

pubs.acs.org/acscatalysis

Aluminum Metal–Organic Framework-Ligated Single-Site Nickel(II)-Hydride for Heterogeneous Chemoselective Catalysis

Neha Antil, Ajay Kumar, Naved Akhtar, Rajashree Newar, Wahida Begum, Ashutosh Dwivedi, and Kuntal Manna*



ABSTRACT: The development of chemoselective and heterogeneous earth-abundant metal catalysts is essential for environmentally friendly chemical synthesis. We report a highly efficient, chemoselective, and reusable single-site nickel(II) hydride catalyst based on robust and porous aluminum metal-organic frameworks (MOFs) (DUT-5) for hydrogenation of nitro and nitrile compounds to the corresponding amines and hydrogenolysis of aryl ethers under mild conditions. The nickel-hydride catalyst was prepared by the metalation of aluminum hydroxide secondary building units (SBUs) of DUT-5 having the formula of Al(μ_2 -OH)(bpdc) (bpdc = 4,4'-biphenyldicarboxylate) with NiBr₂ followed by a reaction with NaEt₃BH. DUT-5-NiH has a broad substrate scope with excellent functional group tolerance in the hydrogenation of



aromatic and aliphatic nitro and nitrile compounds under 1 bar H_2 and could be recycled and reused at least 10 times. By changing the reaction conditions of the hydrogenation of nitriles, symmetric or unsymmetric secondary amines were also afforded selectively. The experimental and computational studies suggested reversible nitrile coordination to nickel followed by 1,2-insertion of coordinated nitrile into the nickel-hydride bond occurring in the turnover-limiting step. In addition, DUT-5-NiH is also an active catalyst for chemoselective hydrogenolysis of carbon–oxygen bonds in aryl ethers to afford hydrocarbons under atmospheric hydrogen in the absence of any base, which is important for the generation of fuels from biomass. This work highlights the potential of MOF-based single-site earth-abundant metal catalysts for practical and eco-friendly production of chemical feedstocks and biofuels.

KEYWORDS: nickel-hydride catalyst, metal-organic frameworks, hydrogenation, hydrogenolysis, chemoselectivity

INTRODUCTION

The role of first-row transition-metal hydrides in sustainable catalysis has received increasing attention in recent years due to the low cost and toxicity of the metals and the utilization of dihydrogen as an energy carrier.^{1,2} They often function as key intermediates in the catalytic reactions for transferring protons (H^+) , hydrogen atoms (H^{\bullet}) , or hydrides (H^-) between molecules.^{3,4} Nickel-hydride is of particular interest, primarily driven by the need to develop hydrogen storage materials, understand the active sites of nickel-containing enzymes such as [NiFe]-hydrogenase^{6,7} and methyl-coenzyme M reductase,⁸ and understand its industrial applications in catalytic hydrogenation and olefin oligomerization.⁹ Generally, well-defined nickel-hydride species are afforded using multidentate strong field nitrogen- and phosphorous-donor ligands bearing sterically encumbered bulky substituents.¹⁰ These nickel-hydrides have been investigated as single-site homogeneous catalysts in many organic transformations such as hydrogenation,¹¹⁻¹³ hydroelementation,^{14–16} oligomerization,^{9,17–19} reduction of CO_{21}^{20-22} and dehydrogenation.^{21,23} In contrast, the traditional heterogeneous nickel catalysts that undergo Ni-H bond

participation such as Raney nickel,²⁴ resin-encapsulated nickel nanoparticles,²⁵ and alumina- or silica-supported nickel^{26–28} have multiple sites, leading to give poor selectivity and also complicating the delineation of active sites and reaction mechanisms. Therefore, the development of chemoselective and heterogeneous single-site nickel catalysts is essential for sustainable chemical synthesis.

Nonreducible γ -Al₂O₃ is one of the most studied oxides as support for Ni catalysts because of its high thermal and chemical stability, high surface area (80–250 m²/g), and high ability to disperse Ni nanoparticles.^{29,30} However, the intrinsic heterogeneity of the γ -alumina surface originating from the presence of different coordination numbers (Al_{IV} and Al_{VI}) of aluminum ions and varied surface OH coordination modes

Received: October 9, 2020 Revised: February 11, 2021 Published: March 16, 2021







Figure 1. Schematic showing the development of robust and porous single-site nickel-hydride catalyst based on DUT-5. The isolation of active nickel sites prevents oligomerization, the formation of multiple catalytic sites or intermolecular decomposition. The heterogeneous and uniformly distributed single-site nickel-hydrides are active in catalytic chemoselective hydrogenation of nitro and nitrile compounds and also hydrogenolysis of aryl ethers in mild conditions.



Figure 2. (a) DUT-5 and its metalation at SBUs with nickel. (b) PXRD patterns simulated from the CIF file of DUT-5 (black)^{78,79} and of freshly prepared DUT-5 (blue), DUT-5-NiBr (red), and DUT-5-NiH (green). (c) Nitrogen sorption isotherms (77 K) of DUT-5 and DUT-5-NiBr. (d) Ni K-edge XANES spectra of NiBr₂ (black), DUT-5-NiBr (red), DUT-5-NiH (blue), and DUT-5-Ni after hydrogenation of benzonitrile (magenta). (e) Extended X-ray absorption fine structure (EXAFS) spectra and fits in *R*-space at the Ni K-edge of DUT-5-NiH showing the magnitude (hollow squares, blue) and real component (solid squares, blue) of Fourier transformation. The fitting range is 1-4 Å in *R*-space (within the gray lines).

(terminal, μ_2 , and μ_3) to the Al centers presents a challenge to afford single-site solid catalysts.^{31,32} To circumvent such difficulties, the design and synthesis of single-site heterogeneous catalysts based on the inorganic metal-oxo-nodes of

metal–organic frameworks (MOF) have drawn considerable interest recently.^{33–40} Constructed from metal cluster secondary building units (SBUs) and organic linkers, MOF provides highly porous and tunable support for stabilizing active species or affording solution-inaccessible molecular catalysts via active-site isolation.^{41–48} The inorganic nodes of many MOFs feature functional OH groups to mimic metal oxides/hydroxides. Due to the presence of highly disperse and uniform OH groups at the nodes, tunable pores, thermal and chemical stability, and predictable structures, MOFs offer a unique platform to develop robust single-site nickel-hydride catalysts.^{35,36,49,50}

Moreover, unlike the traditional supported catalysts, MOF catalysts combine advantages offered by heterogeneous catalysts, such as high stability, facile catalyst separation and recovery, and less leaching, and those provided by their homogeneous counterparts, such as homogeneity of the active sites, reproducibility, and selectivity.^{S1–S5} Aluminum MOF, owing to its simple and economical synthesis, high thermal stability, large pore size, and electrophilic nature of the hydroxy groups at SBUs, offers superior support to develop highly electrophilic nickel-hydride catalysts at SBUs. Herein, we report a highly chemoselective and reusable single-site nickel(II) hydride catalyst supported by the nodes of a robust and porous aluminum metal—organic framework (DUT-5) for hydrogenation of nitro and nitrile compounds to the corresponding amines and also for hydrogenolysis of aryl ethers under mild reaction conditions (Figure 1).

