hcp-phased Ni nanoparticles with generic catalytic hydrogenation activities toward different functional groups

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ABSTRACT Catalytic hydrogenation is a vital industrial means to produce value-added fuels and fine chemicals, however, requiring highly efficient catalysts, especially the nonprecious ones. To date, the majority of high-performance industrial hydrogenation catalysts are made of precious metals-based materials, and any given catalyst could only be used to catalyze one or few specific reactions. Herein, we exemplify a crystal phase engineering approach to empower Ni nanoparticles (NPs) with superb intrinsic catalytic activities toward a wide spectrum of hydrogenation reactions. A facile pyrolysis approach is used to directly convert a Ni-imidazole MOF precursor into hexagonal close-packed (hcp)-phased Ni NPs on carbon support. The as-synthesized hcp-phased Ni NPs exhibit unprecedented hydrogenation catalytic activities in pure water towards nitro-, aldehyde-, ketone-, alkene- and N heterocyclic-compounds, outperforming the face-centered cubic (fcc)-Ni counterpart and the reported transition metals-based catalysts. The density functional theory calculations unveil that the presence of hcp-Ni boosts the intrinsic catalytic hydrogenation activity by coherently enhancing the substrate adsorption strength and lowering the reaction barrier energy of the rate-determining step. We anticipate that the crystal phase engineering design approach unveiled in this work would be adoptable to other types of reactions.

Keywords: crystal phase engineering, hcp-phased Ni nanoparticles, catalytic hydrogenation, DFT calculations, H₂O solvent

INTRODUCTION

Catalytic hydrogenation (CH) of nitro-, aldehyde-, ketone- and alkene-functional groups and N-containing heterocyclic compounds is a vital industrial means to produce high value-added fuels and fine chemicals, however, requiring cheap and highly efficient CH catalysts [1–13]. Enormous efforts have been devoted to exploring different activation approaches capable of boosting the CH activity of cheap and plentiful transition-metal

(TM) catalysts, including alloying/de-alloying [14–16], defect and strain engineering [17,18], structure and composition manipulations [19,20]. A promising strategy that has recently received increasing attention is engineering TM nanoparticles (NPs) with hexagonal close-packed (hcp) crystal phase to enhance the intrinsic CH performance [21–24]. For instance, Bao and Zhu's group [21,22] reported a non-hydrolytic thermal decomposition approach to controllably synthesize hcp-Ni NPs from Ni(COOH)₂ as a CH catalyst to efficiently hydrogenate nitrophenols to aminophenols. Janiak and co-workers [23] demonstrated a synthetic method based on the microwave-induced decomposition of Ni-containing salts to synthesize the metastable hcp-Ni NPs. Under 100°C and 5 bar H₂ pressure, the synthesized hcp-Ni NPs can hydrogenate 1-hexene and benzene with 90% conversion efficiencies within 1 and 60 h, respectively. Very recently, a reductive pyrolysis of metal-organic framework (MOF) approach was reported by Fan's group [24] to fabricate graphene-encapsulated hcp-Co with outstanding CH performance towards a wide spectrum of carboxyl-containing compounds. In addition to thermo-catalytic hydrogenation, engineering TM with hcp phases has also been applied to photo- and electro-catalysis [25–27]. For example, Yan's group [25] demonstrated a “phase-mediated” strategy, where hcp-Co@NC and face-centered cubic (fcc)-Co@NC have been employed for hydrogen and oxygen evolution reactions (HER/OER). They demonstrated that when fcc-Co@NC was converted to hcp-Co@NC, both HER and OER over-potentials could be dramatically decreased, confirming the effectiveness of hcp phase for overall water splitting. These successful exemplifications have been systematically reviewed by Zhang's group [27], which depicted that engineering nanomaterials' crystal phase is an effective approach to endow nanomaterials with promising catalytic properties.

Despite the noticeable progress, the controllable synthesis of hcp-phased TM catalysts remains a challenging task. To date, the reported TM catalysts with hcp crystal phases are almost exclusively synthesized by wet-chemical methods that require

