. Below 120 °C, there is no production of desirable product 1, in which compounds 3 and 4 were the main products. Along with the elevation of reaction temperature, the conversion of vanillin was gradually increased, and the total selectivity of 2 and 1 was increased, while the selectivity of **3** and **4** was decreased. In particular, when the temperature was increased to more than 160 °C, it should be no longer detected for 3 and 4 after 4 h. In the temperature range of 140 °C~160 °C, a large quantity of ether (2) was obtained. The full conversion of vanillin was acquired at 160 °C. If the temperature continues to be raised, the selectivity of 2 was gradually decreased and the selectivity of 1 was increased.

Supplementary Fig. S16 showed the selectivity of **1** increased and **2** slowly decreased along with the prolonging of time. As a result, a full conversion of vanillin and a 96.5% selectivity for **1** was acquired at 200 °C for 10 h. Moreover, the Ni-MFC-700 and Ni-MFC-500 catalyst are easily separated by the filtration process and the activity keeps almost unchanged after being recycled for 5 times which proves its good stability and recyclability (see Fig. S17 in Supporting Information).

**Reaction mechanism.** The traditional hydrogenation and deoxygenation route of vanillin in aqueous media could proceed via (a~a') (The red section in Scheme 3).<sup>25, 26</sup> However, acetal (3), ether (2) and 2-methyl-4-methylphenol (1) were detected as the main products in our catalytic system (vanillin +  $H_2$  + methanol). With this in mind, a new possible pathway for the transformation of vanillin to 1 was proposed. The transformation of vanillin to 1 proceeds via the ether hydrogenolysis pathway and compound 2 should be the main reaction intermediate, and generated from the reductive etherification of vanillin (The green section in Scheme 3). The detail steps may include: (i) Self-catalytic condensation into acetal or hemiacetal. In methanol media, furfural reacted with

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methanol to produce into acetal or hemiacetal via selfcatalytic pathway due to the acidity of para-phenolic hydroxyl group on the substrate. (ii) Reduction acetal or hemiacetal to ether (2); (iii) Hydrogenolysis ether -CH<sub>2</sub>O-R (2) bond into methyl group. For further evidence, we have performed the kinetic experiments and the kinetic curves of the transformation were shown Fig. 4. At the initial stage, compound **3** is the main product. As reaction time was prolonged, the selectivity of compound **2** and **1** increased, while the selectivity of **2** reached the maximum value, and then selectivity of compound **2** decreased greatly. After 1.5 h, the selectivity of compound **2** decreased. Based on the above characters, it is concluded that the transformation of vanillin to compound **1** proceeds via the ether hydrogenolysis pathway (path b<sub>4</sub> in Scheme 3).

In addition, a series of control experiments have been performed and the results were shown in Table 2. The vanillin, vanillyl alcohol (4) and ether (2) were respectively selected as the substrates (Note: compound 2 was acquired from the reaction system of vanillin and methanol with Ni-MFC-700 as the catalyst by using silica gel column chromatography. <sup>1</sup>HNMR spectrum of 2 was provided in Supplementary Fig. S18). It was found that the yield of 1 was listed in the order of from 2 (28.4%) > from vanillin (26.4%)> from vanillyl alcohol (10.4%), which suggested that hydrogenolysis of 2 into 1 should be easier than the hydrogenolysis of vanillyl alcohol (Entries 3, 7 and 8 in Table 2). Comparison the data from Entry 9 and 12 in Table 1, it was found conversion 2 to 1 was feasible by prolonging the reaction time and raising the reaction temperature. We also performed the following reaction: the vanillin was firstly reacted in the N<sub>2</sub> atmosphere for 4 h. Then, the N<sub>2</sub> gas was totally replaced by H<sub>2</sub> gas. After being further reduced for 4 h, it was found that the full conversion of vanillin, 39.3% selectivity of 1 and 56.8% selectivity of 2 were obtained (Entry 10 in Table 2). Obviously, compound **3** can be converted to 2, which can be further transformed to 1 during the selective reduction of vanillin.