Primary and secondary amines including anilines are key intermediates in the synthesis of fine chemicals, pharmaceuticals, agrochemicals, and industrial materials.⁵⁶⁻⁵⁸ Among many methods, earth-abundant metal-catalyzed chemoselective hydrogenation of nitro or nitrile compounds is one of the most sustainable and economic methods due to the availability of starting materials, low price, and high atom efficiency.⁵ Methods for such transformations generally require high hydrogen pressure and high temperature and also often necessitate the addition of a base and thus have potential safety issues.⁵⁹⁻⁶⁸ Despite significant progress with non-noble metal nanoparticles in recent years,69 ⁻⁷² the development of single-site well-defined heterogeneous and chemoselective base-metal catalysts with excellent tolerance of functional groups under mild reaction conditions is a challenge. Our single-site DUT-5-supported nickel catalyst is not only highly active for hydrogenation of nitroarenes and nitriles to give primary amines under 1 bar H₂ in the absence of any base but also affords symmetric and unsymmetric secondary amines selectively in similar mild conditions (Figure 1). Our straightforward, atom-efficient, and environmentally friendly protocols using the easily affordable MOF catalyst are able to hydrogenate not only common aromatic and aliphatic nitro and nitrile substrates but also several industrially important dinitriles and active pharmaceutical ingredients. Moreover, the same MOF catalyst is also efficient for selective hydrogenolysis of ether bonds of aryl ethers as models for lignin under 1 bar H_2 at temperatures as low as 70 °C without the addition of a base, which is important for the production of value-added 5073-77chemicals from biomass.50,73

RESULTS AND DISCUSSION

Synthesis and Characterization of DUT-5 and Nickel-Metalated DUT-5. The solvothermal synthesis between aluminum trichloride hexahydrate and 4,4'-biphenyldicarboxylic acid in DMF at 120 °C for 48 h afforded DUT-5 (DUT-5) as a white crystalline solid with the formula of Al(OH)(bpdc) (Figure 2a).⁷⁸ The crystallinity and structure of DUT-5 were established by the similarity of its Powder X-ray diffraction (PXRD) pattern to that obtained after the simulation of aluminum MOF using the structure of MIL-53(Al)-MOF (Figure 2b).^{78,79} DUT-5 has one-dimensional chains of μ_{2^-} hydroxide-bridged, octahedrally coordinated Al³⁺ cations that are linked via bpdc²⁻ linkers to give a three-dimensional framework with rhombic channels. The solid-state infrared (KBr) spectrum of DUT-5 showed the $v_{\mu_{2^-}O-H}$ stretching band at 3700 cm⁻¹ and strong carboxylate stretching bands at 1598 cm⁻¹ (Figure S6, Supporting Information (SI)).⁴⁹ Nitrogen adsorption isotherms indicated a highly porous structure with a Brunauer–Emmett–Teller (BET) surface of 1618 m²/g, a pore volume of 0.91 cm³/g, and a pore size of 1.2 nm (Figure 2c).⁷⁸

Nickel-functionalized DUT-5 (DUT-5-NiBr) was synthesized by metalation of the SBUs via deprotonation of μ_2 -OH followed by coordination of μ_2 -O⁻ to a nickel ion. DUT-5 was first treated with 1.5 equiv of n-BuLi in THF at room temperature to give an intermediate Al(OLi)(bpdc)^{35,80} and then reacted with NiBr₂ to afford DUT-5-NiBr as an off-white solid via a salt-metathesis reaction. Transmission electron microscopy showed that the DUT-5-NiBr particles have a platelike morphology and an average diameter of the particles of 0.9 nm (Figure S3, SI). Both the organic linker and carboxylate groups remained intact upon lithiation and metalation of SBUs as evidenced by the ¹H NMR spectrum of the digested MOF (Figures S4, SI) and by the retention of carbonyl stretching frequency of carboxylates in the IR spectrum (Figure S6, SI). The crystallinity of DUT-5 was maintained upon metalation as evidenced by similarity in the PXRD pattern of freshly prepared DUT-5-NiBr to that of pristine DUT-5 (Figure 2b). Inductively coupled plasma optical emission spectroscopy (ICP-OES) showed 70% nickel loading with respect to the μ_2 -OH moiety. DUT-5-NiBr is thermally stable up to 450 °C as evaluated by thermogravimetric analysis (Figure S5, SI). The estimated BET surface area and pore size of DUT-5-NiBr are 1252 m²/g and 1.1 nm, respectively (Figure 2c). The reduction of surface area and pore size of DUT-5-NiBr as compared to those of pristine DUT-5 is attributed to the partial filling of the void space of MOF with the nickel bromide moiety. The coordination environment of nickel in DUT-5-NiBr was optimized by the density functional theory (DFT) method (B3LYP) and a basis set of 6-311G(d,p) using the Gaussian 09 software suite. The DFT-optimized structure revealed a slightly distorted squareplanar nickel ion, which is ligated with one anionic bridging oxo (from the deprotonation of the μ_2 -OH group), two carboxylate oxygen, and one bromide to afford the $[(\mu_3$ - O^{-})(carboxylate-O)₂NiBr] species. The Ni-(μ_3 - O^{-}) distance is 1.85 Å, while the Ni-O(carboxylate) distances are 1.91 and 1.88 Å (Figure S19, SI).

The treatment of DUT-5-NiBr with 1.2 equiv of NaBEt₃H resulted in the formation of DUT-5-NiH as a black solid. Heating the mixture of DUT-5-NiH and 1 equiv of H_2O leads to the formation of 1.0 equiv of H_2 as analyzed by gas chromatography (GC). The similarity of the PXRD pattern implies that the crystallinity and the structural integrity of the MOF are maintained during the bromide/hydride exchange. X-ray absorption near-edge structure (XANES) analysis indicated that the oxidation state of the nickel centers in both DUT-5-NiBr and DUT-5-NiH is +2, as determined by comparing their energies of the pre-edge peaks to NiBr₂ as the reference compound (Figure 2d). The Ni coordination in the DFT-optimized structure of DUT-5-NiH converged at a

distorted square-planar geometry similar to that of DUT-5-NiBr. The distances of Ni– $(\mu_3$ -O⁻) and Ni–H are 1.94 and 1.48 Å, respectively, while the Ni–O(carboxylate) distances are 1.88 and 1.89 Å (Figure S20, SI). This DFT-optimized model fitted well to the Ni K-edge absorption of extended Xray fine spectroscopy data of DUT-5-NiH with an R factor of 0.008, indicating the formation of $(\mu_3$ –O)(O-carboxylate)₂NiH species in DUT-5-NiH (Figure 2e and Table S9, SI).

