

Solvent-Controlled Product Distribution in Vanillin Hydrogenation over a N-Doped Carbon-Supported Nickel Catalyst

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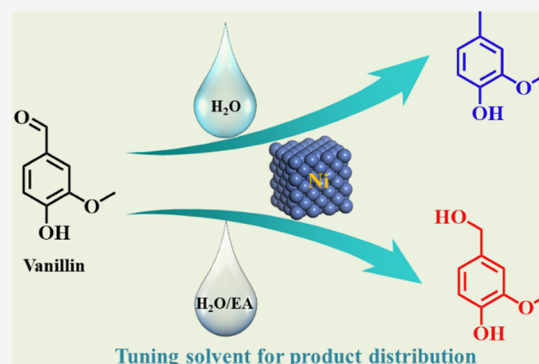


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Supporting Information

ABSTRACT: Solvent-controlled hydrogenation of vanillin to 4-hydroxymethyl-2-methoxyphenol (HMP) or 2-methoxy-4-methylphenol (MMP) is an attractive topic in the field of bio-oil utilization. Herein, a nickel-based catalyst supported on a N-doped carbon material (Ni-N-C) was prepared by facile ball milling and subsequent high-temperature calcination. The as-prepared Ni-N-C₈₀₀ catalyst showed more than 99% MMP yield and good stability using pure H₂O as a solvent under the given conditions. By using the mixed solvent H₂O/ethyl acetate with a volume ratio of 1:5, the hydrogenation was conveniently tuned to produce the intermediate product HMP. Density functional theory (DFT) calculations further showed that the intermolecular forces of HMP interacting with ethyl acetate were much stronger than those interacting with H₂O. Ethyl acetate could raise the energy barrier to keep vanillin hydrogenation in the intermediate HMP stage, and H₂O reduced the energy barrier to accelerate the final product MMP formation.

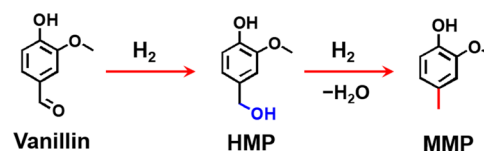


INTRODUCTION

With gradual exhaustion of fossil fuels and increasing demand for environmental protection, finding a green renewable energy source has received increasing attention of many researchers worldwide. The bio-oil derived from biomass pyrolysis is considered to be one of the most promising fuel candidates to replace the traditional fossil energy.¹ However, the complex bio-oil usually contains various chemicals rich in O element such as furans, phenols, aldehydes, ketones, etc., in which O almost accounts for more than 60% in total mass.^{2–4} The excessive oxygenates will inevitably lead to low energy density, poor thermal stability, bad mutual solubility, and strong corrosiveness to equipment, which block its application as an alternative energy source to replace finite fossil fuel reserves.^{5,6} Therefore, hydrodeoxygenation (HDO) is one of the most effective approaches in upgrading the quality of bio-oil with tremendous interest.^{7–9}

As a common component in bio-pyrolysis oil, vanillin is a typically investigated molecule in biomass refining by means of hydrodeoxygenation.^{1,10} MMP is the final product obtained by further hydrodehydrogenation of HMP, which is produced from hydrogenation of the aldehyde group on vanillin (Scheme 1). It is widely used in the synthesis of drugs and fragrances and recognized as a potential biofuel. So far, various transition metal catalysts such as Pd,¹¹ Co,^{12,13} Cu,^{14,15} and Ni^{16,17} have been widely employed for efficient hydrogenation of vanillin to produce MMP. For example, Cai and his co-workers prepared g-C₃N₄-supported Pd–Au bimetallic catalysts for the HDO of

Scheme 1. Hydrogenation of Vanillin to Produce HMP and MMP



vanillin and achieved 100% MMP yield at room temperature.¹⁸ Zhang et al. reported that the catalyst Co/N-C-600 exhibited a vanillin conversion of 99% and MMP yield of 98.6% at 150 °C and 20 bar H₂ pressure for 10 h.¹⁶ Li et al. synthesized a Ni-supported ZrP catalyst for obtaining 97.25% vanillin conversion with a MMP yield of 88.39% under the conditions of 220 °C and 0.5 MPa H₂ for 0.5 h.¹⁹ However, the intermediate HMP is also an important raw chemical for the synthesis of many functional materials such as renewable epoxy thermosets, polymers, and medicines.^{20–24} The above-mentioned progresses show that most of the reported catalysts are based on MMP as the terminal product instead of the

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intermediate HMP. According to various production requirements, facile tuning the excellent yield of HMP or MMP on one catalyst in the HDO of vanillin is still challenging.

Solvents play important roles in chemical synthesis by changing the reaction pathway in some cases. Modulation of product selectivity by the solvent in organic synthesis is a topic of great interest. Lei and his co-workers reported the switchable selective synthesis of β -oxy sulfoxides and β -hydroxy sulfides by solvent selection under mild conditions.²⁵ Fu et al. investigated the selective CO₂ photoreduction on SBA-15-supported CoP catalysts using different solvents, and 76.3% CO selectivity was achieved in acetonitrile.²⁶ These studies make us aware that screening and finding a suitable solvent could have the potential for efficient hydrogenation of vanillin with tunable product selectivity. It is also well known that the N-doped mesoporous carbon has a large specific surface area and abundant mesopores, which can provide more anchored sites for metal nanoparticles and benefit reaction diffusion.²⁷ Doping of the appropriate amount of nitrogen can effectively tune the electronic properties and geometry of metal nanoparticles to improve its catalytic activity.

Herein, a kind of N-doped carbon-supported Ni nanoparticle catalysts was prepared by ball milling of solid precursors and subsequent high-temperature annealing treatment. The catalyst calcined at 800 °C (Ni-N-C₈₀₀) showed good catalytic performance in the hydrogenation of vanillin to MMP under mild conditions with H₂O as a solo solvent. By using the mixed solvent H₂O/ethyl acetate with a volume ratio of 1:5, the hydrogenation was conveniently tuned to produce the intermediate product HMP with a good yield. In addition, the mechanism of the product modulation by the solvents was further investigated through density functional theory (DFT) simulation, and the catalytic reproducibility of Ni-N-C₈₀₀ was finally examined.