The aforementioned results exhibited that hydrogenolysis of **2** into **1** is the most efficient route for the reduction of vanillin in alcohol. Compound **2** should be the main reaction intermediate, and generated from reductive etherification of vanillin, in which acetal (**3**) formation as an intermediate for

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producing **2** was detected. Herein, the catalytic Areaction proceeds via hemiacetal and/or acetal pathway (the green as section path b~b1 and path b~b2~b3 in Scheme 3) was proposed.<sup>47-49</sup> Vanillin can be converted to the acetal (**3**) without Ni-MFC-700 under the N<sub>2</sub> atmosphere by comparison the data from Entries 2 and 4 in Table 2. We speculated that **3** was the self-catalytic condensation product, in which the acidity of phenolic hydroxyl group on the para-position may be responsible for forming product **3**.

Generally, the transformation from vanillin to ether (2) can be performed on the following pathways: (i) hydrogenation of vanillin to vanillyl alcohol, then vanillyl alcohol react with methanol to produce ether [see routes (a)~(d')] (see Entry 5 and 6 in Table 2); (ii) hydrogenation of hemiacetal and acetal to ether [see routes (b)  $\sim$ (b<sub>1</sub>) or (b)~(b<sub>2</sub>)~(b<sub>3</sub>)]. Here, when we performed the catalytic experiments using vanillin as the substrate, no alcohol was detected, ether (2) and acetal (3) were the main by-products. Transformation acetal (3) to ether (2) can't do without  $H_2$ , while the catalyst can promote this process (Entries 1, 2 and 3 in Table 2). Transformation (4) to (2) can do without  $H_2$  and the catalyst (Entries 5 and 6 in table 2). If the path  $b_2 \sim b \sim a \sim d'$ (3~4~2) is the main pathway in our reaction system, the yield of 1 would be in the order: vanillyl alcohol > vanillin. But the opposite is true. So the tandem reductive etherification pathway was more favorable in our reaction system. But we really can not preclude the pathway 3~4~2.

At last, we used other solvents with vanillin, vanillyl alcohol and ether as starting materials for the determination of the mechanistic pathway and the results were shown in Table 3. When the reaction with the other solvents (THF and CH<sub>3</sub>CN) shows no evidence of product (**2**) formation, it may be to the fact step (i) and (ii) can't proceed in THF and CH<sub>3</sub>CN. So in the methanol, hydrogenolysis vanillin into **1** may proceed in pathway (ii), While in THF and CH<sub>3</sub>CN, hydrogenolysis vanillin into **1** may proceed in pathway (i). At the same time, the order for producing **1** was found in tetrahydrofuran (THF): **2** (30.7%) > vanillyl alcohol (22.8%) > vanillin (11.4%) (Entries 3, 4, 5 in Table 3). While the yield of **1** in methanol is: **2**> vanillin > vanillyl alcohol. Hydrogenolysis ether to **1** is much easier. In methanol, the yield of **1** is from vanillin > vanillyl alcohol, which can be ascribed to the occurrence of the tandem reductive etherification.

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Scheme 3. The different routes for hydrogenation of vanillin.



Fig. 4 The kinetic curves of the transformation of vanillin in methanol (reaction conditions: 0.1 g vanillin, 0.025 g catalyst, in 15 mL methanol, under 2 MPa of H<sub>2</sub>, at 200 °C).

Table 2. Some blank and controlled experiments for investigat	ion the reaction mechanism <sup>a</sup>
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Entry	Substrata	Catalyst	Atmosphere	$C_{ODV}$ $(9/1)^{b}$		Selectivity (%) <sup>b</sup>			
Entry	Substrate	Calalysi	Atmosphere	Atmosphere Conv. (%) <sup>5</sup>		2	3	others	
1	Vanillin	No	2MPa H <sub>2</sub>	62.0	0.0	12.1	87.9	-	
2	Vanillin	No	1MPa N <sub>2</sub>	71.5	-	0.6	96.7	2.7	
3	Vanillin	Ni-MFC-700	2MPa H <sub>2</sub>	100	26.4	72.5	0.4	0.7	
4	Vanillin	Ni-MFC-700	1MPa N <sub>2</sub>	63.1	-	1.0	97.4	1.6	
5	4	No	1MPa N <sub>2</sub>	100	1.6	97.8	0.3	0.3	
6	4	No	2MPa H <sub>2</sub>	100	1.9	97.6	0	0.5	
7	4	Ni-MFC-700	2MPa H <sub>2</sub>	100	10.4	88.7	0.3	0.6	
8	2	Ni-MFC-700	2MPa H <sub>2</sub>	29.2	97.3	-	-	2.7	
10 <sup>c</sup>	vanillin	Ni-MFC-700	1MPa N <sub>2</sub> -2MPa H <sub>2</sub>	100	39.3	56.8	3.9	-	

<sup>a</sup> Reaction conditions: 0.1 g substrate, 0.025 g catalyst, in 15 mL methanol, at 160 °C for 4 h.