DUT-5-NiH-Catalyzed Hydrogenation of Nitroarenes. DUT-5-NiH is an active catalyst for the selective hydrogenation of aromatic and aliphatic nitro compounds to the corresponding amines. The screening experiments with nitrobenzene revealed that the highest turnover frequency was obtained when the hydrogenation reaction was carried out at 130 °C under 1 bar of H₂ using toluene or *p*-xylene as the solvent. The analogous DUT-5-supported Fe and Co hydrides, DUT-5-FeH and DUT-5-CoH, were less efficient catalysts for hydrogenation of nitroarenes (Table S1, SI). Under the optimized reaction conditions, the hydrogenation of nitrobenzene with 1 mol % of nickel loading resulted in 100% conversion to aniline (2a) in 6 h (Scheme 1). Pure aniline was isolated in the quantitative yield via simply centrifugation to remove the solid catalyst followed by the evaporation of the volatiles. DUT-5-Ni-catalyzed hydrogenation of nitro groups had a wide range of substrate scope with excellent compatibility with various auxiliary functional groups (Schemes 1, $2\mathbf{b}-\mathbf{z}$). Both the electron-donating groups, such as methyl (2b), hydroxo (2c), and amino (2e), and electronpoor groups, such as halo (2d), ester (2s-u), aldehyde (2g), and cyano (2p), are well tolerated in the reaction conditions. The nitro substrates bearing electron-withdrawing groups were more active, allowing us to carry out the reduction at a lower temperature (90 °C). Hydrogenation of N-(4-nitrophenyl)benzamide, 3-nitro-o-xylene, 1-nitronapthalene and p-nitrophenylacetate gave N-(4-aminophenyl)benzamide (2i), 3amino-o-xylene (2j), 1-aminonapthalene (2k), and p-aminophenylacetate (21), respectively, in 75-100% isolated yields. Importantly, DUT-5-NiH was also highly chemoselective in the hydrogenation of nitroarene-bearing groups sensitive to reduction such as iodo, aldehyde, keto, nitrile, and thio. At a 2.0 mol % loading, the hydrogenation of bis(2-nitrophenyl)sulfane at 120 °C under 1 bar of H₂ afforded 2,2'-thiodianiline (2q) in 70% yield, and no cleavage of the arene-sulfur bond was detected. However, 2-((2-nitrophenyl)thio)aniline (2r)was obtained in 90% yield when the reaction was performed at a lower temperature of 110 °C. Three amine-functionalized dicarboxylates, dimethyl-2-aminoterephthalate (2s), dimethyl-2-amino-[1,1'-biphenyl]-4,4'-dicarboxylate (2t), and dimethyl-2,2'-diamino-[1,1'-biphenyl]-4,4'-dicarboxylate (2u), were prepared in excellent yields from the corresponding nitro derivatives using our standard protocol under 1 bar H₂. In all of the cases, pure products were obtained by removal of the solid MOF catalyst via centrifugation followed by the evaporation of volatiles. The compatibility with borane and acid functionalities and heteroarenes was also striking. For example, 4-nitrophenylboronic acid pinacol ester, 2-nitrobenzoic acid, and bis(4-nitrophenyl) hydrogen phosphate were reduced efficiently to afford 4-aminophenylboronic acid pinacol ester (2w), 2-aminobenzoic acid (2h), and 4aminophenyl (4-nitrophenyl) hydrogen phosphate (2v), respectively. Heterocyclic nitro compounds such as 2-chloro-4-nitropyridine and 5-nitroindole were hydrogenated to the corresponding amino compounds, 2-chloropyridin-4-amine





⁶90 °C, 30 h. ^dSubstrate: *p*-nitroaniline. ^e0.2 mol % Ni, 40 h. ^fSubstrate: 1,3-dinitrobenzene, 3 h. ^gSubstrate: 5-chloro-2-nitroaniline. ^hSubstrate: bis(2-nitrophenyl)sulfane, 2 mol % Ni, 120 °C, 30 h. ⁱSubstrate: bis(2-nitrophenyl)sulfane, 110 °C, 30 h. ^jSubstrate: dimethyl-2,2'-dinitro-[1,1'-biphenyl]-4,4'-dicarboxylate. ^kSubstrate: bis(4-nitrophenyl)hydrogen phosphate, 24 h, NMR yield. ^aReaction conditions: DUT-5-NiH (1.0 mol % Ni), 0.243 mmol nitroarene, 1 bar H₂, 3.0 mL of toluene or *p*-xylene, 130 °C, 6 h. ^b100% conversion; isolated yields are shown.

(2x) and 5-aminoindole (2y) with 85–100% yield without any side products. DUT-5-NiH was also efficient in the hydrogenation of aliphatic nitro compounds such as nitro



Figure 3. (a) Plot for the %GC yield of aniline at various runs in the recycle and reuse of DUT-5-Ni (1.0 mol % Ni) for hydrogenation of nitrobenzene. (b) PXRD patterns of DUT-5-NiH (black) and DUT-5-Ni recovered after run 12 of hydrogenation of nitrobenzene (green), hydrogenation of benzonitrile (red), and hydrogenolysis of diphenyl ether (blue). (c) Plots of %GC yield of 2u (A–C) after hydrogenation of dimethyl-2,2'-dinitro-[1,1'-biphenyl]-4,4'-dicarboxylate and 8d (D–F; gray, 8d; red, 4-acetyl-benzylamine) after hydrogenation of 4-acetylbenzonitrile in the presence of benzylamine, respectively, using DUT-5-NiH (1.0 mol % Ni, A and D), MIL-53(Al)-Ni (1.0 mol % Ni, B and E), and Ni nanoparticles (C and F) as catalysts under identical conditions. (d) Plot for the %GC yield of *N*-benzylacetamide at various runs in the recycle and reuse of DUT-5-NiH (0.1 mol % Ni) for hydrogenation of benzonitrile.

cyclopentane (1z), and cyclopentyl amine was isolated as HCl salt in 95% yield. The hydrogenation of nitroarenes also works well with 0.1 mol % Ni loading, albeit with a longer reaction time (Scheme S1, SI).

We have performed a number of experiments to test the heterogeneous nature of the DUT-5-NiH catalyst. The catalytic activity of DUT-5-NiH for hydrogenation of nitroarenes was unaffected in the presence of metallic mercury (Figure S9, SI). In addition, Ni nanoparticles generated from the reaction of NiBr2 and NaBEt3H both in solution as well as within DUT-5 were almost inactive, thus excluding the potential of any in situ generated Ni nanoparticles or leached Ni particles responsible for catalysis (Figures 3c and S12, SI). Moreover, no further conversion was observed upon removal of the MOF catalyst from the reaction mixture during the course of hydrogenation reaction (Figure S8, SI). Importantly, at 1 mol % Ni loading, DUT-5-NiH was recycled and reused at least 9 times for the hydrogenation of nitrobenzene without apparent loss of catalytic activity (Figure 3a and Table S2, SI). The supernatant of the reaction mixture showed leaching of Ni and Al of 0.13 and 0.06% after the first run and of 0.32 and 0.07% after the fourth run, respectively. The PXRD pattern of DUT-5-NiH recovered after the hydrogenation reaction remained unchanged (Figure 3b), indicating the robustness of the MOF frameworks under the reaction conditions. The effect of pore sizes of MOF on hydrogenation reactions was further studied by comparing the catalytic activity of DUT-5NiH with that of the nickel-metallated MIL-53(Al) MOF having a similar topology but smaller pore size (Figure 3c). Under identical reaction conditions, DUT-5-NiH had almost two times higher activity than MIL-53(Al)-NiH in the hydrogenation of dimethyl-2,2'-dinitro-[1,1'-biphenyl]-4,4'-dicarboxylate, indicating that the catalysis facilitated by DUT-5-NiH was both on the surface and inside of the pores (Figure S12, SI).

DUT-5-Ni-Catalyzed Hydrogenation of Arene Nitriles. DUT-5-NiH was also an active catalyst for chemoselective hydrogenation of aliphatic and aromatic nitriles to give corresponding amines. Interestingly, either primary or secondary amines were afforded selectively depending on the reaction conditions. At a 1.0 mol % Ni loading, dibenzylamine was obtained quantitatively from the hydrogenation of benzonitrile at 90 °C under 1 bar of H₂ (entry 1, Table 1). In contrast, benzylamine was afforded quantitatively when the same catalytic reaction was carried out at 130 °C in the presence of 1.1 equiv of di-tert-butyl dicarbonate (Boc_2O) or acetic anhydride (Ac_2O) with respect to benzonitrile under 1 bar of H_2 followed by acid hydrolysis (entry 2, Table 1). Nitriles bearing alkyl, halo, methoxy, and amino functional groups were fully converted to the corresponding substituted symmetric dibenzyl amines at 90 °C in 90-100% yields (entries 3, 5, 7, 9, and 11, Table 1). In all cases, the pure product was isolated from the reaction mixture simply by centrifugation of the reaction mixture followed by evaporation