EXPERIMENTAL SECTION

Materials. Vanillin (99%), nickel (II) nitrate hexahydrate Ni(NO₃)₂·6H₂O (98%), ethyl acetate (EA, 99.9%), and folic acid (99.9%) were purchased from Shanghai Titan Scientific Co. Ltd. α -Cellulose (250 μ m) was bought from Shanghai Aladdin Co. Ltd. H₂ with a grade of 99.99% was supplied by Jiangxi Huahong Gas Co., Ltd. All the chemicals were used as purchased without further treatment.

Catalyst Preparation. Typically, folic acid (1.0 g), α -cellulose (2.0 g), and Ni(NO₃)₂·6H₂O (0.45 g) were added to a jar (50 mL) of a planetary ball mill (YXQM-1L, MITR). Then, the high-energy ball milling procedure was performed at 200 rpm for 4 h. The resulting yellow powder was calcined in a tube furnace at a heating rate of 10 °C/min in an argon flow at 800 °C for 2 h. After cooling to room temperature, the black powder was obtained and labeled as Ni-N-C₈₀₀. Similarly, Ni-N-C₇₀₀ and Ni-N-C₉₀₀ samples were also prepared by the same procedure at the pyrolysis temperatures of 700 and 900 °C, respectively. For comparison, the Ni-C₈₀₀ sample was also prepared by the same procedure without folic acid addition at the pyrolysis temperature of 800 °C. Ni(NO₃)₂·6H₂O was directly calcined in a muffle furnace with a heating rate of 10 °C/min at 400 °C for 1 h, and the gray powder sample was obtained after cooling to room temperature, which was labeled as NiO.

Catalyst Characterization. XRD patterns of samples were obtained on a Rigaku RINT-2200 X-ray diffractometer with a Cu K α source at 40 kV and 20 mA. The scanning angle was 5–

80° with a scanning rate of 5°/min. The average size of the Ni nanoparticles was calculated by the Scherrer equation based on the Ni (111) ($2\theta = 44.5^\circ$) crystal plane from the XRD signal. The surface area and pore size distribution of the catalysts were recorded by N₂ adsorption/desorption analysis at –196 °C on a Micromeritics Tristar II 3020 instrument. The morphology and sizes of the catalysts were characterized by transmission electron microscopy (TEM) on a JEOL JEM-2100 microscope at 200 kV. The sample powder was ground in a corundum mortar. An appropriate amount of the sample was dispersed in ethanol and subjected to ultrasonic treatment for 0.5 h. Then, the above-mentioned dispersion was dispersed on copper grids and dried in a vacuum oven at 60 °C for 24 h. X-ray photoelectron spectroscopy (XPS) was performed to analyze the surface elemental composition and valence state of the sample on an AXIS Supra instrument (Kratos Analytical) equipped with Al K α under vacuum conditions of 5.0×10^{-8} Pa. The sample powder was placed on a 5×5 mm² two-sided conductive adhesive tape and wrapped in aluminum foil for the tablet press under a pressure of 8.0 MPa. To investigate the reduction performance of catalysts, H₂-TPR was conducted on a Micromeritics Autochem II 2920 instrument with TCD. For H₂-TPR, the sample (10 mg) was heated to 150 °C at a heating rate of 10 °C/min under He conditions at a flow rate of 30 mL/min and held for 2 h to remove water or volatiles adsorbed on the surface of the catalyst. The sample was naturally cooled to 70 °C and purged with 10% H₂–Ar at a rate of 50 mL/min and waited for 20 min. Then, the temperature of the sample tube was increased to 800 °C at a heating rate of 10 °C/min under a 10% H₂/Ar flow at 30 mL/min for the H₂-TPR analysis. The total H₂ consumption was monitored by TCD and recorded as a function of temperature.

Catalyst Evaluation. In a typical run of selective hydrodeoxygenation of vanillin, vanillin (0.05 g), the nickel-based catalyst (50.0 mg), and solvent (6.0 mL) were charged into a 25 mL stainless-steel high-pressure reactor. Then, the reactor was flushed with pure H₂ for 10 min to remove the air in the reactor, and subsequently, the reactor was pressurized with H₂ (1 MPa) and retained at 110 °C for 6 h with stirring at 600 rpm.

After the reaction, the reactor was cooled to room temperature. The spent catalyst was separated and recovered from the reaction mixture by filtration, washed with ethanol and water three times, and dried in a vacuum oven for 2 h at 70 °C for the next run. Since the catalyst would be inevitably lost (about 2%) during the recovery process, the lost amount of the fresh catalyst is added before the next cycle reaction to avoid the problem of activity decline caused by catalyst loss. The liquid product was identified by gas chromatography–mass spectrometry (GC-MS, Thermo Trace 1300) using dodecane as an internal standard. The determination of reaction conversion and selectivity was performed on a Thermo Trace 1310 gas chromatograph.