<sup>b</sup> The results are obtained by GC analysis with the internal standard technique, 1,3-dichlorobenzene as internal standard.

 $^{\rm c}$  The reaction was performed in  $N_2$  for 4 h, then  $N_2$  was replaced by  $H_2.$ 

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Table 3. Effect of solvents on hydrogenolysis of vanillin, 4 and 2 a								
Entry	Substrate	Solvent	Conv. (%) <sup>b</sup> —	Selectivity (%) <sup>b</sup>				
Entry				1	3	4	Others	
1 <sup>c</sup>	Vanillin	CH₃CN	96.1	0	0	0	100	
2 <sup>c</sup>	Vanillin	THF	13.1	27.5	0	64.9	7.6	
3 <sup>d</sup>	Vanillin	THF	13.2	86.4	0	0	13.6	
4 <sup>d</sup>	4	THF	25.3	90.2	0	0	9.8	
5 <sup>d</sup>	2	THF	30.7	100	0	0	0	

<sup>a</sup> Reaction conditions: 0.1 g substrate, 0.025 g catalyst, in 15 mL solvent, for 4 h;

<sup>b</sup> The results are obtained by GC analysis with the internal standard technique, 1,3-dichlorobenzene as internal standard.

<sup>c</sup> Reaction temperature is 160 °C;

<sup>d</sup> Reaction temperature is 200 °C.

Scopes of Substrate. In order to reveal the advantage of this catalytic system, the selective reduction of different aldehydes 4-hydroxybenzaldehyde such as (5), 3-chloro-4hydroxybenzaldehyde (6), 4-hydroxy-3, 5dimethoxybenzaldehyde (7), p-methoxy bezaldehyde (8), 3hydroxy-4-methoxybenzaldehyde (9), and 3, 4, 5-trimethoxy benzaldehyde (10) were studied, and the data are presented in Table 4. Interestingly, the hydrogenation of the substrates 5, 6 and 7 with phenolic hydroxyl group in the para-position afforded the main methylated products. The sequence of methylated product yield is from 7 > from 5 > from 6. Notably, the reduction of compound 7 could give the methylated product in 51.5% yield at 160°C, 2 MPa H<sub>2</sub> for 4 h in (see Table S4 in Supporting Information), which is much higher than the hydrogenation of vanillin under the similar reaction conditions. However, the yields of the corresponding alcohol were mainly generated and the relatively low methylated products were obtained when compound 8 and 10 was used as the substrate, which indicates that the existence of phenolic hydroxyl is beneficial to transform -CHO to CH<sub>3</sub> in hydrogenation of aldehydes. Furthermore, the hydrogenation of compound 9 provide a moderate yield of methylated product that proves that the hydroxyl at the para-position is more desirable than that at meta position to this catalytic process. When the reaction was performed at 200 °C for 10 h, the reduction of the substrates 5, 6 and 7 afforded the higher yields of methylated products. Especially for 6 and 7, no ether as the intermediate was detected. A small quantity of unknown byproduct would be the deep hydrolysis products. Also, higher yields of methylated products were obtained during the

selective reduction of 8 and 9 at 200 °C for 10 h. The corresponding yields of methylated product are 62.1% and 68.2%, respectively. For the reduction of 10, the selectivity of methylated product was 34.9% where 53.0% selectivity of alcohol and 12.1% selectivity of ether were achieved. While, for the hydrogenation of 8 and 9, the selectivity of ether was respectively 37.9% and 29.5% in the catalytic reaction system. Obviously, the yield of methylated products was consistent with the occurrence of reduced etherification of substrates, which further verified the aforementioned reaction pathway (Route (b) in Scheme 3). The obtained methylated product could mainly be attained via reductive etherification route during the catalytic process, indicating that the transformation of the aldehyde group to the methyl group via the hydrogenolysis of ether is more favorable than that via the hydrogenolysis of alcohol.