"Reaction conditions: DUT-5-NiH (1.0 mol % Ni), 0.243 mmol nitrile, 1 bar H_2 , 3.0 mL of toluene or *p*-xylene. ^b100% conversion, isolated yields are shown. "Reaction was performed at 110 °C.

of the volatiles without any chromatographic purification. At a 1.0 mol % Ni loading, DUT-5-NiH also gave complete conversion of various substituted nitriles at 130 °C in the presence of Boc₂O to give the corresponding N-Boc-benzylamines within 6 h, and the corresponding primary amines were isolated as HCl salts after carbamate hydrolysis in acidic conditions. A range of substituted benzylamines bearing functional groups such as methyl, bromo, fluoro, methoxy, amino, keto, and thio were afforded in 80-100% yields (entries 4, 6, 8, 10, and 12-17, Table 1). No side products such as N-benzylidenebenzylamine, dibenzylamine, or their derivatives were formed as analyzed by GC-mass spectrometry (GC-MS). Heterocyclic nitriles such as 2-pyridylnitrile, 3-pyridylnitrile, and indole-5-carbonitrile were reduced to 2picolylamine, 3-picolylamine, and 5-(aminomethyl)indole, respectively, in excellent yields (entries 19-21, Table 1). Importantly, at a 0.1 mol % Ni loading, DUT-5-NiH was recycled and reused at least 7 times for the reduction of benzonitrile to N-benzylacetamide (Figure 3d). The leached nickel and aluminum into the supernatant after run 1 were 0.22

and 0.04%, respectively. The crystallinity of the MOF remained the same after the hydrogenation of benzonitrile as shown by the PXRD of the recovered MOF (Figure 3b).

Hydrogenation of Aliphatic Nitriles and Dinitriles. The chemoselective hydrogenation of aliphatic nitriles is more challenging due to base-induced side reactions using common hydrogenation catalysts. Importantly, several aliphatic nitriles such as benzyl cyanide, 4-chloro-benzyl cyanide, pentanenitrile, and cyclohexyl carbonitrile were selectively reduced to the corresponding primary amines in nearly quantitative yields with 1.0 mol % DUT-5-NiH at 130 °C under 1 bar H₂ (entries 1, 2, 4, and 5, Table 2). The amines with high NMR purity were obtained after simply removal of the MOF solid by centrifugation followed by either removal of the volatiles in vacuo or isolation as the HCl salt. Using the same protocol, several dinitriles were also efficiently reduced to corresponding diamines. For example, adiponitrile, which is hydrogenated at elevated pressures in the polymer industry on a ton scale annually to give 1,6-hexamethylenediamine, an essential building block for the production of Nylon 6,6, was readily

	R CN + H ₂ 6 (1 bar	DUT-5-NiH (1.0 mol% Ni) toluene or xylene) 130 °C 7	,NH₂
Entry	Arene	Product	%Conversion (Yield) ^b
1	CN	NH ₂	100 (95)
2	CI	CI NH2	100 (99)
3 ^c	·	CI C	100 (99)
4	CN	NH ₂	100 (99) ^d
5	CN	NH ₂	100 (76) ^d
6	NC 4 CN	H ₂ N ⁺ NH ₂	100 (95) ^e
7		$H_2N \xrightarrow{4}_3 NH_2$	100 (99) ^e
8		H ₂ N	100 (91) ^e

Table 2. DUT-5-NiH-Catalyzed Hydrogenation of AliphaticNitriles and Dinitriles a,b,c,d,e

^{*a*}Reaction conditions: DUT-5-NiH (1.0 mol % Ni), 0.243 mmol nitrile, 1 bar H_{22} 3.0 mL of toluene or *p*-xylene, 20 h. ^{*b*}Isolated yield in the parentheses. ^{*c*}Reaction was performed at 90 °C. ^{*d*}Isolated as HCl salt. ^{*e*}GC yield.

hydrogenated under 1 bar of H_2 (entry 6, Table 2). The hydrogenation of malononitrile and 1,4-dicyanobenzene attained full conversion, giving 1,3-trimethylenediamine and 1,4-bis(aminomethyl)-benzene, respectively, in excellent yields (entries 7 and 8, Table 2).

Mechanistic Investigation into DUT-5-NiH-Catalyzed Hydrogenation of Aryl Nitriles. The presence of Ni^{II} centers in DUT-5-NiH and DUT-5-Ni after catalysis based on the XANES analysis (Figure 2d) and control experiments (Figure S12, SI) precludes the contribution of any Ni nanoparticles within the MOFs to the hydrogenation of aryl nitriles. Furthermore, the absence of any reflection peaks of Ni nanoparticles with $2\theta > 30^{\circ}$ in the PXRD pattern rules out the formation of any Ni particulates upon treatment of NaEt₃BH and during catalysis (Figure 3b). We thus infer that the SBUsupported Ni^{II} hydride was the actual catalytic species, and the proposed pathways of hydrogenation of nitriles are summarized in Figure 4. As discussed before, the hydrogenation of benzonitrile at 80-90 °C produces only dibenzylamine. Upon increasing the reaction temperature, a mixture of benzylamine and dibenzylamine was formed, and benzylamine was the major product at 130 °C. We thus infer that the Ni-catalyzed hydrogenation of benzonitrile gives the putative phenylmethanimine as the key intermediate in the first step, which undergoes further hydrogenation to produce benzylamine (A pathway). The reaction between the benzylamine product and phenylmethanimine intermediate gives dibenzylamine (B pathway). The selectivity of the products depends on the relative rate of the individual steps. We propose that at low temperatures (80–90 °C), the rate of the A pathway is slower than that of the B pathway; thus, the nucleophilic attack of benzylamine to the imine intermediate gives a secondary amine with the liberation of ammonia (B pathway). The nucleophilic attack of benzylamine became restricted in the presence of acetic anhydride leads to the formation of only Nbenzylacetamide (A pathway).

We have further characterized the reaction pathway of hydrogenation of aryl nitrile to the corresponding benzylamine by kinetic and computational studies. The empirical rate law was determined by investigating the instantaneous rate dependence on the average initial substrate concentration, and the concentration of benzonitrile was determined by GC-FID analysis. At low initial concentrations (0.048-0.28 M) of the substrate, the average initial substrate conversion rates increase linearly as the substrate concentration increases; however, at higher substrate concentrations (>0.28 M), the initial rates reach a maximum. Plots of initial rates versus substrate concentration thus show saturation in high substrate concentrations (Figure 5a). This saturation kinetics implies reversible nitrile coordination to nickel followed by the turnover-limiting step. In addition, the initial substrate conversion rates had first-order rate dependence on nickel concentrations (Figure 5a) and zeroth-order dependence on the pressure of H₂ (Figure S18, SI). Our kinetic data indicates that a substrate molecule and the nickel catalyst are involved in



Figure 4. Proposed pathways for DUT-5-NiH-catalyzed hydrogenation of nitriles to primary and secondary amines.



Figure 5. (a) Kinetic plots of initial rates -(d[substrate]/dt) for hydrogenation of benzonitrile versus initial concentrations of nickel and benzonitrile for the first 8 min. (b) Proposed catalytic cycle of DUT-5-NiH-catalyzed hydrogenation of aryl nitriles to corresponding benzylamines based on the kinetic and computational studies. (c) DFT-calculated reaction energy profile of DUT-5-NiH-catalyzed hydrogenation of benzonitriles. See the Supporting Information for computational details.

the turnover-limiting state of the catalytic cycle in the hydrogenation of aryl nitriles.