Computational Details. DFT calculations were conducted to investigate the possible mechanism of solvent effects on the yield of hydrogenation products. Structures and related energy calculation analysis of vanillin and HMP interacting with the solvent (H₂O or EA) were optimized using the Gaussian 16 software package.²⁸ All simulations were performed using the M06-2X functional combined with 3-zeta basis sets. Geometry optimization was carried out with the def2SVP basis set, and to get more accurate data in the energy, single-point calculations were performed in the M06-2X/

def2TZVP level.^{29–31} The binding energy (ΔE_b) was corrected by the basis set superposition error (BSSE) of vanillin and HMP interacting with the solvent, defined as follows: $\Delta E_s = E_{VS} - E_V - nE_S + \Delta E_{BSSE}$. In the BSSE, two fragments were separately defined as vanillin or vanillyl (V) and solvent (S). Isosurface maps of electrostatic potential (ESP) were displayed by means of the VMD visualization program³² based on the files exported using the Multiwfn 3.8(dev) code.³³

Considering the periodic structure of metallic Ni, DFT calculation for transition-state analysis was implemented in the CASTEP package employing the GGA functional in the PBE form.^{34–37} The typical (1 1 1) surface of Ni was created in a 4×4 supercell with a vacuum slab (15 Å thick) for the surface catalytic reaction. Spin-polarized calculation using formal spin as initial was considered since Ni is a magnetic transition metal.³⁸ Grimme DFT-D dispersion correction was used to reflect the weak interaction in the system.³⁹ The convergence standards of energy and force were defined in the fine level. A cutoff energy of 400 eV and the SCF tolerance of 1.0×10^{-6} eV/atom were adopted in all computations. A k -point mesh of $2 \times 2 \times 1$ was set for optimization, and transition states (TSs) are located by the LST/QST method.^{40,41}

RESULTS AND DISCUSSION

Characterization of Catalysts. Figure 1 shows the XRD patterns of Ni-N-C₇₀₀, Ni-N-C₈₀₀, Ni-N-C₉₀₀, Ni-C₈₀₀, and NiO.

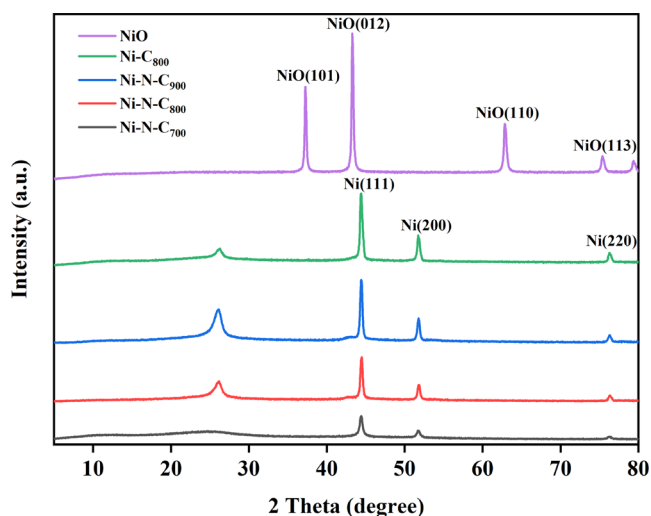


Figure 1. XRD patterns of Ni-N-C₇₀₀, Ni-N-C₈₀₀, Ni-N-C₉₀₀, Ni-C₈₀₀, and NiO.

NiO samples. A broad peak located around 26° is attributed to the (002) crystal plane of graphite-like carbon (JCPDS No. 41-1487). Peaks located at $2\theta = 44.5$, 51.8 , and 76.4° were assigned to the Ni (111), Ni (200), and Ni (220) crystalline planes (JCPDS No. 04-0850), respectively, indicating that metal Ni is formed after pyrolysis with folic acid and α -cellulose, and its peak strength gradually increases with pyrolysis temperature. The average size of Ni nanoparticles of Ni-N-C₇₀₀, Ni-N-C₈₀₀, Ni-N-C₉₀₀, and Ni-C₈₀₀ evaluated based on the Scherrer formula is 19.9, 33.5, 33.8, and 49.3 nm, respectively. From the XRD pattern of Ni-C₈₀₀, the absence of addition of the nitrogen source for calcination improved the peak intensity of metal Ni, which implies that the size of Ni particles in the Ni-C₈₀₀ sample is larger. Furthermore, direct calcination of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at high temperature in air can only obtain NiO, and no Ni (0) was detected.

The morphology of Ni-N-C samples can be seen in TEM images shown in Figure 2. It can be observed that the nanoparticles on the Ni-N-C₈₀₀ sample displayed more homogeneous size than that on Ni-N-C₇₀₀ and Ni-N-C₉₀₀. The HRTEM image (inset in Figure 2a) showed a crystal plane distance of 0.202 nm, which belongs to the cubic Ni (111) planes.^{42,43} Statistically obtained particle size distribution (Figure S1) showed that more than 88% of the Ni nanoparticles on Ni-N-C₈₀₀ are between 10 and 50 nm. For comparison, Ni nanoparticles on Ni-N-C₉₀₀ samples were severely aggregated into larger clusters because of higher pyrolysis temperature, which is in accordance with the XRD results. It is also shown that Ni particles were seriously aggregated in a distribution of much larger size on Ni-C₈₀₀ (Figure S2). Table 1 shows the actual Ni content on the four

Table 1. Element (C, N, O, Ni) Content on the Prepared Catalysts

entry	catalyst	C (wt %) ^a	N (wt %) ^a	O (wt %) ^a	Ni (wt %) ^b
1	Ni-N-C ₇₀₀	75.47	4.18	7.43	12.92
2	Ni-N-C ₈₀₀	78.01	3.80	6.01	12.18
3	Ni-N-C ₉₀₀	83.60	0.42	5.68	10.30
4	Ni-C ₈₀₀	76.59	0.00	5.30	18.11

^aDetermined by XPS. ^bDetermined by ICP-OES.

carbon material-supported Ni catalysts. It could be found that the contents of metal Ni supported by the three N-doped carbon materials obtained by calcination at different temperatures are relatively similar. Ni-C₈₀₀ contains more Ni (18.11 wt %), which is due to the absence of folic acid in the preparation process.

