Supplementary Information

Highly dispersed nickel anchored on N-doped carbon molecular sieve derived from metal-organic frameworks for efficient hydrodeoxygenation in aqueous-phase

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Experimental section

The description of using ZIFs as template to fabricate metal-carbon catalysts: Zeolitic imidazolate frameworks (ZIFs) are a special subclass of metal organic frameworks (MOFs), displaying a tetrahedral structures very much like those found in inorganic zeolites, featuring large cages connecting through narrow windows. Indeed, ZIFs derived metal-carbon catalysts have been fairly reported, because direct pyrolysis of MOFs is a straightforward and facile method to construct carbon supported metal catalysts. However, the zeolite-type structure of ZIFs are generally destroyed during pyrogenic decomposition. It not only dramatically decreases the surface area of catalyst but also destroy the rare and well-defined MOF pore/channel structures. In addition, the derived metal usually involves uneven size distribution scaled from atom to tens of nanometer. In order to obtain high dispersed metal catalyst (especially atomic metal), the unstable particles located on the external surface should be removed by extra treatment, such as acid pickling. In this work, one of the main reasons for using ZIF-8 as a template is pyrolyzed ZIF-8 can obtain a zeolite-type carbon molecular sieve (CMS), which can still inherit the morphology (rhombic-dodecahedral) and pore structure of ZIF-8 perfectly after high temperature pyrolysis. More importantly, using ZIF-8 as template can contribute abundant N defects, which are generated through the evaporation of Zn ions in Zn-N-Zn nodes (a typical unit in ZIF-8). These electron-rich N left by the evaporation of Zn can easily capture and integrate with adjacent Ni^{2+} ions, therefore stabilizing as Ni-N coordination configuration during thermal treating, achieving a high dispersion of Ni at atomic-level. This strategy does not involve extra expensive and environmentally unfriendly treatment, and the Ni content in catalyst is quantitative controllable.

Chemicals and reagents

All solvents were analytical grade and used without further purification. Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), nickel(II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), 2-methylimidazole (MeIM) and vanillin were purchased from Aladdin Industrial Corporation. n-hexane, methanol were derived from Sinopharm Chemical Reagent. Deionized (DI) water with 18.2 MΩ resistance is required.

Preparation of catalyst precursor: ZIF-8 was first synthesized via a facile method. Briefly, 0.558 g

$Zn(NO_3)_2 \cdot 6H_2O$ was first dissolved in 15 mL methanol, and then 15 mL methanol containing 0.616 g

MeIM was quickly added and stirred at room temperature for 3 h. The ZIF-8 was then grown under

static at room temperature for 10 h. The as-obtained precipitates were centrifuged and washed with

methanol three times and dried in vacuum at 60 ^{o}C for overnight.

Preparation of HD-Ni/N-CMS catalyst: The powder of ZIF-8 (100 mg) was dispersed in n-hexane (10 mL)

under ultrasound for 5 min at room temperature. After forming a homogeneous solution, an aqueous

solution of $Ni(NO_3)_2 \cdot 6H_2O$ (100 mg·mL^{-1} 50 uL) was injected drop by drop into the mixture and

dispersed by ultrasound for 2 min at room temperature. Next, the mix solution was under vigorous

stirring for 3 h at room temperature in order to make the double solution be absorbed completely.

Then the sample was centrifuged and washed with methanol and dried in vacuum at 60 ^{o}C for 6 h. The

sample was placed in a tube furnace and heated to 1000 ^{o}C (heating rate 5 ^{o}C·min^{-1}) for 2 h in a stream

of Ar (25 mL·min^{-1}) to yield HD-Ni/N-CMS. The Ni content was measured to be 0.56 wt% based on

ICP-AES analysis.

The preparation of other samples (HD-Ni/N-CMS-1, Ni-CNT/NC, Ni-NPs/NC and Ni-NPs/NC-1)

were the same as HD-Ni/N-CMS catalyst except that the addition amount of $Ni(NO_3)_2 \cdot 6H_2O$ is

different.