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the use of organic ligands to stabilize the hcp phase [28]. It is known that the presence of such organic ligands inevitably slows the reactant transport to the catalyst active sites, leading to the decreased catalytic performance and potential contamination of the final products. To this end, MOFs with metal-nodes and carbon containing organic ligands have shown notable advantages for the fabrication of highly dispersed TM NPs with unique crystal structures for important catalytic reactions [29,30]. So far, the successful examples of using MOFs as precursors to directly synthesize hcp-phased TM catalysts are mostly for Co NPs [24,25,29]. For instance, $\text{Co}_3[\text{Co}(\text{CN})_6]_2$ MOF was used to synthesize hcp-Co NPs *via* a carbonization process under N_2 protective atmosphere at 800°C ; nevertheless, Ru doping was required to trigger the growth of hcp-phased Co [24]. Zhang and co-workers [29] reported the use of chemical vapor deposition of ethyne to controllably reduce Co-MOF precursor to Co NPs with fcc and hcp phases. They unveiled that the ratio of hcp and fcc phases in the resultant Co NPs can be controlled by precisely controlling the deposition temperatures. Nonetheless, using MOFs as precursors to directly synthesize hcp-phased Ni NPs *via* a one-step process has yet been reported, which is due mainly to the comparatively high stability of fcc-phased Ni over hcp-phased Ni [31].

Herein, we report a facile pyrolysis approach to directly convert a Ni-imidazole ($\text{Ni}(\text{im})_x$) MOF precursor into hcp-phased Ni NPs covered by a thin N-doped carbon layer (denoted as hcp/fcc-Ni). Notably, the obtained hcp/fcc-Ni exhibits the unprecedented CH activities towards a wide spectrum of substrates including nitro-, aldehyde-, ketone-, alkene- and N heterocyclic-compounds. Density functional theory (DFT) calculations demonstrate that the presence of hcp phase enhances the substrate adsorption strength and lowers the reaction barrier energy of the rate-determining step.

EXPERIMENTAL SECTION

Chemicals

Imidazole and nitric acid (HNO_3) were purchased from Aladdin Reagent Company. Nickel acetate tetrahydrate ($\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$), ethanol and ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$) were purchased from Sinopharm Chemical Reagent Co. Ltd. Unless otherwise stated, all other solvents and chemicals were of commercially available analytical grade and used without further purification. All solutions were prepared using deionized water ($>18.2 \text{ M}\Omega$).

Synthesis of $\text{Ni}(\text{im})_x$

In a typical synthesis, imidazole (1.17 g, 17 mmol) was added to 50 mL of aqueous solution containing 2.83 mmol of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, and quickly mixed with 5 mL of $\text{NH}_3 \cdot \text{H}_2\text{O}$. The resultant solution was transferred into a 100-mL vial and stirred for 20 min. The vial was then placed in a Teflon-lined stainless-steel autoclave and heated at 90°C for 6 h. The as-obtained yellow precipitates were collected by air pump filtration, washed by deionized water and ethanol three times, and dried at 60°C for 24 h in a vacuum oven.

Synthesis of hcp/fcc-Ni and fcc-Ni

To synthesize hcp/fcc-Ni, 500 mg of the synthesized $\text{Ni}(\text{im})_x$ precursor was placed in a ceramic boat and heated to 400°C with a heating ramp of 2°C min^{-1} under 10 vol% H_2/Ar flow and

maintained at this condition for 2 h. After naturally cooling down to the room temperature, the black powder was obtained and labelled as hcp/fcc-Ni. The fcc-Ni was synthesized *via* the same procedure as that used for hcp/fcc-Ni, except that Ar was used to replace 10 vol% H_2/Ar during the pyrolysis.

Catalyst characterizations

Field emission scanning electron microscopy (FESEM) measurements were performed on an FESEM (SU8020) operated at an accelerating voltage of 5.0 kV. Powder X-ray diffraction (XRD) patterns were recorded on a Philips X-Pert Pro X-ray diffractometer using Ni-filtered monochromatic Cu K α radiation ($\lambda_{\text{K}\alpha 1} = 1.5418 \text{ \AA}$) at 40 kV and 40 mA. Transmission electron microscopy (TEM) tests were carried out using JEOL-2010 at 200 kV. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images were carried out on Philips TecnaiG2 F20 operated at an acceleration voltage of 200 kV with an EDS Oxford, Link ISIS. AC HAADF-STEM images were recorded by a JEOL JEM-ARM 200F field-emission transmission electron microscope with a spherical aberration corrector. The specific surface area, pore volume and pore size of the catalysts were calculated using a BET (Brunauer-Emmett-Teller) instrument (Autosorb iQ Station 2). X-ray photoelectron spectroscopy (XPS) spectra were performed by an ESCALAB 250 X-ray photoelectron spectrometer (Thermo, USA) equipped with Al K $\alpha_{1,2}$ monochromatized radiation at 1486.6 eV X-ray source. The metal contents in different samples were determined by inductively coupled plasma mass spectrometer (ICP 6300, Thermo Fisher Scientific).

