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hydrodeoxygenation in aqueous-phase

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

ZIF-8 was employed as template to synthesize HD-Ni/N-CMS containing highly dispersed Ni at atomic-level anchored on N-doped carbon molecular sieve for vanillin hydrodeoxygenation. The ZIF-8 structure was inherited and Ni-N bonds were formed by coordination of Ni with N-rich defects, therefore exhibiting high turnover frequency (1047.1 h^{-1}) and good stability.

Catalytic hydrotreating is a promising strategy for activation of C=O and C-O bonds. it is an important process for upgrading biomass and its intermediates with oxygen-rich functional groups.¹ This can be accomplished by liquid-phase reaction of hydrodeoxygenation (HDO) via selective hydrogenation of the C=O bond, split of the C-O bond, and simultaneous saturation with active hydrogen to form the desired product. $^{\rm 1b,\ 1c,\ 2}$ Predictably, it puts forward a strict requirement for corresponding catalysts which can simultaneously realize the three-step catalytic process. Considerable efforts have been made to explore such multi-functional catalysts for activation of C=O and C-O bonds, especially the heterogeneous transition metal catalysts.³ Currently, the widely studied catalysts are still the noble metals (Pt, Pd, Ru) because of their outstanding activity. However, the application of noble metals is limited due to their high cost, limited reserves, and complicated synthesis. In addition, the hyperactivity of noble metals is prone to side reactions, poor selectivity for the desired product, and deactivation.⁴

In recent years, several non-noble transition metals (e.g. Ni,

Co, Cu, Fe) attracted great attention and showed tuneable catalytic performances in the reduction reactions such as hydrogenation, hydrogenolysis, and HDO.⁵ Among them, Nibased heterogeneous catalysts exhibit most striking features of versatile activities, for instance, activities in the synthesis of bio-derived compounds. Xia et al. reported that HDO of vanillin to 2-methoxy-4-methylphenol (MMP) in liquid-phase can be achieved with selectivity of 64.6% over a highly dispersed Ni/N-doped carbon black catalyst.^{5a} Wang and co-workers pointed out that the sub-nanometre-scale NiCo bimetallic alloy immobilized on SiO₂ support using NiCo-MOFs as a precursor, exhibited excellent activity and stability in furfural alcohol hydrogenation reaction under mild conditions.⁶ Li et al. reported Ni single atoms distributed in N-doped porous carbon for active CO₂ reduction.⁷ Our group also did the relevant research work and reported our findings.⁸ It is noteworthy that the activity of Ni catalysts dispersion (based on TOF) is magnitudes lower than that of counterpart noble metal catalysts. This could be attributed to non-uniform size distribution and low dispersion caused by high Ni loading (higher than 10 wt%). In addition, high metal loading would lead to Ni leaching into the reaction mixture, consequently results in catalyst deactivation as well as the possibility of product contamination. The most effective and challenging way is to reduce the size of the Ni catalyst to increase atom utilization. Therefore, the Ni-based catalyst can achieve the activity similar to that of the precious metals while reducing Ni loading. For instance, single atom catalysts (SACs), as a new popular field in catalysis with high atom utilization, have displayed attractive catalytic activity compared to nanoparticle type metal catalyst. Wu et al. reported a two-step strategy to synthesize Ni SACs by thermal transforming N-doped carbon sunken Ni nanoparticles (NPs) and displayed excellent activity of C-H bond activation.⁹ Li et al. developed Ni SACs by a threestep strategy using Ni(phen)₃ as a precursor and showed high activities for hydrogenation of various unsaturated substrates.¹⁰ However, the synthesis of SACs with catalytic stability is still a very challenging work.