The catalytic hydrogenation of vanillin

The description of using vanillin HDO as model reaction: Lignocellulosic biomass feedstocks are a complex mixture of three structural biopolymers (lignin, cellulose and hemicellulose) with oxygenated complex macromolecules. Lignin, constituting approximately 30 wt% of woody biomass, is much more challenging to convert due to its highly complex structure compared to cellulose and hemicellulose. Because of the oxygen-rich functionalized features, catalytic hydrotreating is a promising strategy for activating of C=O and C-O bonds, which is essential for upgrading of biomass and its intermediates. This issue generally experiences liquid-phase reaction of hydrodeoxygenation (HDO) via selective hydrogenation of C=O bond, splitting of C-O bond, and simultaneous saturating by active hydrogen to form a desired product. Vanillin has been recognized as a representative lignin derived product, because it is not only one of the major products from the oxidative lignin transformation but also the only molecular phenolic compounds manufactured on an industrial scale from biomass. It possesses three typical oxygenate functional groups, hydroxyl, methoxy, and formyl on a benzene ring, which are recognized as one of best model compounds for studying selective HDO. Therefore, HDO of vanillin (a typical model compound of lignin) was chosen as the model reaction to explore the principal C=O and C-O bond activation over Ni-based catalysts via hydrogenation and hydrogenolysis route, which would pave a way for in-depth and systematic investigation on catalytic conversion of oxygen-rich functionalized biomass and their intermediates.

Here, The catalytic HDO reactions were carried out in a 25 or 100 mL stainless steel autoclave equipped with a mechanical stirrer, a pressure gauge, and automatic temperature control apparatus. In typical experiment, the reaction solutions of vanillin/Ni (substrate/catalyst) molar ratio of S/C = 300. When the reactor had been pressurized with H_2 to a relevant pressure 2.0 MPa, the reactor was heated to a setting temperature (80-150 ^{o}C) and maintained at this temperature for a setting reaction time with 600 rpm stirring. After reaction, the reactor was cooled down quickly. The product mixture and used catalyst were separated by centrifugation. The products were extracted by ethyl acetate from the liquid. The liquid product was identified by gas chromatography–mass spectrometry (GC-MS, Thermo Fisher Scientific-TXQ Quantum XLS, column-TG-WAXMS, 30 m × 0.25 mm × 0.25 μm), and was

quantitatively analyzed by GC (Shimadzu, GC-2010 Plus), equipped with flame ionization detector and a 30 m × 0.25 mm × 0.25 μm KB-WAX capillary column (Kromat Corporation, USA). The mass balance (based on carbon) was checked in every experimental run and detected to be higher than 98%.

During the catalyst stability test, the catalyst was reused without any further treatment. More specifically, following the first hydrogenation reaction, the reaction mixture was centrifuged or filtered to recover the catalyst, which was washed first with water and then with ethanol followed by drying under vacuum oven at 60 ^{o}C and employed for the next test.
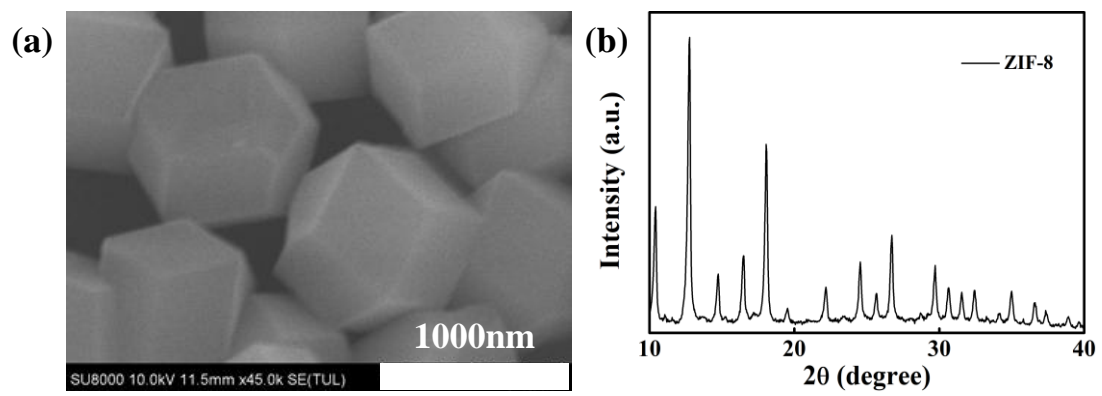
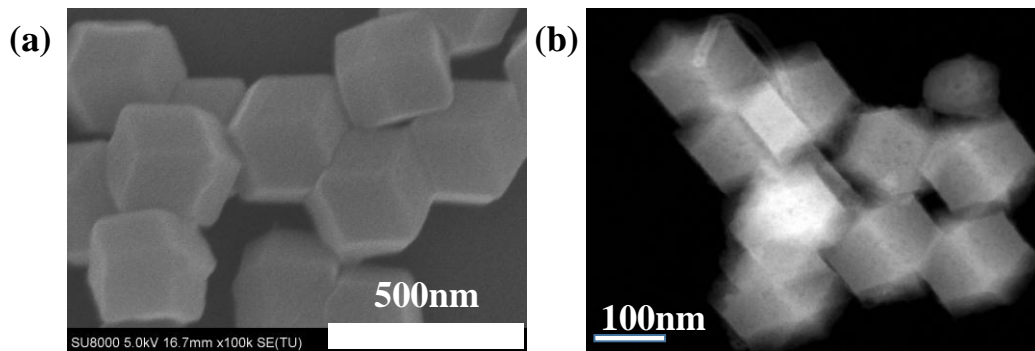**Fig. S1** (a) SEM image and (b) XRD pattern of ZIF-8.