In order to further verify the catalytic results, the isolated yields of methylated products for the reduction of vanillin, compoud **5** and **7** (200 °C, 10 h) were obtained based on the silica gel column chromatography with the mixture of ethyl acetate and petroleum ether as eluent. Therein, the isolated yield of MMP (**1**), 4-methyl phenol and 2,6-dimethoxy-4-methylphenol is 82%, 78% and 85%, respectively (see the last column in Table 4). The isolated yields are a slightly lower than the yields obtained from GC detection, which may be ascribed to the adsorption of silica gel. But the <sup>1</sup>HNMR spectra of corresponding products were attained and shown in Fig. S19, S20 and S21 of Supporting Information, which shows the data from the GC analysis are reliable.

	Та	ble 4. Hydrogend	olysis of other lig	nin models using	g Ni-MFC-700 as	s catalyst <sup>a</sup>	View Article Online DOI: 10.1039/C9GC01116A
Substrates	Conv. (%) <sup>b</sup>		Product	distribution (%) <sup>E</sup>	)		Isolated yield(%)
СНО		OH			HO	Others	ОН
(5)	100	83.1	15.9		О	1.0	78.0
ОН		CI	CI	CI	ОН	Others	/
(6)	100	75.3	0	0	0	24.7	/
CHO OH OH		O OH	O OH	O CH	HO O O O H	Others	OH OH
(7)	100	92.1	0	0	0	7.9	85.0
CHO O					HO	Others	/
(8)	100	62.1	37.9	0	0	<u>0</u>	L
CHO		С	ОН	С	HO	Others	/
(9)	100	68.2	29.5	0	<b>О</b> но	2.3	/
		° ° °				Others	/
(10)	100	34.9	12.1	0	53.0	0	_
CHO OH		OH OH			HO	Others	OH OF
Vanillin	100	96.5	3.1	0.4	0	0	82.0

 $^{\it a}$  Reaction conditions: 0.1 g substrate, 0.025 g catalyst, in 15 mL methanol, at 160 °C for 4 h.

<sup>b</sup> The results were obtained by GC analysis with the internal standard technique, 1,3-dichlorobenzene as internal standard.

### Experimental

**Materials.** Vanillyl alcohol (99.0%), vanillin (98.0%), 3,4,5trimethoxybenzaldehyde (99.0%), p-methoxybezaldehyde (99.0%), 4-hydroxybenzaldehyde (99.0%), 3-chloro-4hydroxybenzaldehyde (99.0%), MMP (99.0%), 1,3dichlorobenzene (99.0%) were purchased from Alfa Aesar. Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (98.0%), NaN<sub>3</sub> (98.0%), NaNO<sub>2</sub>·6H<sub>2</sub>O (98.0%), sodium ascorbate (97.0%), NaOH (98.0%), CuSO<sub>4</sub>·5H<sub>2</sub>O (98.0%),  $\gamma$ -AL<sub>2</sub>O<sub>3</sub>, activated carbon, nano graphite, ZrO<sub>2</sub>, TiO<sub>2</sub> and MgO were purchased from Shanghai Aladding Bio-Chem. Technology Co. Ltd. The reaction solvents were chromatography reagents and used without further purification.

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and Ni-MOF Catalyst preparation characterization. ([Ni(tia)(H<sub>2</sub>O)<sub>2</sub>]) was fabricated according to our previous report <sup>28</sup>. Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.4 mmol, (0.1162 g), NaOH (0.8 mmol, 0.032 g), and H<sub>3</sub>ctia (0.4 mmol, 0.1108 g) was added into a Teflon-lined pressure vessel, and then the mixture was heated to 180°C and kept at 180°C for 72 h. After being cooled to room temperature at a rate of 2.5°C/h, green block-shaped crystals were acquired, collected, washed with distilled water, and then dried in the air.

The as-synthesized Ni-MOFs were added in a quartz boat, and placed in the tubular furnace. The MOFs were calcined under N<sub>2</sub> flow (50 mL/min) for 4 h at different temperature (300, 350, 400, 500, 600, 700 and 800°C). After being cooled to room temperature, Ni-MFC-300, 350, 400, 500, 600, 700 and 800 catalysts were obtained.