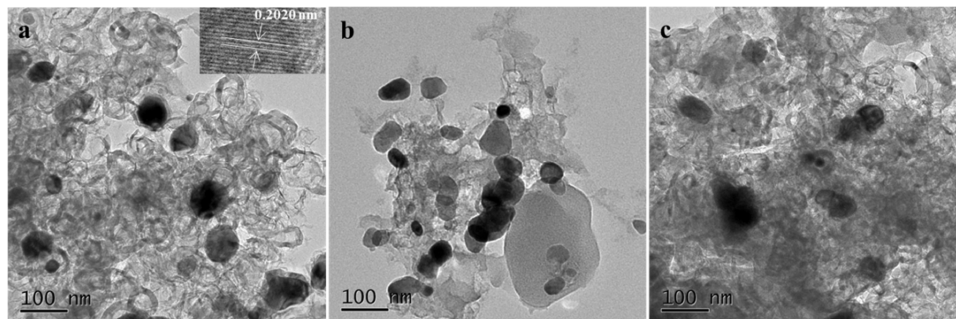


Figure 2. TEM images of (a) Ni-N-C₈₀₀, (b) Ni-N-C₇₀₀, and (c) Ni-N-C₉₀₀.

N₂ adsorption/desorption isotherms of Ni-N-C samples are shown in Figure 3. Isotherms of these three samples were all

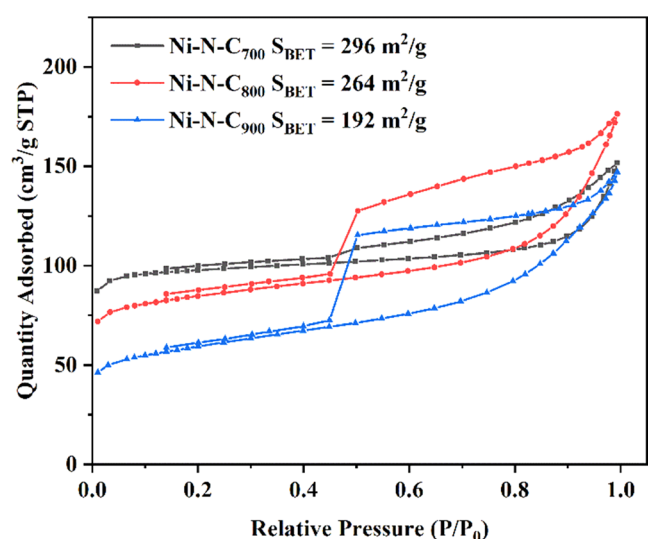


Figure 3. N₂ adsorption–desorption isotherms of Ni-N-C₇₀₀, Ni-N-C₈₀₀, and Ni-N-C₉₀₀.

type IV, which indicates the presence of mesoporous structure. The appearance of H4 hysteresis loops demonstrated the formation of narrow slit-like mesopores.^{44,45} Pore diameter distributions of Ni-N-C₇₀₀, Ni-N-C₈₀₀, and Ni-N-C₉₀₀ (Figure S3) also showed the above-mentioned characteristics. The specific surface area was calculated to be 296, 264, and 192 m²·g^{−1} using the Brunauer–Emmett–Teller (BET) model for Ni-N-C₇₀₀, Ni-N-C₈₀₀, and Ni-N-C₉₀₀, respectively. Ni-N-C₈₀₀ showed a much larger specific surface area than that of Ni-C₈₀₀ (193.3 m²·g^{−1}, Figure S4), which probably originated from the addition of folic acid in calcination. Ni-N-C₉₀₀ displayed the smallest specific surface area, which indicates that higher annealing temperature would lead to the mesoporous structure collapse.

The surface element valence states of Ni-N-C₇₀₀, Ni-N-C₈₀₀, and Ni-C₈₀₀ samples were further investigated by XPS. The Ni 2p_{3/2} XPS spectra of Ni-N-C (Figure 4a) could be fitted into four peaks at 853.1, 854.2, 856.9, and 860.3 eV, corresponding to Ni⁰, NiO, and the satellite peaks.^{46–48} Ni-N-C₈₀₀ possessed a higher proportion of Ni⁰ species compared with Ni-N-C₇₀₀,

which indicates that it tends to form Ni metal at higher annealing temperature. Compared with Ni-N-C₇₀₀ and Ni-N-C₈₀₀, there were more Ni⁰ species on the Ni-C₈₀₀ sample without folic acid addition for calcination. This is likely to be due to the coordination effect between Ni²⁺ and N/O atoms in folic acid after long-time severe ball milling. In the subsequent heating and reduction process, the Ni²⁺ is easily reduced to Ni⁰ due to the lack of such coordination in the samples without folic acid. However, the sample added with folic acid will not be reduced rapidly due to the strong coordination between Ni²⁺ and the ligands. At the same time, the carbon material obtained by pyrolysis is N-doped and contains more O atoms (Table 1). This favors the formation of many coordination interactions between the support and Ni, which would reduce the content of Ni⁰. Figure 4b shows the N 1s spectra of Ni-N-C₇₀₀ and Ni-N-C₈₀₀. Four distinct peaks were found at 398.6, 400.3, 401.5, and 404.4 eV, corresponding to pyridine-N, pyrrole-N, graphite-N, and oxide-N.^{49–51}

H₂-TPR measurements were further performed, and the results are illustrated in Figure 5. A sharp peak between 260

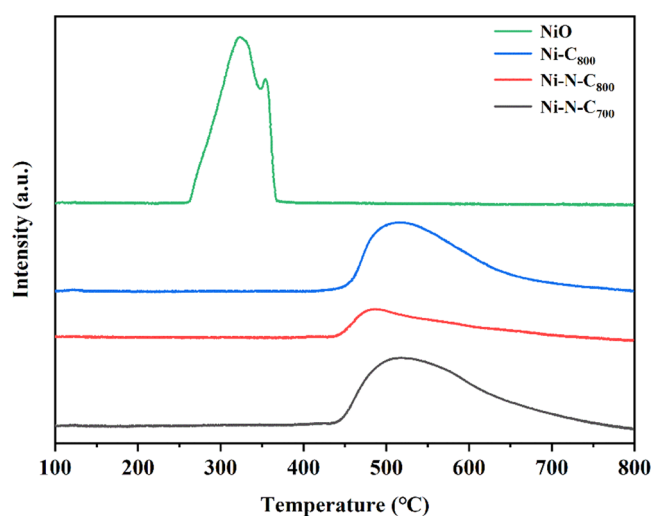


Figure 5. H₂-TPR of Ni-N-C₇₀₀, Ni-N-C₈₀₀, Ni-C₈₀₀, and NiO.