Performance evaluations

All catalytic hydrogenation reactions were carried out in a 25-mL stainless steel autoclave equipped with a mechanical stirrer, a pressure gauge, and automatic temperature control apparatus (Anhui Kemi Machinery Technology Co., Ltd). For a typical run, 0.5 mmol of reaction substrate, 20 mg of catalyst, and 10 mL of solvent were added into the reactor. The air in the reactor was thoroughly replaced by 1 MPa N_2 three times. The reactor was firstly pressurized with H_2 to a desired pressure, then heated to a required temperature and maintained the temperature for a pre-determined period (the reaction time). A stirring speed of 700 r min^{-1} was used for all the experiments. The obtained reaction solution was filtered through a filter membrane ($0.22 \mu\text{m}$) and extracted by ethyl acetate for three times. The reaction products in the extraction solution were identified by gas chromatography mass spectrometry (GC-MS, Thermo Fisher Scientific-TXQ), and then quantitatively analyzed by GC (Shimadzu, GC-2010 Plus) using *n*-octanol as an internal standard. For cycling tests, the used catalyst was collected by an external magnet, washed by ethanol, and dried at 60°C for 24 h in a vacuum oven.

DFT calculations

Density functional theory as implemented in the Vienna *ab-initio* Simulation Package (VASP) was employed to optimize geometry structures [32,33]. The exchange-correlation interactions were described by the generalised gradient approximation (GGA) [34] in the form of the Perdew-Burke-Ernzerhof (PBE) functional [35]. A cut-off energy of 500 eV for plain-wave basis sets was adopted and the convergence threshold was set to 10^{-5} eV , and $5 \times 10^{-3} \text{ eV \AA}^{-1}$ for energy and force, respectively.

The weak interaction was described by DFT+D3 method using empirical correction in Grimme's scheme [36]. The vacuum space was set to be more than 20 Å, which was enough to avoid the interaction between periodical images. For fcc-Ni and hcp-Ni models, a four layer of 6×6 supercell was used with the last two layers fixed. The minimum energy pathway for the oxidation process was determined by using a climbing image nudged elastic band method (CINBE) implemented in the VASP code

[37,38].

RESULTS AND DISCUSSION

Synthesis and structural characteristics of hcp/fcc-Ni

Fig. 1a schematically illustrates the typical synthetic procedure for the fabrication of hcp/fcc-Ni. In brief, the polycrystalline-structured $\text{Ni}(\text{im})_x$ MOF nanofiber precursor having 50–100 μm

Figure 1 (a) Schematic illustrating the synthetic procedure of hcp/fcc-Ni. (b) XRD pattern (inset: hcp-Ni crystal structure model). (c) TEM image (insets: high-magnification TEM image and size distribution) and (d) HRTEM image (dotted yellow and white cycles indicating the outer profiles of Ni-NP and graphitic carbon layer, respectively) of hcp/fcc-Ni. (e) HAADF-STEM image of a typical Ni-NP in hcp/fcc-Ni. (f) Magnified HAADF-STEM image of Ni NPs with domains highlighted and (g) corresponding atomic scale schematics showing the stacking sequence of fcc (blue dots), hcp (red dots) phase and domain boundary (purple dots).