To further study the mechanism of DUT-5-NiH-catalyzed hydrogenation of nitriles, we performed DFT calculations, and the calculated energy profile are shown in Figure 5c. The catalytic cycle commences with the 16-electron d⁸-nickelhydride complex (DUT-5-NiH) as the catalyst and benzonitrile (cycle 1, Figure 5b). The coordination of benzonitrile to nickel forms an 18-electron nickel intermediate (INT-1), which is 2.6 kcal lower in energy than DUT-5-NiH (Figure 5c). INT-1 then transformed into phenylmethaniminecoordinated nickel species (INT-2) via a transitional state (TS-1) involving 1,2-insertion of the coordinated nitrile into the nickel-hydride bond, requiring an activation free energy of 16.5 kcal/mol. The subsequent σ -bond metathesis of the Ni-N bond of INT-2 and the H-H bond of molecular dihydrogen associated with a barrier of 13.0 kcal/mol leads to the formation of phenylmethanimine and the regeneration of the DUT-5-NiH catalyst. DUT-5-NiH further catalyzes the hydrogenation of phenylmethanimine to give benzylamine (cycle 2, Figure 5b). The coordination of phenylmethanimine to nickel of DUT-5-NiH forms INT-3, and this step is exergonic by 12.5 kcal/mol. Then, 1,2-insertion of the coordinated imine into the nickel-hydride bond transforms INT-3 to INT-4 via TS-3, requiring an activation free energy of 12.8 kcal/mol. INT-4 then undergoes a σ -bond metathesis

reaction with dihydrogen that leads to the production of benzylamine and the regeneration of DUT-5-NiH. The calculated energy profile diagram reveals that the transformation of INT-1 to INT-2 via TS-1 is the turnover-limiting step. The DFT calculation identifies TS-1 as a four-member cyclic transition state involving 1,2-insertion of the coordinated nitrile into the nickel-hydride bond with the dissociation of a labile Ni-O(carboxylate) bond. In our kinetic studies, the plots of initial rate versus [substrate] showed a rate dependence that evolved from first order at low concentrations to zero order at high concentrations, and this was consistent with reversible nickel-nitrile interaction to give INT-1 preceding the irreversible turnover-limiting step. The firstorder dependence on the concentrations of nickel and the substrate saturation kinetics further support the involvement of nickel and nitrile in the turnover-limiting step. The proposed catalytic cycle is thus in good agreement with the theoretical and kinetic studies (Figure 5b).

DUT-5-NiH-Catalyzed Synthesis of Unsymmetric Secondary Amines. As discussed above, DUT-5-NiHcatalyzed hydrogenation of aryl nitrile at 90 °C produces symmetric diarylamine selectively due to the coupling between benzylamine and the phenylmethanimine intermediate. We surmised that the hydrogenation of substituted aryl nitriles in the presence of benzylic primary amines under identical reaction conditions would give unsymmetric secondary amines by the reaction of benzylic primary amines and the arylmethanimine intermediate. Indeed, at a 1.0 mol % Ni loading, the reaction of 4-methoxy-benzonitrile with 1.5 equiv of benzylamine under 1 bar of H₂ in toluene or *p*-xylene at 90 °C gave *N*-benzyl-1-(4-methoxyphenyl)methanamine as the sole product in 80% isolated yield (**8a**, Scheme 2). An excess





^{*a*}Reaction conditions: DUT-5-NiH (1.0 mol % Ni), 0.243 mmol R– CN, 0.365 mmol R'–NH₂, 1 bar H₂, 3.0 mL of *p*-xylene, 20 h. ^{*b*}Isolated yield in the parentheses.

amount (1.5 equiv) of benzylamine was found to improve the selectivity of product 8. Several unsymmetric secondary amines (8b-d, Scheme 2) were afforded by the reaction of various substituted aryl nitriles and benzylamine in good yields. The formation of any symmetric secondary amines or substituted benzylamines was not observed in all of the reactions as determined by GC-MS. The reaction of 4-methoxy-benzylamine with benzonitrile or substituted benzonitriles bearing bromo, fluoro, acetyl, or acetamide functional groups also produced the corresponding unsymmetric secondary amines in 80-94% isolated yields with excellent chemoselectivity (8e-i, Scheme 2). At a 1.0 mol % Ni loading, indole- and pyridylsubstituted nitriles or aliphatic nitrile such as benzyl cyanide selectively yielded unsymmetric secondary amine products 8k-o by the reaction with benzylamine or 4-methoxybenzylamine. Other amines such as furfuryl amine and anilines also react smoothly (8p-s, Scheme 2) under identical reaction conditions. However, a significant decrease in the reaction rate with anilines was observed presumably due to their lower nucleophilicity.

Hydrogenation of Nitro and Cyano Groups of Pharmaceutical Compounds. The conditions for the hydrogenation of nitroarenes and arene nitriles were appropriate for the functionalization of the active pharmaceutical ingredients (APIs) in some of the prescribed drugs, indicating that the scope of the reaction is suitable for applications in medicinal chemistry (Scheme 3). Our protocol

Scheme 3. DUT-5-NiH-Catalyzed Hydrogenation of Nitro and Cyano Groups of Pharmaceutical Compounds a



^{*a*}Reaction conditions: DUT-5-NiH (1.0 mol % Ni), 0.243 mmol substrate, 1 bar H_2 , 3.0 mL of *p*-xylene, 130 °C, 24 h; isolated yields are shown. ^{*b*}Substrate: 4-nitrophenol, 1.2 equiv of Ac₂O with respect to substrate was added in situ.

enables us to produce paracetamol by one-pot hydrogenative amidation of 4-nitrophenol with Ac_2O . At a 1 mol % Ni loading, the hydrogenation of *p*-nitrophenol in presence of 1.2 equiv of Ac_2O in *p*-xylene at 130 °C produced paracetamol, which was isolated in 95% yield and excellent purity. Using the methodology of nitro reduction, marketed nitro-substituted drugs such as Ornidazole, Flutamide, and Niclosamide were hydrogenated to the respective amines (10–12, Scheme 3) with high selectivity. Citalopram (13), a cyano-substituted drug, was also hydrogenated to afford the corresponding benzylamine in 75% yield.

DUT-5-NiH-Catalyzed Hydrogenolysis of Aryl Ethers. We next tested the catalytic activity of DUT-5-NiH in hydrogenolysis of aryl ethers, commonly found in lignin linkage structures (Figure S16, SI).⁸¹ β -O-4, α -O-4, and 4-O-5 linkages are three of the most frequent types of C-O bonds present in the structure of hardwood lignin contributing to 45-62%, 3-12% and 4-9% of ether bonds, respectively.⁸² Due to the high strength and stability of its aryl ether bonds, their cleavage by base-metal catalysts generally requires harsh conditions such as a high catalyst loading,^{73,83} a high pressure of H₂,^{74,75} and a high temperature (120–180 °C).^{50,74,75,83} Despite significant improvement with recently developed Ni nanoparticles,^{76,84} the requirement of excess base and the presence of multiple sites limit their practical applicability as well as the scope of mechanistic investigations. Therefore, the development of single-site earth-abundant metal catalysts for selective depolymerization of lignin into small molecules under mild conditions and for understanding the C-O cleavage mechanism is highly desirable. Hydrogenolysis of diphenyl ether as a model compound for the 4-O-5 linkage of lignin was first studied to optimize the reaction conditions. At a 1 mol % Ni loading, DUT-5-NiH completely cleaved diphenyl ether to DUT-5-NiH

Table 3. I	DUT-5-NiH-Cat	alyzed Hyd	irogenolysis	of Aryl Ethers"
------------	---------------	------------	--------------	-----------------