Controllable and facile synthesis of supported Ni with unsaturated coordination can not only maximize Ni atom utilization efficiency but also provide stable reaction sites. Recently reported direct pyrolysis of MOFs seems a straightforward and facile method to construct carbon

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⁺ Electronic Supplementary Information (ESI) available: Supporting SEM image, TEM image, HAADF-TEM image and corresponding energy-dispersive X-ray spectroscopy (EDX) mapping, XRD patterns, Magnetic testing.

supported metal SACs. However, a complete decomposition of MOFs usually leads to structural collapse, which not only dramatically decreases the surface area but also destroys the rare and well-defined MOF pore/channel structures.

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In the present work, we prepared a HD-Ni/N-CMS (highly dispersed Ni at atomic-level anchored on N-doped carbon molecular sieve) through a simple thermal ionic-exchange method using ZIF-8 as a sacrificed template, in which Ni ions exchanged with Zn nodes via ionic exchange during pyrolysis.' The catalyst not only inherited the morphology and pore structure of ZIF-8, but also exhibited atomic dispersion of Ni via Ni-N bonds formed by coordination of Ni with N-rich defects. Therefore, it displayed excellent activity and waterphase stability in vanillin HDO. The highly dispersed Ni at atomic-level and low Ni-N coordination could ensure a high metal-atom utilization. More importantly, the derived N-CMS with zeolite-type structure could create a favorable microenvironment which benefited the aqueous-phase reaction and prevented the leaching of Ni. The turnover frequency (TOF) normalized to metal Ni reached a value of 1041.7 h^{-1} .

First, ZIF-8 was synthesized in a mixture of Zn²⁺, methanol, and 2-methylimidazole at room temperature similar to the reported method.^{7, 11} The synthesized white powder had a monodisperse rhombic-dodecahedral shape with uniform size of 280-300 nm (Fig. S1a, ESI⁺) and XRD structure of typical ZIF-8 crystal (Fig. S1b, ESI⁺). Then, the precursor of HD-Ni/N-CMS was obtained by homogeneously dispersing ZIF-8 in a nonpolar solvent (n-hexane), followed by adding Ni(NO₃)₂ aqueous solution dropwise (the molar ratio of adsorbed Ni ions to ZIF-8 was 1/20). Through solvent extraction effect, Ni ions were confined within the pore channel of ZIF-8.⁷ After washing away a tiny amount of unstable Ni ions on surface of ZIF-8, the mixture was subjected to pyrolysis at 1000° C for 2 h under an argon (Ar) atmosphere to yield the HD-Ni/N-CMS catalyst.

For such prepared HD-Ni/N-CMS catalyst, no Ni characteristic peaks were observed in the XRD profiles (similar to pyrolyzed ZIF-8 in Fig. 1a), demonstrating its poor crystallinity or high dispersion.7, 12 Fig. 1b showed the pyrogenic decomposition profiles of pure ZIF-8 and precursor of HD-Ni/N-CMS (ZIF-8 of adsorbed Ni ions) detected by thermogravimetric (TGA) analysis. For the precursor of HD-Ni/N-CMS, it showed a higher decomposition temperature at the first stage of weight loss than ZIF-8 because of the removal of free organic solvent adsorbed on the ZIF-8 during Ni ions loading. The precursor of HD-Ni/N-CMS also showed a higher weight loss due to carbon evaporation catalyzed by Ni. As can be seen in Fig. 1c and Fig. S2, Table S1 (ESI⁺), the HD-Ni/N-CMS sample almost perfectly inherited the morphology (rhombicdodecahedral) and pore structures of ZIF-8 as the form of N-CMS, with only a slight shrinkage in average size (200-230 nm). The formed N-CMS support could provide large surface area and abundant pore channels for active metal. More importantly, Ni, N and C were homogeneously dispersed over the whole architecture (Fig. 1d) revealed by energy-dispersive X-ray spectroscopy (EDX) in high-angle annular dark field scanning TEM (HAADF-STEM). The actual Ni and Zn loading in

HD-Ni/N-CMS catalyst were 0.56% and 0% byinductively coupled plasma atomic emission spectresterpy (ICP) 24259.