in lengths and 100–300 nm in diameters (Fig. S1) was firstly synthesized by reacting imidazole (im) with $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ under solvothermal conditions [39]. The obtained $\text{Ni}(\text{im})_x$ nanofiber precursor was then converted to hcp/fcc-Ni *via* a simple pyrolysis process under a 10 vol% H_2/Ar atmosphere. The X-ray diffraction (XRD) pattern (Fig. 1b) of hcp/fcc-Ni shows diffraction peaks at 41.5° , 44.5° and 47.5° , respectively, assignable to the (002), (001) and (101) planes of hcp-Ni crystal phase [28] (JCPDS: 45-1027), while the relatively weak diffraction peaks at 51.8° and 76.4° indicate the co-existence of fcc-Ni (JCPDS: 04-0850). A broad peak centered at $\sim 26.3^\circ$ can be attributed to the presence of graphitic carbon (JCPDS: 41-1487) [40]. A typical scanning electron microscopy (SEM) image of hcp/fcc-Ni (Fig. S2) indicates that the shape of $\text{Ni}(\text{im})_x$ nanofiber precursor is retained by hcp/fcc-Ni. The transmission electron microscopy (TEM) images (Fig. 1c) unveil that the Ni NPs in hcp/fcc-Ni with an average diameter of 9.1 nm are uniformly distributed in the carbon matrix. The high-resolution TEM (HRTEM) image (Fig. 1d) displays that the Ni NPs in hcp/fcc-Ni are covered by a thin carbon layer. The HAADF-STEM image of a typical NP in hcp/fcc-Ni (Fig. 1e) unveils an alternative hcp/fcc domain structure and the two neighboring hcp domains are separated by a fcc lamellae. The lattice spacings of 2.10 and 2.00 Å with an interplanar angle of 62.1° are measured from the hcp-Ni domain. The corresponding fast Fourier transformation (FFT) image (top right inset of Fig. 1e) can be indexed to the pattern with a [100] zone axis. The lattice spacings of 2.05 and 1.77 Å with an interplanar angle of 54.8° were measured from the fcc-Ni domain and the corresponding FFT image (bottom left inset of Fig. 1e) is assignable to the pattern with [10–1] zone axis. The magnified HAADF-STEM image of a Ni NP in hcp/fcc-Ni (Fig. 1f) and the corresponding fcc/hcp stacking sequence (Fig. 1g) confirm a distinctive atomic lamellae stacking with clear domain boundaries (purple). The high resolution Ni 2p X-ray photoelectron spectroscopic (XPS) spectrum (Fig. S3a) unveils the presence of Ni^0 and Ni^{2+} in hcp/fcc-Ni [41,42], while the high-resolution C 1s spectrum (Fig. S4a) discloses the presence of C–N bonds [43]. The Raman spectrum (Fig. S5) displays two peaks centered at 1360 and 1589 cm^{-1} , assignable respectively to the D and G bands of graphitic carbons ($I_D/I_G = 1.02$) [44,45]. The BET surface area of hcp/fcc-Ni is measured to be $104.6\text{ m}^2\text{ g}^{-1}$ and the corresponding pore size distribution confirms the existence of microporous and mesoporous structures (Fig. S6a, b) [46]. The Ni content in hcp/fcc-Ni NPs is determined by the ICP analysis to be 48.38 wt.%.

Hydrogenation performance

The CH performance of hcp/fcc-Ni was firstly evaluated using hydrogenation of nitrobenzene (NB) to aniline (AN) as a model reaction. Unless otherwise stated, all catalytic experiments were conducted in a mechanically stirred thermal reactor loaded with 10 mL solvent containing 20 mg catalyst and 0.5 mmol substrate. It has been widely reported that the hydrogenation of NB to AN involves multiple steps and intermediates as illustrated in

Scheme 1 [45].

The effect of reaction conditions on the catalytic performance and reaction process was elaborately investigated. First, it can be found that the sample calcined at 400°C give the optimum hydrogenation performance (Fig. S7). The effect of reaction temperature was examined under 1 MPa H_2 pressure within a 2-h reaction period (Fig. 2a). An increase in the reaction temperature from 20 to 30°C leads to the increased NB conversion from 65.6% to 100%. When the reaction temperature is increased from 20 to 40°C , the AN selectivity is increased from 72.3% to 100%, accompanying a decreased nitrosobenzene (NSB) selectivity from 27.7% to 0%. This suggests that higher temperature favors the hydrogenation of NSB. Notably, the other intermediate, phenylhydroxylamine (PAN), is undetectable under the experimental temperatures, which is likely due to the strong adsorption of PAN on the catalyst surface [47]. It is well known that when NSB and PAN co-exist, the condensation reaction occurs spontaneously to form azoxybenzene without the presence of any catalyst (Fig. S8). However, the formation of azoxybenzene is undetectable in our experiments (Fig. 2a and Fig. S9), confirming that the condensation of PAN and NSB intermediates is inhibited during the hydrogenation of NB due to the strong adsorption of PAN on the catalyst surface [47]. Fig. 2b shows the effect of H_2 pressure under 40°C within a 2-h reaction period. It unveils that an increase in H_2 pressure leads to an increase in NB conversion, and 100% NB conversion can be reached under 1 MPa H_2 . Compared with the effect on NB conversion, the effect of H_2 pressure on AN selectivity is less dramatic. The AN selectivity of 80.4% can be achieved under a low H_2 pressure of 0.1 MPa and increases gradually to 100% at 0.8 MPa, which accompanies a decreased NSB selectivity from 19.6% to 0%. These results suggest that higher H_2 pressures are favorable for hydrogenation of NSB to AN. The effect of reaction time was then evaluated under 40°C and 1 MPa H_2 (Fig. 2c). The NB conversion increases from 35.2% to 100% when the reaction time is increased from 10 to 120 min, accompanying an increase in AN selectivity from 76.6% to 100% and an decrease in NSB selectivity from 23.4% to 0%. Additionally, the CH performance of hcp/fcc-Ni in different solvents was studied (Fig. 2d). Under the experimental conditions, both NB conversion efficiency and AN selectivity follow the same trend of H_2O (100%/100%) > methanol (95.8%/100%) > ethanol (67.2%/91.7%) > 2-propanol (35.2%/89.8%) > 1-butanol (30.8%/87.5%), implying that the solvent with high polarity favors the CH of NB to AN. Such a correlation between the solvent polarity and NB conversion efficiency was also observed by others [48]. Such a polarity-dependent performance order would also be due to the improved hydrophilicity of the N-doped carbon support [49,50]. The stability of hcp/fcc-Ni was also examined (Fig. S10). The perfectly retained NB conversion and AN selectivity over six consecutive catalytic cycles confirm an excellent stability of hcp/fcc-Ni. The excellent catalytic stability of hcp/fcc-Ni can be attributed to its excellent structural stability as evidenced by the perfectly retained morphological, structural and crystal phases