and 365 °C centered at 323 °C appeared in the H₂-TPR profile of the sample NiO, corresponding to the reduction of bulk NiO species, which had no interaction with the support,^{52,53} while the peaks of Ni-N-C₇₀₀, Ni-N-C₈₀₀, and Ni-N-C₉₀₀

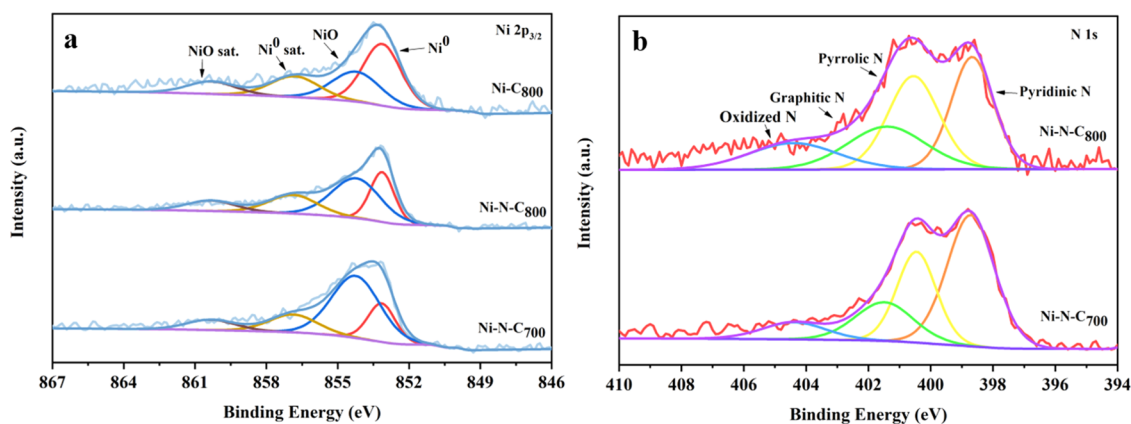


Figure 4. XPS spectra of (a) Ni 2p and (b) for Ni-N-C₇₀₀, Ni-N-C₈₀₀, and Ni-C₈₀₀.

attributed to NiO reduction were shifted to higher temperatures ($>450\text{ }^{\circ}\text{C}$) with broader peak width. In particular, the peak intensity of Ni-N-C₈₀₀ was obviously weaker than that of Ni-N-C₇₀₀ and Ni-N-C₉₀₀. This indicates that Ni-N-C₈₀₀ had a lower content of NiO species, which is in accordance with the XPS characterization results that more Ni⁰ species existed in Ni-N-C₈₀₀.

Tuning the Solvent for Vanillin Hydrogenation. The catalytic performance of Ni-N-C catalysts for selective hydrodeoxygenation of vanillin was evaluated (Table 2).

Table 2. Catalytic Activity of Vanillin Hydrogenation on the Prepared Catalysts^a

entry	catalyst	solvent	conversion (%)	yield (%)	
				HMP	MMP
1	Ni-N-C ₇₀₀	H ₂ O	82.7	9.3	73.4
2	Ni-N-C ₈₀₀	H ₂ O	100	0.9	99.1
3	Ni-N-C ₉₀₀	H ₂ O	97.8	12.5	85.3
4	Ni-C ₈₀₀	H ₂ O	100	15.4	84.6
5	NiO	H ₂ O	1.3	0.9	0.4

^aReaction conditions: vanillin (0.05 g), catalyst (50 mg), solvent (6 mL), H₂ (1 MPa), 110 $^{\circ}\text{C}$, and 6 h.

Among the Ni-N-C catalysts (Table 2, entries 1–3), Ni-N-C₈₀₀ showed the most excellent catalytic performance with a vanillin conversion of 100% and MMP yield of 99.1% at 110 $^{\circ}\text{C}$ for 6 h. Vanillin conversion on Ni-N-C₉₀₀ was slightly lower at 97.8%, and the yield of MMP was reduced to 87.2%. Ni-N-C₇₀₀ exhibited the lowest vanillin conversion of 82.7%, and the yield of MMP was only 73.4%. The outstanding performance of the Ni-N-C₈₀₀ catalyst probably originates from the larger specific surface area, high proportion of Ni⁰ species, and uniform size of Ni nanoparticles. In addition, the reference catalysts (Table 2, entries 4–5) were also studied to elucidate the excellent catalytic activity of Ni-N-C₈₀₀. The yield of MMP on the Ni-C₈₀₀ catalyst decreased to 84.6% under the same reaction conditions, although vanillin was completely converted in the reaction. The lower MMP selectivity is probably attributed to the severe agglomeration of Ni nanoparticles on Ni-C₈₀₀. In contrast, the conversion of vanillin on the NiO catalyst was only 1.3% under the same conditions (Table 2, entry 5), indicating that Ni⁰ is the key catalytic active site during the hydrogenation.

The recyclability of the Ni-N-C₈₀₀ catalyst were investigated, as shown in Figure 6. After six consecutive cycles, the yield of MMP still remained at more than 95% at 110 $^{\circ}\text{C}$ for 6 h, indicating the excellent stability of Ni-N-C₈₀₀. Compared with the fresh catalyst, the XRD pattern of the regenerated Ni-N-C₈₀₀ catalyst showed that the diffraction peak of Ni⁰ nanoparticles was better preserved (Figure S5). This demonstrates that the Ni-N-C₈₀₀ catalyst is stable enough for hydrodeoxygenation of vanillin.