Fig.1 (a) XRD spectra of pyrolyzed ZIF-8 and HD-Ni/N-CMS catalyst, (b) TGA curve of precursor of HD-Ni/N-CMS (red line) and ZIF-8 (black line), (c) TEM image and (d) HAADF-STEM image of HD-Ni/N-CMS and corresponding energy-dispersive X-ray spectroscopy (EDX) mapping, C (red), N (blue), and Ni (green), (e) Ni L-edge XANES spectra of HD-Ni/N-CMS, (f) The high-resolution XPS N 1s spectrum.

Based on HAADF-STEM and ICP-AES, the Zn nodes (existing as Zn-N bonds) in ZIF-8¹¹ were completely evaporated when the pyrolysis temperature was elevated over 920 °C, leaving the Nrich defects. These electron-rich N left by the evaporation of Zn could be easily integrated with adjacent Ni^{2+} ions and stabilized as Ni-N coordination configuration during thermal treating, achieving a high dispersion of Ni at the atomic-level. Additionally, the Ni L-edge X-ray absorption near edge structure (XANES) was used to characterize the valence state of the HD-Ni/N-CMS catalyst. Based on Ni L-edge XANES spectra (Fig. 1e), the valence of the Ni atom in the HD-Ni/N-CMS catalyst should be situated between Ni⁰ (852.5-853.0 eV) and Ni²⁺ (855.5-856.0 eV) in phthalocyanine nickel (NiPc), indicating an electronic structure of Ni^{δ +} (0< δ < 2).^{7, 13} The detail information of Ni species coordination was further revealed by the high-resolution XPS N1s spectrum (Fig. 1f). The high-resolution XPS N1s spectrum exhibited dominant Ni-N coordination with a peak at 399.3 eV.¹⁴ This observation also agreed well with other characterization results (Fig. 1). According to above results, we confirmed that HD-Ni/N-CMS catalyst achieved a high dispersion of Ni at atomic level through Ni-N coordination and can retain the original morphology and pore structures of ZIF-8. The unsaturated coordination of Ni-N could promote atomic-level dispersion of Ni, and more importantly, it also offered high-efficient active sites with fantastic properties for HDO.

Due to the unique electronic structure and geometry of the HD-Ni/N-CMS catalyst, we employed it as the HDO catalyst in aqueous-phase hydrogenation of vanillin (a model unsaturated compound derived from lignin), and the results were shown in Fig. 2. The molar ratio of vanillin to catalyst (based on Ni determined by ICP) was 300:1. At such a low dose, the catalyst was still active enough to reduce the carbonyl group (C=O) in vanillin and transformed it into MMP. The starting reaction temperature was 110°C, which showed 5.2% vanillin conversion and 93.2% MMP selectivity within a short reaction time (1 h). The vanillin conversion was steadily enhanced as reaction temperature increased from 110 to 150°C and the

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converted vanillin was almost completely transformed into MMP.



Fig. 2 (a) Effect of reaction temperature and (b) Reusability of HD-Ni/N-CMS. (Reaction conditions: vanillin/Ni (substrate/catalyst) molar ratio of S/C = 300, defined amount of water, $130 \,^{\circ}$ C, 2.0 MPa H₂, 1h).

More importantly, the catalyst still showed good stability in aqueous-phase hydrogenation at such a harsh reaction temperature after 5 cycles. Compared with other reported non-noble catalysts,^{5a, 5c} HD-Ni/N-CMS offered competitive activity and stability when molar ratio of vanillin to catalyst was 300:1 or above.