Scheme 1 The reaction path of NB hydrogenation to AN.

Figure 2 Effects of (a) reaction temperature (2 h, 1 MPa H₂, H₂O), (b) H₂ pressure (40°C, 2 h, H₂O), (c) reaction time (40°C, 1 MPa H₂, H₂O) and (d) solvent (40°C, 1 MPa H₂, 2 h) on NB conversion and AN selectivity for hcp/fcc-Ni-catalyzed hydrogenation of NB.

(Figs S11 and S12). The above results demonstrate the superiority of hcp/fcc-Ni toward hydrogenation of NB to AN in H₂O. In fact, among the reported catalysts to date, hcp/fcc-Ni is the best performed nonprecious catalyst for hydrogenation of NB to AN in H₂O (Table S1).

It has been widely reported that the catalytic performance of TM catalysts can be strongly affected by their crystal phases [21–23]. For comparative purpose, the pure fcc-phased Ni NPs (denoted as fcc-Ni) was synthesized by the same synthetic procedure as that used to synthesize hcp/fcc-Ni, except the H₂/Ar mixed gas was replaced by pure Ar gas during pyrolysis (Fig. S13). The obtained fcc-Ni consists of pure fcc-Ni NPs (Fig. S14a) with similar morphology, porous structure and Ni NP sizes (Figs S3b, S4b, S5, S6c, d and S14b–h) as that of hcp/fcc-Ni. The Ni content in fcc-Ni determined by ICP is 40.96 wt.%, slightly lower than the Ni content in hcp/fcc-Ni (48.38 wt.%). The CH performance of the resultant fcc-Ni toward NB was investigated. Fig. S15 shows the effect of reaction temperature on NB conversion and AN selectivity over a 2-h reaction period under 1 MPa H₂ in H₂O. In strong contrast to hcp/fcc-Ni, under 40°C, fcc-Ni can only achieve a 25.4% NB conversion with an AN selectivity of 74.7%. A high reaction temperature of 70°C is required for fcc-Ni to achieve a complete NB conversion with 100% AN selectivity, which is 30°C higher than that of hcp/fcc-Ni, confirming a poor CH activity of fcc-Ni NPs toward hydrogenation of NB.

To gain further insights, the kinetic studies were carried out. Fig. S16 shows the plots of NB conversion against reaction time under different reaction temperatures for hcp/fcc-Ni and fcc-Ni, respectively. The $-\ln(C_t/C_0)$ values derived from Fig. S16 are

plotted against the reaction time under different reaction temperatures (Fig. 3a, c). The obtained linear relationships from all investigated reaction temperatures imply that the hydrogenation of NB catalyzed by both hcp/fcc-Ni and fcc-Ni follow the first-order kinetics. The reaction rate constants (k) are derived from the slopes of $-\ln(C_t/C_0)$ versus time plots. At 50°C, hcp/fcc-Ni displays a k_{50} of $9.96 \times 10^{-3} \text{ min}^{-1}$, which is nearly seven times that for fcc-Ni ($k_{50} = 1.49 \times 10^{-3} \text{ min}^{-1}$). Furthermore, the apparent activation energies (E_a) of 37.5 and 57.1 kJ mol⁻¹ for hcp/fcc-Ni and fcc-Ni are derived from the corresponding Arrhenius plots (Fig. 3b, d), further confirming the superior kinetics of hcp/fcc-Ni over fcc-Ni. Considering both catalysts possess similar morphology, porous structure, Ni-NP sizes and Ni contents, it is very reasonable to attribute the superior hydrogenation performance of hcp/fcc-Ni to the presence of hcp-phased Ni [51,52].