$R + H_{2} \xrightarrow[(1 \text{ bar})]{\text{DUT-5-NiH}} R + H_{2} \xrightarrow[(1 \text{ or mol% Ni})]{\text{heptane}} R + H_{2} \xrightarrow[(1 or mol%$										
Entry	Aryl ether	Product	T (°C)	Time (h)	Conversion (%)	%GC (14	Yield) ^b 15	TOF (h ⁻¹)		
1		+ OH	140	12	100	97	97	8.3		
2 ^b	MeO OMe	MeO HO OMe	160	24	85	83	80	1.8		
3	F ₃ C	CF ₃ OH	140	12	100	99	99	8.3		
4		С + ОН	140	18	100	99	99	5.6		
5		+ OH	70	36	100	99	99	2.8		
6	C OH	+ HO	70	36	100	99	99	2.8		
7		+ ОН	140	12	100	99	95	8.3		
8	° C		100	24	100	97		4.2		
9	Ph	+OH	140	12	90	87	87	7.5		

^aReaction conditions: DUT-5-NiH (1.0 mol % Ni), 0.24 mmol aryl ether, 1 bar H₂, 3.0 mL of heptane. ^b2 mol % Ni was used.

give benzene and cyclohexanol as the sole products in 12 h under 1 bar of H_2 in heptane at 140 °C (Table 3, entry 1). Importantly, no base was required in this hydrogenolysis reaction. Although phenol was nearly completely hydrogenated to afford cyclohexanol, no competing hydrogenation of benzene was observed under these conditions. However, the formation of cyclohexyl phenyl ether was observed at a higher pressure of hydrogen due to the partial hydrogenation of diphenyl ether. Unsymmetrical diaryl ethers were dissociated at the C–O bond adjacent to the more electron-poor aryl ring (Table 3, entry 3).

DUT-5-NiH was also active under comparable conditions for the selective hydrogenolysis of a number of α -O-4 and β -O-4 lignin model compounds. For example, hydrogenolysis of α -O-4 lignin model compounds such as benzyl phenyl ether and 4-(benzyloxy)phenol with 1 mol % Ni catalyst under 1 bar of H₂ in heptane led to the formation of toluene and corresponding cyclohexanol in nearly quantitative yields (Table 3, entries 4 and 6) via cleavage of alkyl C–O bonds. Importantly, DUT-5-NiH-catalyzed hydrogenolysis of benzyl phenyl ether could be done at a temperature as low as 70 °C presumably due to the presence of weaker alkyl C-O bonds in the α -O-4 linkage (Table 3, entry 5). Moreover, the hydrogenolysis of similar alkyl ethers such as dibenzyl ether and benzyl acetate also progressed well under similar reaction

conditions (Table 3, entries 7 and 8). The hydrogenolysis of 2phenylethyl phenyl ether (β -O-4) proceeded to full conversion to form cyclohexanol and ethylbenzene in 87 and 87% yields, respectively (Table 3, entry 9). The TOFs of the model compounds agree with the trend of bond-dissociation energies: 4-O-5 (314 kJ/mol) > β -O-4 (289 kJ/mol) > α -O-4 (218 kJ/ mol).7

Investigation into the Mechanism of DUT-5-NiH-Catalyzed Hydrogenolysis of Aryl Ethers. We first investigated the reaction pathway of DUT-5-NiH-catalyzed hydrogenolysis of diphenyl ether by kinetics using the method of initial rates. The average initial substrate conversion rates increase linearly with initial concentrations of diphenyl ether and nickel, indicating first-order rate dependence on both substrate and catalyst concentrations (Figure 6a). However, the initial rate of the hydrogenolysis of diphenyl ether showed zeroth-order dependence on hydrogen concentrations (Figure 6b). This empirical rate law supports the involvement of diphenyl ether and nickel in the turnover-limiting step. The oxidative addition of the aryl C–O bond of diphenyl ether to the Ni(II) center is unlikely to occur in the turnover-limiting step because the oxo-ligated Ni⁺² center is electron-poor. Instead, DUT-5-NiH-catalyzed hydrogenolysis of diphenyl ether likely proceeds via σ -bond metathesis pathways (Figure 6c). On the basis of our experimental observations, we propose

Research Article



Figure 6. (a) Kinetic plots of initial rates -(d[substrate]/dt) for hydrogenolysis of diphenyl ether versus initial concentrations of nickel and diphenyl ether (<10% conversion), showing first-order dependence on both components. (b) Plot of initial rate -(d[substrate]/dt) versus $(P_{H2})_{initial}$ showing independence of initial rates on hydrogen pressure. (c) Proposed mechanism for the hydrogenolysis of aryl ether catalyzed by DUT-5-NiH. (d) DFT-computed minimum-energy reaction path diagram for catalytic hydrogenolysis of diphenyl ether. See the Supporting Information for computational details.

that the reaction of DUT-5-NiH with diphenyl ether produces the DUT-5-Ni(OPh) intermediate and benzene via a fourcentered turnover-limiting step, involving $[2\sigma + 2\sigma]$ cycloaddition of a "Ni–H" bond with a "C–O" bond of diphenyl ether. Then, the σ -bond metathesis between Ni–OPh and H₂ furnishes phenol and regenerates DUT-5-NiH. The DFT calculation revealed that $[2\sigma + 2\sigma]$ cycloaddition in TS-A requires an activation free energy of 24.8 kcal/mol and the transformation of DUT-5-NiH to DUT-5-Ni(OPh) is exergonic by 21.8 kcal/mol. The weak coordination of H₂ gives INT-B, which undergoes σ -bond metathesis to give DUT-5-NiH and phenol via TS-B, requiring an activation free energy of 19.0 kcal/mol (Figure 6d). The proposed catalytic

cycle is thus in good agreement with our theoretical and kinetic studies (Figure 6c).

Role of MOF in the Kinetics and Chemoselectivity. To understand the reason for the excellent chemoselectivity and high activity of DUT-5-NiH under atmospheric hydrogen pressure, we performed comparative studies of the formation of unsymmetric secondary amine 8d from 4-acetylbenzonitrile and benzylamine catalyzed by DUT-5-NiH, MIL-53-(Al)-NiH, and Ni nanoparticles under identical reaction conditions (Figures 3c and S15, SI). DUT-5-NiH produced 8d with 100% chemoselectivity, in contrast, MIL-53(Al)-NiH and Ninanoparticles gave a mixture of 8d and primary amine. We thus infer that the well-defined large pores of DUT-5-NiH facilitate the intermolecular reactions in the confined space and thus enhance chemoselectivity. The pore confinement and steric protection around nickel also likely to increase the activation energy of the binding of bulky substrates compared to that of smaller dihydrogen, resulting in zeroth-order dependence on the concentration of H₂. Our computational studies showed that the labile Ni-O(carboxylate) bonds not only stabilize the active nickel-hydride site but also dissociate in a sterically congested transition state for creating vacant coordination sites at the nickel center. In addition, DUT-5-NiH features electronrich hydride and bridged μ_3 -oxo sites with NBO charge of -0.381 and -1.396, respectively, thus affording a reactive Ni-H species for substrate activation. We thus believe that the high stability, chemoselectivity, and reactivity of the nickel catalyst originates due to high electrophilicity of the nickel center, site isolation and uniform distribution of the active sites within the MOF, the presence of single-site catalytic species, and the large size and confinement effect of the pores within DUT-5 (Figure 7).



Figure 7. Origin of the robustness, high reactivity, and chemo-selectivity of DUT-5-NiH.