As mentioned, the HD-Ni/N-CMS catalyst was obtained by pyrolysis of Ni²⁺ ions adsorbed ZIF-8. The loading of Ni ions is an important parameter affecting the morphological, chemical and electronic structures of Ni catalysts, thus affecting the catalytic behaviour in aqueous-phase HDO. The original rhombic-dodecahedral structure of ZIF-8 could be retained as the form of N-CMS when the molar ratio of Ni ions to ZIF-8 was lower than 1/10. There were almost no characteristic peaks of Ni crystals in XRD pattern (Fig. 3 and Fig. S3, ESI⁺), indicating Ni was dispersed at the atomic-level in the catalyst, like the HD-Ni/N-CMS (the molar ratio of Ni ions to ZIF-8 was 1/20) and HD-Ni/N-CMS-1 (the molar ratio of Ni ions to ZIF-8 was 1/10) samples. On this basis, the surface area (S_{BET}) and pore size distribution of HD-Ni/N-CMS and HD-Ni/N-CMS-1 were also similar to pyrolytic ZIF-8 (Table. S1, ESI⁺). When the ratio of Ni ions to ZIF-8 was in the range of 1/10-1/4, there was still no obvious diffraction peak of Ni crystals in XRD pattern, but a sharp diffraction peak at $2\theta = 23.0^{\circ}$. This could be attributed to the characteristic peak of carbon nanotube (CNT). The TEM image of the catalyst (Fig. 3) further indicated that it was composed of dodecahedron and CNT, defined as Ni-CNT/NC (the molar ratio of Ni ions to ZIF-8 was 1/4), and the content of CNT was directly proportional to Ni ions in carbon. The Ni-CNT/NC catalyst obtained under this condition showed lower S_{BET} than that of HD-Ni/N-CMS because of the Ni overlapping in the pore channel and partial disintegration of the structure (Table. S1, ESI⁺). For further increasing Ni ions loading, such as Ni ions to ZIF-8 higher than 1/4 (Fig.S4, ESI⁺ and Fig. 3), the obtained sample Ni-NPs/NC (the molar ratio of Ni ions to ZIF-8 was 1/1) and Ni-NPs/NC-1 (the molar ratio of Ni ions to ZIF-8 was 1/2) both displayed the characteristic peaks at 44.3° and 51.7° attributing to face-centered-cubic Ni, indicating the formation of Ni NPs.The N and Ni-N XPS spectra and contents were shown in Fig.S5 and Table S2 (ESI). The Ni-N contents were significantly influenced, for instance the Ni-N content of HD-Ni/N-CMS is 44.6 % (based on N), which is far higher than those of Ni-CNT/NC (22.3%) and Ni-NPs/NC (11.7 %). Combined with TEM, it was evident that the structure of ZIF-8 completely collapsed and Ni NPs were agglomerated, which



Additionally, the structure transition with Ni content could also

Fig. 3 Schematic illustration of the Ni catalysts under different molar ratio of Ni $^{2+}$ and ZIF-8 (calcined at 1000 $^{\circ}$ C for 2 h in Ar atmosphere).

be related to their magnetic properties. As shown in Fig. S6 (ESI⁺), it was known that the metal almost showed no magnetism when it existed as highly dispersed at atomic-level, such as magnetic profiles of HD-Ni/N-CMS, HD-Ni/N-CMS-1 and Ni-CNT/NC. However, a strong magnetism would appear when the atomic metal assembled as particles, such as Ni-NPs/NC and Ni-NPs/NC-1. The magnetic characterization results also confirmed that the HD-Ni/N-CMS catalyst achieved high dispersion at Ni atomic level.