Computational studies

DFT calculations were performed to depict the mechanistic insight of CH of NB on fcc- and hcp-Ni. Based on the structural characterization results, the (111) plane of fcc-Ni and the (011) plane of hcp-Ni were chosen for the DFT calculations. Fig. 4a shows the DFT-optimized stable NB parallel and vertical adsorption configurations on (011) plane of hcp-Ni and (111) plane of fcc-Ni, respectively. The calculated parallel and vertical NB adsorption energies are -1.93 and -1.32 eV for hcp-Ni and -1.54 and -0.90 eV for fcc-Ni, respectively. Compared with the vertical NB adsorptions, the parallel NB adsorptions on both catalyst surfaces are obviously stronger. The parallel adsorptions of NB on the hcp (011) and fcc (111) surfaces elongate the N–O

Figure 3 First-order kinetic fittings and corresponding Arrhenius plots for (a, b) hcp/fcc-Ni and (c, d) fcc-Ni-catalyzed hydrogenation of NB under different reaction temperatures. Reaction conditions: 0.2 MPa H_2 , H_2O .

bonds in the nitro group from 1.250 to 1.332 and 1.256 Å, respectively, indicating a stronger interaction between NB and hcp (011), favorable for the subsequent hydrogenation of the nitro group [1,53,54]. It has been widely reported that CH of nitro group in NB to form AN involves multiple sequential hydrogenation steps and each involves an transition state (TS)/intermediate [55,56]: $PhNO_2^* \rightarrow PhNOOH^*$ (via TS1) $\rightarrow PhN(OH)_2^*$ (via TS2) $\rightarrow PhNOH^*$ (via TS3) $\rightarrow PhNHOH^*$ (via TS4) $\rightarrow PhNH^*$ (via TS5) $\rightarrow PhNH_2^*$ (via TS6). Therefore, in this work, we calculated the TS structures and relative energies corresponding to each hydrogenation step of hcp-Ni- and fcc-Ni-catalyzed hydrogenation of nitro group in NB via the parallel adsorption reaction pathway. The DFT-optimized TS structures on the (011) plane of hcp-Ni and (111) plane of fcc-Ni are shown in Fig. 4b and Fig. S17, respectively, while the relative energies are summarized in Fig. 4c. Firstly, NB and H_2 (a in Fig. 4c) adsorb on both hcp-Ni (011) and fcc-Ni (111) to form $PhNO_2^*$ and H^* (b in Fig. 4c). The 1st hydrogenation is to form $PhNOOH^*$ (b $\rightarrow$ c via TS1) on hcp-Ni (011) and fcc-Ni (111), which requires to overcome an energy barrier of 0.34 and 0.40 eV, respectively. The 2nd hydrogenation forms $PhN(OH)_2^*$ (d $\rightarrow$ e via TS2) and needs to overcome an energy barrier of 0.28 and 0.31 eV on the hcp-Ni (011) and fcc-Ni (111), respectively. Our calculations unveil that due to the special confrontations of the two attached hydroxyl groups on N, $PhN(OH)_2^*$ is a highly active intermediate. Therefore, hcp-Ni (011)/fcc-Ni (111)-catalyzed activations of N–O of $PhN(OH)_2^*$ to yield $PhNOH^*$ and OH^* (e $\rightarrow$ f via TS3) are exothermic by -1.63 and -2.81 eV,

with a low energy barrier of 0.33 and 0.58 eV, respectively. The calculated energy barriers involving in the processes of TS1-3 suggest an unambiguous thermodynamical favor of hcp-Ni (011) over fcc-Ni (111). It is worth noting that the generated OH^* can be spontaneously reduced to H_2O by fcc-Ni(111) and desorbed into the solution, while for hcp-Ni (011), a small energy input of 0.12 eV is required. However, $PhNOH^*$ (g in Fig. 4c) remains on the catalyst surface and reacts with H^* to form $PhNHOH^*$ (h $\rightarrow$ i via TS4) that needs to overcome an energy barrier of 0.59 and 0.82 eV on hcp-Ni (011) and fcc-Ni (111), respectively. This is followed by the cleavage of the remaining N–O to form $PhNH^*$ and OH^* (i $\rightarrow$ j via TS5), which involves an energy barrier of 0.64 and 1.15 eV for hcp-Ni (011) and fcc-Ni (111), respectively. In fact, the energy barrier involved in this reaction step is the highest of the entire reaction process. As such, the significantly reduced energy barrier by hcp-Ni (011) reflects its superiority over fcc-Ni (111) for CH of NB to AN. The desorption of OH^* to form $PhNH^*$ (k in Fig. 4c) is a spontaneous process for both hcp-Ni (011) and fcc-Ni (111). The subsequent hydrogenation to form $PhNH_2^*$ (l $\rightarrow$ m via TS6) needs to overcome an energy barrier of 0.55 and 0.62 eV for hcp-Ni (011) and fcc-Ni (111), respectively.