Fig. S2 (a) SEM image of HD-Ni/N-CMS. (b) HAADF-STEM image HAADF-STEM of HD-Ni/N-CMS.
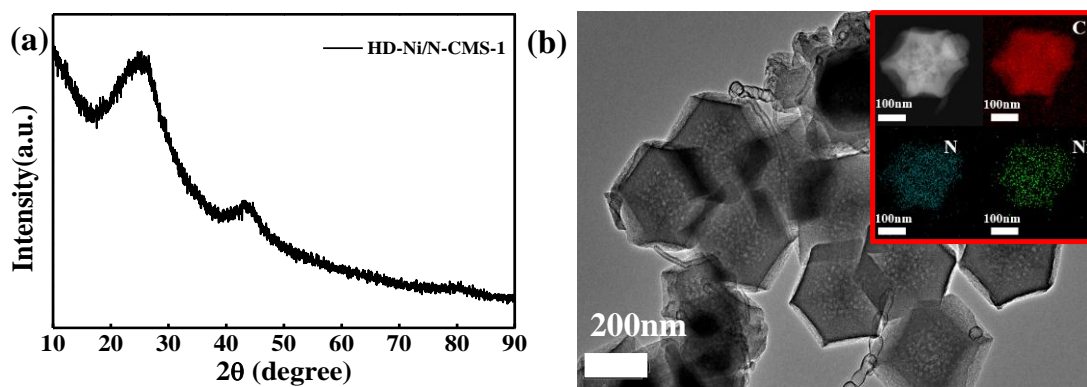
Fig. S3. (a) XRD pattern of HD-Ni/N-CMS-1. (b) TEM image of HD-Ni/N-CMS-1, insert HAADF-STEM image of HD-Ni/N-CMS-1 and corresponding energy-dispersive X-ray spectroscopy (EDX) mapping, C (red), N (cyan), and Ni (green).
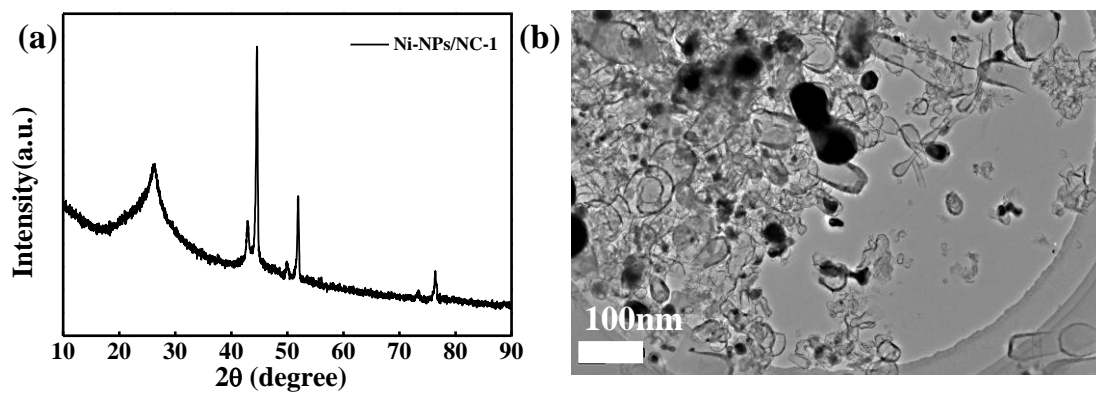
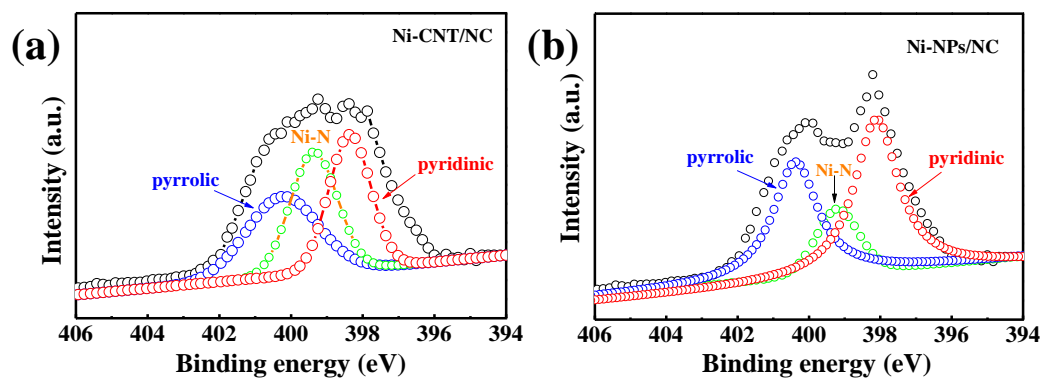**Fig. S4** (a) XRD pattern and (b) TEM image of Ni-NPs/NC-1.