The catalyst Ni-N-C₈₀₀ was further tested to investigate the solvent effect on the hydrogenation of vanillin to HMP, and the results are shown in Figures 7 and 8. Figure 7 shows vanillin conversion and the yield of HMP or MMP on Ni-N-C₈₀₀ in the solvents with different H₂O/EA volume ratios at 100 $^{\circ}\text{C}$ for 8 h. In pure H₂O, the conversion of vanillin was 98% and the yield of MMP was 79%. However, when pure EA was used as the solo solvent, the conversion of vanillin was reduced significantly to 39%, but the selectivity of HMP was as high as 95% and the yield of HMP was 37%. This shows that

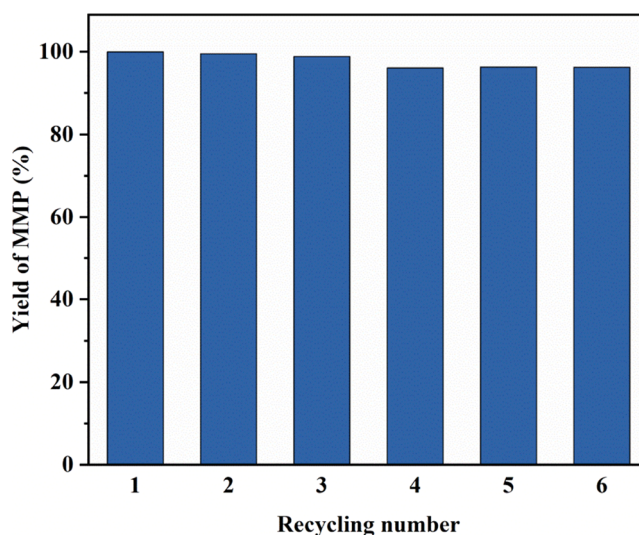


Figure 6. Reusability test of Ni-N-C₈₀₀ in six runs. (Reaction conditions: 0.5 mmol substrate, 50 mg of catalyst, 6 mL of H₂O, 1.0 MPa H₂, 110 $^{\circ}\text{C}$, 6 h, and 600 rpm).

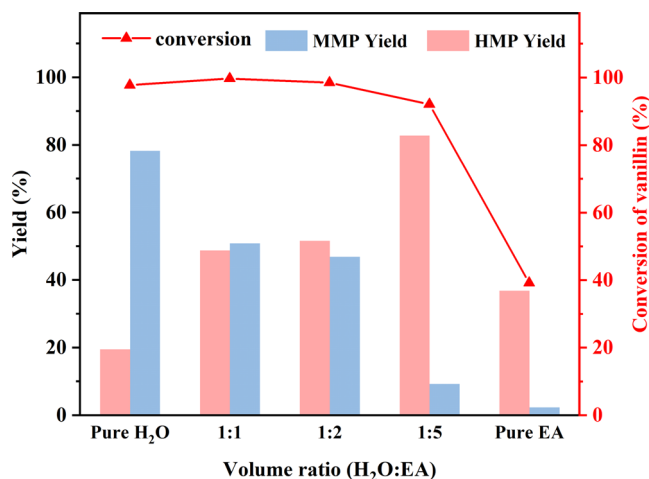


Figure 7. Catalytic activity of vanillin hydrodeoxygenation on Ni-N-C₈₀₀ in the solvents with different H₂O/EA volume ratios.

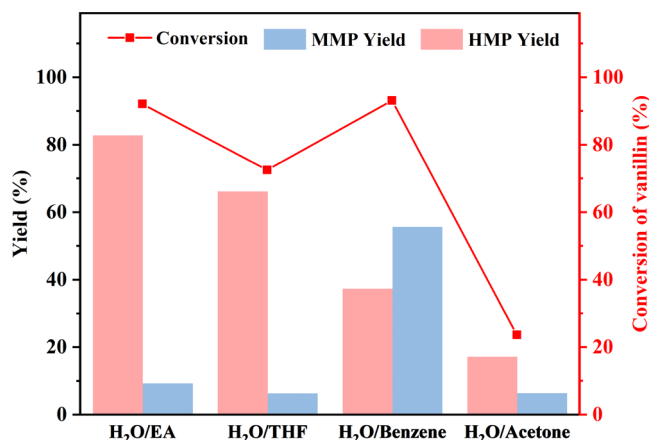


Figure 8. Catalytic activity of vanillin hydrodeoxygenation on Ni-N-C₈₀₀ in various mixed solvents with a volume ratio of 1:5.

EA is suitable to maintain high selectivity of HMP, whereas H₂O is positive to high conversion of vanillin. Subsequently, by

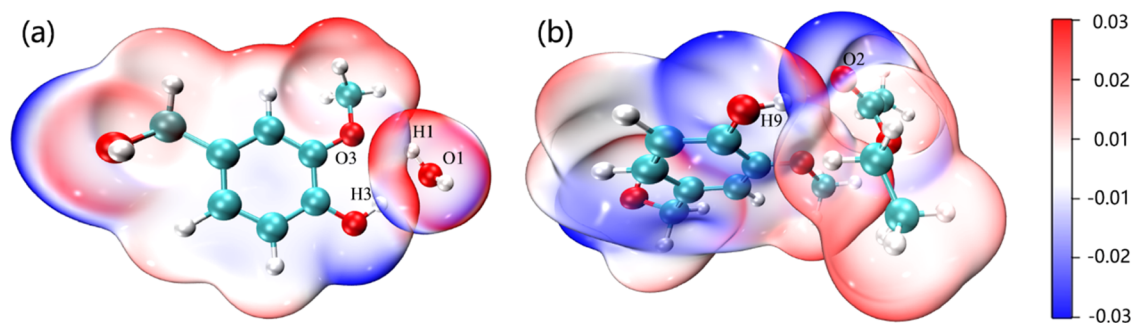


Figure 9. Molecular ESP values mapped on the van der Waals surface of (a) HMP–H₂O and (b) HMP–EA cluster (negative regions are indicated in blue and positive regions are indicated in red).

using the mixed solvent H₂O/EA with a volume ratio of 1:1 or 1:2, the conversion of vanillin retained a high vanillin conversion of 99%, but the yield of HMP was still lower than 55%. When the volume ratio of H₂O/EA was set to 1:5, the product distribution for hydrogenation of vanillin was successfully controlled. HMP became dominant with a yield of 85%, and the conversion of vanillin was 93%. The utilization of the mixed solvent H₂O/EA (1:5) can tune the hydrogenation product to stay mostly in the intermediate HMP.