Catalytic hydrogenation of other substrates

Encouraged by the above results, we further examined the catalytic hydrogenation performance of hcp/fcc-Ni for a wide spectrum of nitro-, aldehyde-, ketone-, alkene- and N heterocyclic-compounds. All experiments were carried out in H_2O

Figure 4 (a) Front and top views of the optimized parallel and vertical NB adsorption structures on hcp-Ni (011) and fcc-Ni (111) surfaces, respectively. (b) Front and top views of the optimized TS structures involving in the hcp-Ni (011)-catalyzed hydrogenation of NB to AN. (c) Energy profiles of the hcp-Ni (011)/fcc-Ni (111)-catalyzed hydrogenation of NB to AN. TS1: PhNO₂* + H* → PhNOOH*; TS2: PhNOOH* + H* → PhN(OH)₂*; TS3: PhN(OH)₂* → PhNOH* + OH*; TS4: PhNOH* + H* → PhNHOH*; TS5: PhNHOH* → PhNH* + OH*; TS6: PhNH* + H* → PhNH₂*. Dark blue, grey, blue, red and white represent Ni, C, N, O and H, respectively.

under 1 MPa H₂ and different temperatures for a reaction period of 2 h. As summarized Table 1, hcp/fcc-Ni overperforms fcc-Ni for all cases investigated. For CH of nitro-containing compounds under 40°C (Entries 1 and 2, Table 1), hcp/fcc-Ni can readily achieve the quantitative substrate conversion and 100% selectivity toward the targeted products for CH of both NB and *m*-nitrotoluene (MNT) with a turnover frequency (TOF) of 217.0 h⁻¹ for CH of NB and 237.9 h⁻¹ for CH of MNT. In strong

contrast, the substrate conversion, targeted product selectivity and TOF achieved by fcc-Ni are approximately half of that achieved by hcp/fcc-Ni, indicating an inferior hydrogenation catalytic activity of fcc-Ni toward nitro-compounds. In fact, compared with the reported TM-based catalysts (Tables S1 and S2), hcp/fcc-Ni is the best performed catalyst for CH of nitro-compounds. Meanwhile, the excellent catalytic activity of hcp/fcc-Ni also allows the hydrogenation to proceed at a significantly

Table 1 Comparative performance of hcp/fcc-Ni and fcc-Ni for CH of various substrates^a

Entry	Substrate	Product	Catalyst	T (°C)	Conv. ^b (%)	Sel. ^b (%)	TOF ^{b, c} (h ⁻¹)
1			hcp/fcc-Ni	40	100	100	217.0
			fcc-Ni	40	50.8	58.4	111.8
2			hcp/fcc-Ni	30	100	100	237.9
			fcc-Ni	30	62.7	46.7	123.3
3			hcp/fcc-Ni	50	99.3	100	69.2
			fcc-Ni	50	1.2	100	0.3
4			hcp/fcc-Ni	60	100	98.8	179.5
			fcc-Ni	60	7.2	31.1	19.6
5			hcp/fcc-Ni	80	91.3	94.2	54.2
			fcc-Ni	80	0	—	—
6			hcp/fcc-Ni	40	99.4	100	66.3
			fcc-Ni	40	0.3	100	0.3
7			hcp/fcc-Ni	40	100	100	349.4
			fcc-Ni	40	10.7	100	68.7
8			hcp/fcc-Ni	90	100	100	35.1
			fcc-Ni	90	6.5	100	0.6

a) Reaction conditions: solvent: H₂O; reaction time: 2 h; H₂ pressure: 1 MPa. b) Determined by GC-MS. c) Reaction time: 5 min.

reduced H₂ pressure with a moderately increased reaction temperature (Fig. S18). In addition, the results (Fig. S19) show that well-known Raney Ni is superior to fcc-Ni but inferior to hcp/fcc-Ni in the hydrogenation of NB, indicating its commercial potential.