CONCLUSIONS

In conclusion, we have developed an aluminum MOF-nodeligated nickel(II)-hydride, which is a versatile chemoselective catalyst for hydrogenation of nitro and nitrile compounds and hydrogenolysis of aryl ethers under mild conditions. This heterogeneous single-site nickel catalyst was easily prepared by metalation of SBUs of DUT-5 with NiBr₂ followed by the activation with NaEt₃BH. The mechanisms of catalytic hydrogenation of aryl nitriles and hydrogenolysis of aryl ethers were investigated in detail by kinetic and computational studies. Highly selective hydrogenation of numerous structurally diverse nitroarenes and nitriles were achieved in high yields with excellent selectivity under atmospheric hydrogen pressure. The zeroth-order dependence of the reaction rate on the pressure of H₂ allowed us to progress all of the reactions under ambient hydrogen pressure. This work has demonstrated that DUT-5 node-ligated single-site base-metal hydrides are

promising catalysts in hydrogenation and hydrogenolysis reactions for sustainable synthesis of biofuels and chemical feedstocks owing to their low cost, excellent stability and reactivity, and usage of cheap and atom-economic reductant hydrogen.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.0c04379.

Synthesis and characterization of DUT-5 and metalated MOF, procedures for catalytic reactions, details for kinetics, NMR and GC analyses, X-ray absorption spectroscopic analysis, and DFT calculations (PDF)

AUTHOR INFORMATION

Corresponding Author

Kuntal Manna – Department of Chemistry, Indian Institute of Technology Delhi, New Delhi 110016, India; orcid.org/ 0000-0002-2924-0353; Email: kmanna@ chemistry.iitd.ac.in

Authors

- Neha Antil Department of Chemistry, Indian Institute of Technology Delhi, New Delhi 110016, India
- Ajay Kumar Department of Chemistry, Indian Institute of Technology Delhi, New Delhi 110016, India
- Naved Akhtar Department of Chemistry, Indian Institute of Technology Delhi, New Delhi 110016, India
- Rajashree Newar Department of Chemistry, Indian Institute of Technology Delhi, New Delhi 110016, India
- Wahida Begum Department of Chemistry, Indian Institute of Technology Delhi, New Delhi 110016, India
- Ashutosh Dwivedi Beamline Development and Application Section, Bhabha Atomic Research Centre, Mumbai 400085, India

Complete contact information is available at: https://pubs.acs.org/10.1021/acscatal.0c04379

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research is supported by the Science and Engineering Research Board (SERB), India (project ECR/2017/001931). R.N. and N.A. acknowledge CSIR, and W.B. acknowledges UGC for financial support. Prof. B. Jayaram is gratefully thanked for providing access to his supercomputing facility. Prof. Sreedevi Upadhyayula is thanked for BET analysis. We acknowledge Raja Ramanna Centre for Advanced Technology, Indore (RRCAT) for providing Indus-2 SRS facility for XAFS measurements. The authors thank Dr. S.N. Jha and Babita for their support during XAFS measurements. Authors acknowledge the Central Research Facility, IIT Delhi, for instrument facilities.

REFERENCES

(1) Nakazawa, H.; Itazaki, M. Fe–H Complexes in Catalysis. In *Iron Catalysis: Fundamentals and Applications*; Plietker, B., Ed.; Springer: Berlin, Heidelberg, 2011; pp 27–81.

(2) Wiegand, A.-K.; Rit, A.; Okuda, J. Molecular zinc hydrides. Coord. Chem. Rev. 2016, 314, 71-82.

(3) Kaesz, H. D.; Saillant, R. B. Hydride complexes of the transition metals. *Chem. Rev.* **1972**, *72*, 231–281.

(4) Straub, B. F. Organotransition Metal Chemistry. From Bonding to Catalysis. Edited by JohnF. Hartwig. *Angew. Chem., Int. Ed.* **2010**, 49, 7622.

(5) Zou, J.; Sun, H.; Meng, F.; Ji, G.; Ding, W. Preparation and Hydrogen Storage Properties of Mg-Rich Mg-Ni Ultrafine Particles. *J. Nanomater.* **2012**, 2012, No. 592147.

(6) Frey, M. Hydrogenases: Hydrogen-Activating Enzymes. *ChemBioChem* **2002**, *3*, 153–160.

(7) Lubitz, W.; Ogata, H.; Rüdiger, O.; Reijerse, E. Hydrogenases. *Chem. Rev.* **2014**, *114*, 4081–4148.

(8) Harmer, J.; Finazzo, C.; Piskorski, R.; Ebner, S.; Duin, E. C.; Goenrich, M.; Thauer, R. K.; Reiher, M.; Schweiger, A.; Hinderberger, D.; Jaun, B. A Nickel Hydride Complex in the Active Site of Methyl-Coenzyme M Reductase: Implications for the Catalytic Cycle. J. Am. Chem. Soc. 2008, 130, 10907–10920.

(9) Kuhn, P.; Sémeril, D.; Matt, D.; Chetcuti, M. J.; Lutz, P. Structure-reactivity relationships in SHOP-type complexes: tunable catalysts for the oligomerisation and polymerisation of ethylene. *Dalton Trans.* **2007**, 515–528.

(10) Eberhardt, N. A.; Guan, H. Nickel Hydride Complexes. *Chem. Rev.* **2016**, *116*, 8373–8426.

(11) Vasudevan, K. V.; Scott, B. L.; Hanson, S. K. Alkene Hydrogenation Catalyzed by Nickel Hydride Complexes of an Aliphatic PNP Pincer Ligand. *Eur. J. Inorg. Chem.* **2012**, 2012, 4898–4906.

(12) Lin, T.-P.; Peters, J. C. Boryl–Metal Bonds Facilitate Cobalt/ Nickel-Catalyzed Olefin Hydrogenation. J. Am. Chem. Soc. 2014, 136, 13672–13683.

(13) Shevlin, M.; Friedfeld, M. R.; Sheng, H.; Pierson, N. A.; Hoyt, J. M.; Campeau, L.-C.; Chirik, P. J. Nickel-Catalyzed Asymmetric Alkene Hydrogenation of α , β -Unsaturated Esters: High-Throughput Experimentation-Enabled Reaction Discovery, Optimization, and Mechanistic Elucidation. *J. Am. Chem. Soc.* **2016**, *138*, 3562–3569.

(14) Tran, B. L.; Pink, M.; Mindiola, D. J. Catalytic Hydrosilylation of the Carbonyl Functionality via a Transient Nickel Hydride Complex. *Organometallics* **2009**, *28*, 2234–2243.

(15) Chakraborty, S.; Krause, J. A.; Guan, H. Hydrosilylation of Aldehydes and Ketones Catalyzed by Nickel PCP-Pincer Hydride Complexes. *Organometallics* **2009**, *28*, 582–586.

(16) Neufeldt, S. R.; Sanford, M. S. Combining Transition Metal Catalysis with Radical Chemistry: Dramatic Acceleration of Palladium-Catalyzed C-H Arylation with Diaryliodonium Salts. *Adv. Synth. Catal.* **2012**, 354, 3517–3522.

(17) Tolman, C. A. Chemistry of tetrakis(triethyl phosphite) nickel hydride, $HNi[P(OEt)_3]^{4+}$. II. Reaction with 1,3-butadiene. Catalytic formation of hexadienes. J. Am. Chem. Soc. **1970**, 92, 6777–6784.

(18) Keim, W.; Kowaldt, F. H.; Goddard, R.; Krüger, C. Novel Coordination of (Benzoylmethylene)triphenylphosphorane in a Nickel Oligomerization Catalyst. *Angew. Chem., Int. Ed.* **1978**, *17*, 466–467.