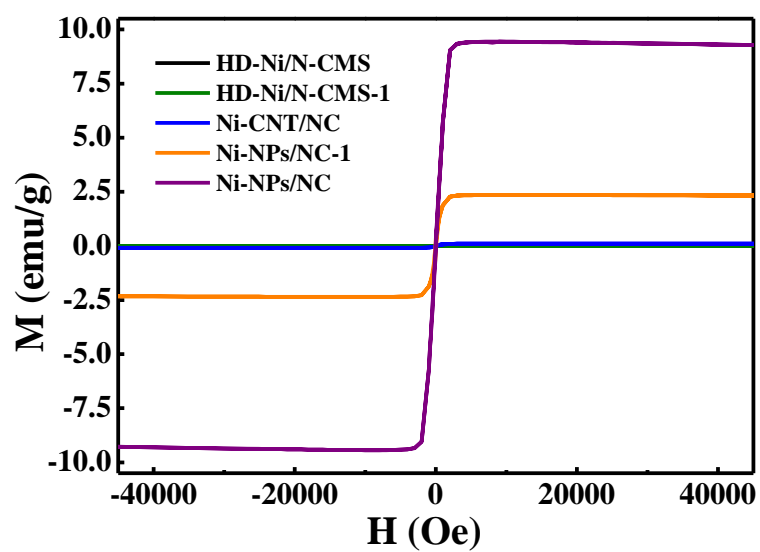**Fig. S5** The high-resolution XPS N 1s spectrum. (a) Ni-CNT/NC, (b) Ni-NPs/NC.

Fig. S6 The hysteresis loop of catalysts (HD-Ni/N-CMS, HD-Ni/N-CMS-1, Ni-CNT/NC, Ni-NPs/NC-1 and Ni-NPs/NC) with different Ni loading.

Table S1. Textural parameters for ZIF-8 and the Ni-x/NC catalysts with different loading.

Sample	S_{BET} $(m^2.g^{-1})$	Pore volume $(cm^3.g^{-1})$	Ni content (wt%)	Mean Size (nm)	Vanillin Conversion (%)	MMP Selectivity (%)	HMP Selectivity (%)
ZIF-8	1671	2.1	-	-	--	--	--
ZIF-8- pyrolysis	869	1.7	-	-	--	--	--
HD-Ni/N-CMS	889	1.9	0.56	<1	100	100	0
HD-Ni/N-CMS-1	832	1.6	1.32	<1	95.7	99.1	0.9
Ni-CNT/NC	769	1.3	4.32	8.6	54.5	97.1	2.9
Ni-NPs/NC-1	494	0.8	10.85	15.4	31.7	91.2	8.8
Ni-NPs/NC	424	0.6	23.41	33.8	17.8	87.8	12.2

Reaction temperature, 130 °C; reaction time, 10 h; $P(H_2)$ = 2.0 MPa; reactant to catalyst (S/C) molar ratio=300, defined amount of water.

Table S2. The elemental contents of samples.

	ICP	TEM-EDX	XPS	XPS
	Ni (wt%)	N (wt%)	N (wt%)	Ni-N (%)
Pyrolytic ZIF-8	0	4.2	--	--
HD-Ni/N-CMS	0.56	4.1	4.4	44.6
Ni-CNT/NC	4.32	3.6	4.1	22.3
Ni-NPs/NC	23.41	3.2	3.9	11.7