The CH of aldehyde-compounds to corresponding alcohols such as furfural (FAL) to furfuryl alcohol (FOL) and cinnamaldehyde (CAL) to hydrocinnamyl alcohol (HCOL) is another class of important hydrogenation reactions to produce fine and bulk chemicals [47,48,51]. For CH of FAL to FOL under 50°C (Entry 3, Table 1), hcp/fcc-Ni can easily achieve 99.3% FAL conversion and 100% FOL selectivity with a TOF of 69.2 h⁻¹, outperforming the reported TM-based catalysts to date (Table S3). In a sharp contrast, under the identical reaction conditions, fcc-Ni can only convert 1.2% FAL to FOL with a low TOF of 0.3 h⁻¹ (Entry 3, Table 1). For CH of CAL to HCOL under 60°C (Entry 4, Table 1), hcp/fcc-Ni can achieve a quantitative CAL conversion and 98.8% HCOL selectivity with a TOF of 179.5 h⁻¹, while fcc-Ni can only convert 7.2% CAL with a poor HCOL selectivity of 31.1% and a low TOF of 19.6 h⁻¹. CH of other substrates including levulinic acid (LA) to γ-valerolactone (GVL), acetophenone (AOP) to 1-phenylethanol (PE), styrene (ST) to ethylbenzene (EBZ) and quinoline (QO) to tetrahydroquinoline (THQ) were also investigated to demonstrate the generic hydrogenation capability of hcp/fcc-Ni toward ketone-, alkene- and N heterocyclic-compounds. For CH of LA under 80°C (Entry 5, Table 1), hcp/fcc-Ni can realize 91.3% LA conversion and 94.2% GVL selectivity with a TOF of 54.2 h⁻¹ that contrast strongly with the catalytic inactivity observed from fcc-Ni. As shown in Table 1 (Entries 6–8), hcp/fcc-Ni can quantitatively hydrogenate CYC to CYH under 40°C with a TOF of 66.3 h⁻¹, ST to EBZ under 40°C with a TOF of 349.4 h⁻¹, and QO to THQ under 90°C with a TOF of 35.1 h⁻¹, while under the corresponding temperatures, fcc-Ni is barely active and can only convert 0.3%–10.7% substrates to the targeted products. These results demonstrate the superb catalytic performance and unprecedented generic applicability of hcp/fcc-Ni for hydro-

genation reactions, and exemplify the effectiveness of engineering Ni NPs with hcp phase to enhance their intrinsic catalytic activity.

CONCLUSIONS

In summary, we have demonstrated a facile pyrolysis approach to directly convert Ni-containing MOF precursor into hcp-phased Ni NPs on carbon support. We theoretically and experimentally exemplified that introducing hcp crystal phase into Ni NPs can dramatically enhance the intrinsic catalytic activity toward a wide spectrum of hydrogenation reactions. We anticipated that the unveiled crystal phase engineering design approach would be adoptable to other types of reactions.

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Author contributions Lv Y carried out the materials fabrication, characterizations and performance measurements, and wrote the initial manuscript; Mao X and Du A performed and guided theoretical analysis; Wang D, Chen C and Lin Y did some characterizations; Liu P, Wang G and Zhang H performed some data analysis; Gong W and Zhao H conceived and supervised this study, and revised the manuscript. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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hcp晶相的Ni纳米颗粒对不同官能团的通用催化加氢活性

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摘要 催化加氢是生产高附加值燃料和精细化学品的重要工业途径, 但需要高效的催化剂, 尤其是廉价的非贵金属催化剂. 迄今为止, 大多数高性能催化加氢催化剂都是由贵金属材料制成, 并且这些催化剂都只能用于催化一种或几种特定的反应. 在这里, 我们例证了一种晶相工程方法, 其能赋予Ni纳米颗粒(NPs)卓越的、广谱的内在催化加氢活性. 这种负载于碳载体上含有hcp晶相的Ni NPs催化剂通过直接碳化热解Ni咪唑MOF前驱体获得. 在纯水中, 含hcp相的Ni NPs对硝基、醛、酮、烯烃和N杂环化合物表现出前所未有的加氢催化活性, 优于类似物fcc-Ni和目前报道的其他过渡金属催化剂. 密度泛函理论计算表明, hcp-Ni通过增强底物吸附强度和降低速率决定步骤的反应势垒能共同来提高内在催化加氢活性. 我们预计这项工作中揭示的晶相工程设计方法将适用于其他类型的反应.