Ni/activated carbon, Ni/y-Al2O3-700, Ni/nano-graphite-700, Ni/TiO<sub>2</sub>-700, Ni/ZrO<sub>2</sub>-700 and Ni/nano-MgO-700 were prepared according to the literature.<sup>29</sup>

X-ray single-crystal diffraction data were collected on a Rigaku SCX-mini diffractometer at 293(2) K with MoKR radiation ( $\lambda$ = 0.71073 Å) by  $\omega$ -scan mode. The powder X-ray diffraction patterns (PXRD) were recorded on Rigaku D/Max 2400 diffractometer with Cu/K $\alpha$  radiation. Fourier transform infrared spectra (FT-IR) were recorded using Bruker EQUINOX55 infrared spectrometer. High resolution scanning electron microscopy (HRSEM) was performed in a JSM 6490LV JEOL microscope at 25 kV. X-ray photoelectron spectroscopy (XPS) was carried out in a 5700 model Physical Electronics apparatus. Temperature programmed desorption (TPD) analysis were carried out using a Micromeritics ChemiSorb 2720 Pulse Chemisorption System with TCD detector. The BET surface areas and pore volumes were measured by N<sub>2</sub> adsorption-desorption at 77 K on a Micromeritics ASAP 2020 instrument at -196°C. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES: Varian 700-ES) was used to measure the metal content of the catalytic materials.

Reaction system and product analysis. The catalytic reaction was performed in 100 mL Parr stainless autoclave equipped with heater and sample port. In a typical experiment, substrate (0.1000 g), catalyst (0.025 g), and methanol (15 mL) were charged into the autoclave and purged with  $N_{\rm 2}$  for several times to remove the air. Then H<sub>2</sub> was purged into the reactor for 4 times to replace  $N_{\rm 2}$  at room temperature. Later, the autoclave was pressurized with H<sub>2</sub> up to 2 MPa and heated to 160 °C under vigorous stirring and held at this temperature for 4 h. After the reaction was over, the reaction mixture was weighed and diluted with methanol. The products were qualitatively analyzed by an Agilent 7890A-5975C gas chromatography-mass spectrometry (GC-MS) equipped with an capillary flow technology to detect multi signal data and quantitatively analyzed by using a GC (Agilent 6820) equipped with a flame ionization detector (FID) and a HP-5MS capillary column (0.25 mm in diameter, 30 m in length). Some GC-MS and GC spectra of the typical reactions were shown in Supporting information (Fig. S22~S37).

### Conclusions

DOI: 10.1039/C9GC01116 Novel Ni-MFC catalysts have been fabricated using 2D Ni-MOFs as precursors. Owing to the well-defined architecture of MOFs, the as-synthesized catalyst possesses the high specific surface area and uniform mesoporous sizes. The catalytic active sites such as Ni(0), NiO, etc., which were originated from metal nodes of MOFs, and the functional ingredient N was incorporated into the co-doped porous carbon matrix composites. All of these endowed Ni-MFC catalysts with good catalytic performance for the efficient transformation of vanillin to 1 or 2. Notably, Ni-MFC-700 was screened as the efficient hydrodeoxygenation catalyst for the transformation of -CHO group to -CH3 group while the Ni-MFC-500 was selective to promote reductive etherification of aldehydes to methyl ether. Moreover, the Ni-MFC catalysts kept stable and recyclable for the catalytic reductive process under the H<sub>2</sub> atmosphere. Furthermore, the mechanism investigations indicated that the transformation of aldehyde group (-CHO) to methyl group (-CH<sub>3</sub>) may proceed via the following steps: (i) Self-catalytic condensation into acetal or hemiacetal; (ii) Reduction acetal or hemiacetal to ether; (iii) Hydrogenolysis ether -CH<sub>2</sub>O-R bond into methyl group. In general, this catalytic system showed better performance for aromatic aldehyde with phenolic hydroxyl groups in the para-position. It provides a new and promising technique for the catalytic valorization of biomass feedstock and biomass-derived aldehyde and ether in chemical industry.

### **Conflicts of interest**

There are no conflicts to declare.

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# Nickel-catalyzed intelligent reductive transformation of View Article Online DOI: 10.1039/C9GC01116A

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# aldehyde group with hydrogen

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A highly efficient and catalytic valorization of lignin-derived aldehhydes to produce value-added chemicals has been developed with the Ni-based catalyst under the H<sub>2</sub> atmosphere.

# **Graphical Abstract**