Furthermore, the effect of other kinds of mixed solvents on hydrogenation of vanillin to HMP was studied as shown in Figure 8. When the mixed solvent H₂O/THF was used with tetrahydrofuran (THF) instead of EA, the intermediate HMP was the dominant product with a yield of 66% along with a vanillin conversion of 74% at 100 °C for 8 h. However, the mixed solvent H₂O/benzene led to the final product MMP with a yield of 55%, and the yield of the intermediate HMP was less than 40%. The use of the mixed solvent H₂O/acetone also resulted in a very low conversion of vanillin and yield of HMP. These findings obviously demonstrate that H₂O and EA play important roles in controlling the product distribution in vanillin hydrogenation. The final product MMP and intermediate HMP in vanillin hydrogenation over the Ni–N–C₈₀₀ catalyst can be effortlessly adjusted by tuning the reaction solvent of pure H₂O or H₂O/EA (1:5).

Mechanism of the H₂O/EA Solvent Effect. The above-mentioned experimental results showed that the mixed solvent H₂O/EA significantly affected the product distribution in vanillin hydrogenation. When H₂O is more in the solvent, the yield of MMP is higher, while HMP is the major product as more EA is added. The contact angle test showed that the catalyst Ni–N–C₈₀₀ was strongly hydrophobic with a contact angle of 140° for pure H₂O (Figure S6). The hydrophobicity of the catalyst surface enables the side product H₂O generated in the hydrodeoxygenation process to get away from the surface quickly, which is conducive to the hydrodeoxygenation reaction of HMP to MMP. Meanwhile, solubility experiments (Figure S7) showed that HMP was more soluble in EA and had little solubility in H₂O. The difference in HMP solubility might be another reason why the intermediate HMP could be obtained with a high yield in the mixed solvent H₂O/EA.

ESP analysis on the van der Waals surface (0.001 au contours electronic density)^{54,55} was further performed. Molecular clusters with the stable structure of HMP interacting with H₂O and EA are shown in Figure 9. The van der Waals surface penetration intuitively indicated the interaction between two molecules. The van der Waals penetration distance of O3–H1 in HMP–H₂O is 1.05 Å. Compared with

HMP–H₂O, the stronger hydrogen bond (O2–H9) with a long van der Waals penetration distance of 1.10 Å was found in the HMP–EA cluster. Then, the calculated energies of the intermolecular interaction (mainly hydrogen bonds) for HMP–H₂O and HMP–EA were –22.4 and –24.8 kJ/mol, respectively. All these results demonstrate that HMP–EA has a stronger interaction than that of HMP–H₂O, which has a very good agreement with the larger HMP solubility in EA than in H₂O.

In addition to the reasons discussed above, the solvent may also affect the activation energy of the reactants on the surface of the catalyst. Therefore, the energy barrier of the hydrodeoxygenation reaction of HMP on the representative Ni (111) surface under solvent-free and solvent-containing (H₂O and EA) conditions was investigated using the first-principles theory. The optimized structure and the searched transition-state (TS) structure are shown in Figures S8–S10. The calculation results shown in Figure 10 demonstrated that the

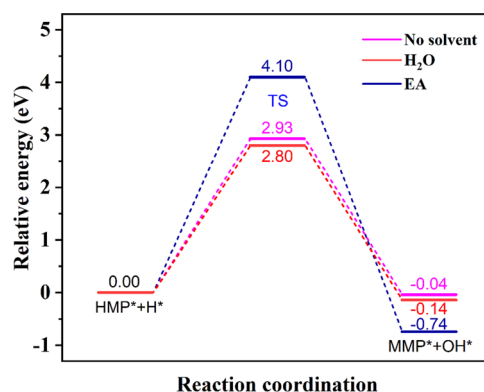


Figure 10. Relative energy profiles of HMP hydrodeoxygenated to MMP on the Ni (111) surface under solvent-free conditions and in the solvent (H₂O or EA).

energy barrier of HMP deoxyhydrogenated to MMP was 2.93 eV under the condition of no solvent, and the energy barrier was reduced to 2.80 eV with H₂O participating. It is obvious that the energy barrier for this reaction increased to 4.10 eV when EA was used as the solvent. This shows that the large steric hindrance of EA has increased the energy barrier of the hydrodeoxygenation reaction of HMP. As a result, the addition of EA inhibits the hydrodeoxygenation of HMP to further generate MMP.

H₂ dissociation has an important impact on the hydrogenation process, sometimes even a controlling step that determines the reaction rate. Therefore, the process of H₂

dissociation was investigated under different solvent conditions (EA and H₂O). The calculation results are shown in Figure 11,

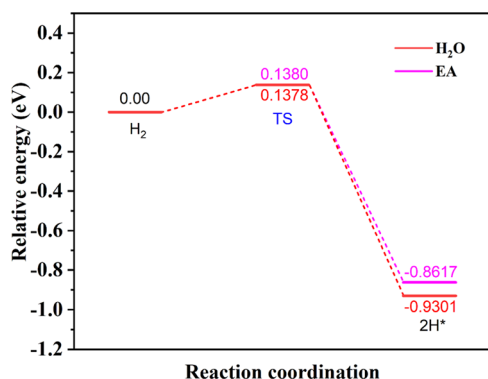


Figure 11. Relative energy profiles of H₂ dissociation into two adsorbed H atoms (2H*) on the Ni (111) surface in different solvents (H₂O or EA).

and the corresponding initial-state, transition-state, and final-state structures are shown in Figures S11 and S12. It can be seen from Figure 11 that the dissociation energy barriers of H₂ in the presence of the two solvents are basically the same (0.1380 and 0.1378 eV), but the dissociation heat of H₂ in the presence of H₂O (−0.9301 eV) is a little higher than the heat release (−0.8617 eV) in the presence of EA, which shows that H₂ is a little easier to dissociate when H₂O is used as a solvent, even if the dissociation energy barrier and dissociation heat difference are relatively small compared with EA as a solvent.