To trace and compare the catalytic activity of the HD-Ni/N-CMS with other Ni catalysts (Ni-NPs/NC and Ni-CNT/NC), the HDO of vanillin (a model compound derived from lignin) was conducted at 130° C and 2 MPa H₂ in aqueous-phase. As expected in Fig. 4a-b, the HD-Ni/N-CMS catalyst displayed the best catalytic performance with complete vanillin conversion and 100% MMP selectivity. The excellent catalytic performance could be attributed to the high dispersion at Ni atomic level via Ni-N coordination (Fig. 1e and 1f), as well as the big surface area and abundant pore structure originated from the retaining of the original morphology and pore structure of ZIF-8 by N-CMS (Fig. S2, Table S1, ESI⁺ and Fig. 1c). As a contrast, the activity lowered to 54.5% vanillin conversion and 97.1% MMP selectivity for the Ni-CNT/NC catalyst. This decreased activity was probably due to the reduced Ni dispersion and the barrier property of carbon layer in CNT. Among them, the Ni-NPs/NC catalyst showed the lowest activity (17.8% vanillin conversion and 87.8% MMP selectivity), which was triggered by the collapse of well-organized dodecahedron structure, metal agglomeration, as well as a significant decrease of Ni dispersion and surface area. According to the Fig. 4 and Table S2. (ESI), the catalytic performances of Ni catalysts are in accord with their Ni-N contents, indicating Ni-N sites play a key role on aqueousphase HDO of vanillin. On these bases, we further correlated the real-time concentration of vanillin with reaction time, and found that they all followed pseudo first-order kinetics for the three types catalysts (HD-Ni/N-CMS, Ni-CNT/NC and Ni-NPs/NC) in Fig. 4c. The slopes of the plots were their rate constants, and the calculated rate constant of HD-Ni/N-CMS catalyst was 0.35 h⁻¹, which was 4 and 17 times higher than the rate constant of Ni-CNT/NC and Ni-NPs/NC catalysts. This further illustrated the importance of metal dispersion at the

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atomic-level and maintaining the multi-channel structure and high specific surface area of ZIF-8 for the HD-Ni/N-CMS catalyst to promote the aqueous-phase HDO of vanillin.



Fig. 4 Catalytic evaluation of HD-Ni/N-CMS, Ni-CNT/NC and Ni-NPs/NC toward convert vanillin to MMP. (a) Conversion vs reaction time, (b) product selectivity for 10 h, (c) ln ($C_{0,vanillin}/C$) vs reaction time, (d) TOF value determined as moles of initial vanillin converted per mole of exposed active sites per hour in dynamic range. (Reaction conditions: vanillin/Ni (substrate/catalyst) molar ratio of S/C = 300, defined amount of water, 130 °C, 2.0 MPa H₂).

Moreover, the TOF based on Ni and vanillin conversion was measured at the initial reaction stage (Fig. 4d). The TOF value of HD-Ni/N-CMS was 1041.7 h^{-1} , which was 3 and 12 times higher than that of the Ni-CNT and Ni-NPs/NC. This TOF value was far larger than that of the conventional Ni/AC catalyst.^{5a}

In summary, we successfully synthesized a HD-Ni/N-CMS catalyst by a simple thermal ionic-exchange method using ZIF-8 as a sacrificed template, in which Ni ion exchanged with Zn nodes during pyrolysis. The unique morphological and electronic structures of the HD-Ni/N-CMS catalyst were verified by HAADF-STEM, and XANES. Compared with Ni-CNT/NC and Ni NPs/NC, the HD-Ni/N-CMS catalyst was capable of highly selective HDO of vanillin with excellent activity and aqueous-phase stability. This was mainly caused by the high dispersion at Ni atomic level via Ni-N coordination, thus ensuring a high metal-atom utilization, as well as retaining the original structure of ZIF-8 by N-CMS. Importantly, the derived zeolite-type N-CMS supplied large surface area and abundant pore channel, which could create a favourable reaction microenvironment benefiting aqueous-phase reaction and overcoming poor stability of traditional carbon-based catalysts. The discovery of this type of catalyst shed light on rational design of highly efficient atomically dispersed non-noble metal catalysts for practical industrial application.

Conflicts of interest

There are no conflicts to declare.

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HD-Ni/N-CMS catalyst exhibited excellent catalytic performance in aqueous-phase hydrodeoxygenation of lignin-derived vanillin through a synergistic effect of zeolite-type N-CMS and unsaturated Ni-N coordination site.