From the above-mentioned discussion, it can be seen that the solvents (EA and H₂O) have a more significant change on the energy barrier of the HMP hydrogenation process and have little effect on the energy barrier of H₂ dissociation. This indicates that the solvents (EA and H₂O) have a certain influence on the dissociation of H₂, but not as much as that on the hydrogenation of HMP to MMP. The effect on the process

of hydrogenation of HMP to MMP is most likely to be the intrinsic mechanism of the solvent effect to change product selectivity.

Applicability to Other Biomass-Derived Aldehydes.

After the success in the hydrogenation of vanillin, the scope of hydrogenation of other biomass-derived aldehydes in pure H₂O and the mixed solvent H₂O/EA was explored over the Ni-N-C₈₀₀ catalyst. These products were determined and confirmed by GC-MS (Figure S13). As seen from Figure 12, the aldehyde group attached to the benzene ring was hydrodeoxygenated to form a methyl group using pure H₂O as a solvent, and the mixed solvent H₂O/EA would bring the product distribution dominated by aromatic alcohol. More obviously, the aromatic aldehydes with large steric hindrance (S3, S4) and 3, 4-dimethylbenzaldehyde (S6) with less activity were also successfully reduced to the intermediate methylation product or the final alcohol product, which were characterized at a high reaction temperature of 130 or 160 °C for at least 12 h. Therefore, the use of pure H₂O and the mixed solvent H₂O/EA is considered to be a good strategy for tuning the product distribution in various biomass-derived aldehyde hydrogenations.

CONCLUSIONS

A series of Ni-based catalysts supported on N-doped carbon materials were prepared and employed for efficient hydrogenation of vanillin. The yield of hydrogenation products can be easily controlled by adjusting the volume ratio of the two solvents—H₂O and EA. Under the given reaction conditions, MMP was mainly produced in the pure H₂O solvent, and the intermediate product HMP was the dominant product upon using the mixed solvent H₂O/EA with a volume ratio of 1:5. Experiments and DFT calculations further showed that both HMP had a stronger interaction with H₂O and H₂O can reduce the energy barrier of HMP to MMP on the Ni surface. On the contrary, the addition of EA would increase the hydrogenation barrier of HMP to MMP. This convenient

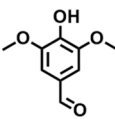
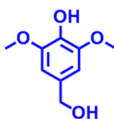
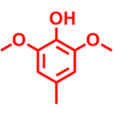
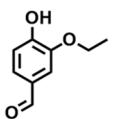
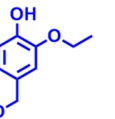
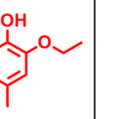
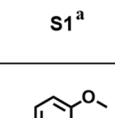
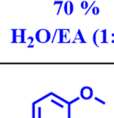
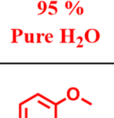
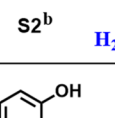
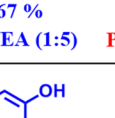
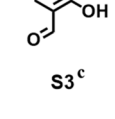
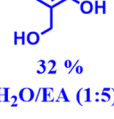
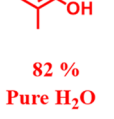
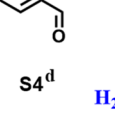
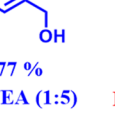
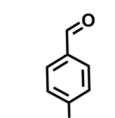
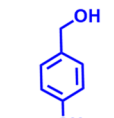
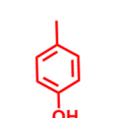
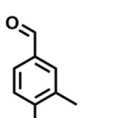
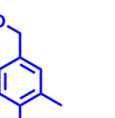
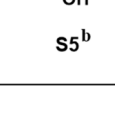
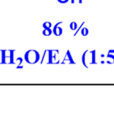
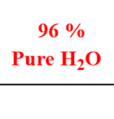
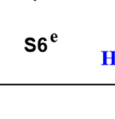
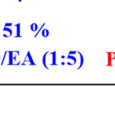
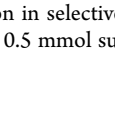
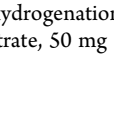
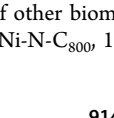
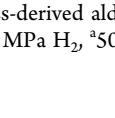
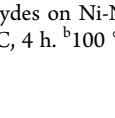
 S1^a	 S2^b	 S3^c	 S4^d	 S5^b	 S6^e
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	 S1^a	 S2^b	 S3^c	 S4^d	 S5^b
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	 S1^a	 S2^b	 S3^c	 S4^d	 S5^b
	 S1^a	 S2^b	 S3^c	 S4^d	 S5^b

Figure 12. Product distribution in selective hydrogenation of other biomass-derived aldehydes on Ni-N-C₈₀₀ using pure H₂O or H₂O/EA mixed solvent. (Reaction conditions: 0.5 mmol substrate, 50 mg of Ni-N-C₈₀₀, 1.0 MPa H₂, ^a50 °C, 4 h. ^b100 °C, 8 h. ^c130 °C, 12 h. ^d110 °C, 16 h. ^e160 °C, and 24 h).

method of solvent-regulated product distribution provides a useful guideline and inspiration for other hydrodeoxygenation reactions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.3c00510>.

Particle size distribution and pore diameter distributions of the prepared Ni catalysts; TEM images and N₂ adsorption–desorption isotherms of Ni-C; XRD pattern of fresh and recycled Ni-N-C₈₀₀ catalysts; contact angle of H₂O/EA (1:5) and pure H₂O on the catalyst Ni-N-C₈₀₀; dissolution photo of HMP in H₂O or EA; structural images of different states in DFT calculation; and GC-MS results of hydrogenation of various biomass-derived aldehydes (PDF)

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Notes

The authors declare no competing financial interest.

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