(19) Escobar, M. A.; Trofymchuk, O. S.; Rodriguez, B. E.; Lopez-Lira, C.; Tapia, R.; Daniliuc, C.; Berke, H.; Nachtigall, F. M.; Santos, L. S.; Rojas, R. S. Lewis Acid Enhanced Ethene Dimerization and Alkene Isomerization—ESI-MS Identification of the Catalytically Active Pyridyldimethoxybenzimidazole Nickel(II) Hydride Species. *ACS Catal.* **2015**, *5*, 7338–7342.

(20) Chakraborty, S.; Zhang, J.; Krause, J. A.; Guan, H. An Efficient Nickel Catalyst for the Reduction of Carbon Dioxide with a Borane. *J. Am. Chem. Soc.* **2010**, *132*, 8872–8873.

(21) Enthaler, S.; Brück, A.; Kammer, A.; Junge, H.; Irran, E.; Gülak, S. Exploring the Reactivity of Nickel Pincer Complexes in the Decomposition of Formic Acid to O_2/H_2 and the Hydrogenation of NaHCO₃ to HCOONa. *ChemCatChem* **2015**, *7*, 65–69.

(22) Ríos, P.; Curado, N.; López-Serrano, J.; Rodríguez, A. Selective reduction of carbon dioxide to bis(silyl)acetal catalyzed by a PBP-supported nickel complex. *Chem. Commun.* **2016**, *52*, 2114–2117.

(23) Wang, Z. J.; Ghasimi, S.; Landfester, K.; Zhang, K. A. I. Highly porous conjugated polymers for selective oxidation of organic sulfides under visible light. *Chem. Commun.* **2014**, *50*, 8177–8180.

(24) Lee, S.-P.; Chen, Y.-W. Nitrobenzene hydrogenation on Ni–P, Ni–B and Ni–P–B ultrafine materials. *J. Mol. Catal. A: Chem.* **2000**, 152, 213–223.

(25) Rani, P.; Singh, K. N.; Kaur, A. Synthesis, characterization, and application of easily accessible resin-encapsulated nickel nanocatalyst for efficient reduction of functionalized nitroarenes under mild conditions. J. Chem. Sci. 2018, 130, No. 160.

(26) Iwamoto, M.; Kosugi, Y. Highly Selective Conversion of Ethene to Propene and Butenes on Nickel Ion-Loaded Mesoporous Silica Catalysts. J. Phys. Chem. C 2007, 111, 13–15.

(27) Li, L.; Abou-Hamad, E.; Anjum, D. H.; Zhou, L.; Laveille, P. V.; Emsley, L.; Basset, J.-M. Well-defined mono(η^3 -allyl)nickel complex \equiv MONi(η^3 -C₃H₅) (M = Si or Al) grafted onto silica or alumina: a molecularly dispersed nickel precursor for syntheses of supported small size nickel nanoparticles. *Chem. Commun.* **2014**, *50*, 7716–7719.

(28) Copéret, C.; Comas-Vives, A.; Conley, M. P.; Estes, D. P.; Fedorov, A.; Mougel, V.; Nagae, H.; Núñez-Zarur, F.; Zhizhko, P. A. Surface Organometallic and Coordination Chemistry toward Single-Site Heterogeneous Catalysts: Strategies, Methods, Structures, and Activities. *Chem. Rev.* **2016**, *116*, 323–421.

(29) Digne, M.; Sautet, P.; Raybaud, P.; Euzen, P.; Toulhoat, H. Hydroxyl Groups on γ -Alumina Surfaces: A DFT Study. *J. Catal.* **2002**, 211, 1–5.

(30) Trueba, M.; Trasatti, S. P. γ-Alumina as a Support for Catalysts: A Review of Fundamental Aspects. *Eur. J. Inorg. Chem.* **2005**, 2005, 3393–3403.

(31) Tsyganenko, A. A.; Mardilovich, P. P. Structure of alumina surfaces. J. Chem. Soc., Faraday Trans. 1996, 92, 4843-4852.

(32) Shirai, T.; Watanabe, H.; Fuji, M.; Takahashi, M. Structural properties and surface characteristics on aluminum oxide powders. *Ceram. Res. Lab.* **2009**, *9*, 23–31.

(33) Yang, D.; Odoh, S. O.; Wang, T. C.; Farha, O. K.; Hupp, J. T.; Cramer, C. J.; Gagliardi, L.; Gates, B. C. Metal–Organic Framework Nodes as Nearly Ideal Supports for Molecular Catalysts: NU-1000and UiO-66-Supported Iridium Complexes. J. Am. Chem. Soc. 2015, 137, 7391–7396.

(34) Manna, K.; Ji, P.; Greene, F. X.; Lin, W. Metal–Organic Framework Nodes Support Single-Site Magnesium–Alkyl Catalysts for Hydroboration and Hydroamination Reactions. *J. Am. Chem. Soc.* **2016**, *138*, 7488–7491.

(35) Manna, K.; Ji, P.; Lin, Z.; Greene, F. X.; Urban, A.; Thacker, N. C.; Lin, W. Chemoselective single-site Earth-abundant metal catalysts at metal–organic framework nodes. *Nat. Commun.* **2016**, *7*, No. 12610.

(36) Ji, P.; Manna, K.; Lin, Z.; Feng, X.; Urban, A.; Song, Y.; Lin, W. Single-Site Cobalt Catalysts at New $Zr_{12}(\mu_3-O)_8(\mu_3-OH)_8(\mu_2-OH)_6$ Metal–Organic Framework Nodes for Highly Active Hydrogenation of Nitroarenes, Nitriles, and Isocyanides. *J. Am. Chem. Soc.* **2017**, *139*, 7004–7011.

(37) Ji, P.; Song, Y.; Drake, T.; Veroneau, S. S.; Lin, Z.; Pan, X.; Lin, W. Titanium(III)-Oxo Clusters in a Metal–Organic Framework Support Single-Site Co(II)-Hydride Catalysts for Arene Hydrogenation. J. Am. Chem. Soc. **2018**, 140, 433–440.

(38) Liu, J.; Ye, J.; Li, Z.; Otake, K.-i.; Liao, Y.; Peters, A. W.; Noh, H.; Truhlar, D. G.; Gagliardi, L.; Cramer, C. J.; Farha, O. K.; Hupp, J. T. Beyond the Active Site: Tuning the Activity and Selectivity of a Metal–Organic Framework-Supported Ni Catalyst for Ethylene Dimerization. J. Am. Chem. Soc. **2018**, *140*, 11174–11178.

(39) Park, H. D.; Dincă, M.; Román-Leshkov, Y. Continuous-Flow Production of Succinic Anhydrides via Catalytic β -Lactone Carbonylation by Co(CO)₄⊂Cr-MIL-101. *J. Am. Chem. Soc.* **2018**, *140*, 10669–10672.

(40) Zheng, J.; Ye, J.; Ortuño, M. A.; Fulton, J. L.; Gutiérrez, O. Y.; Camaioni, D. M.; Motkuri, R. K.; Li, Z.; Webber, T. E.; Mehdi, B. L.; Browning, N. D.; Penn, R. L.; Farha, O. K.; Hupp, J. T.; Truhlar, D. G.; Cramer, C. J.; Lercher, J. A. Selective Methane Oxidation to Methanol on Cu-Oxo Dimers Stabilized by Zirconia Nodes of an NU-1000 Metal–Organic Framework. *J. Am. Chem. Soc.* **2019**, *141*, 9292– 9304.

(41) Lee, J.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. Metal–organic framework materials as catalysts. *Chem. Soc. Rev.* **2009**, *38*, 1450–1459.

(42) Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. The Chemistry and Applications of Metal-Organic Frameworks. *Science* **2013**, *341*, No. 1230444.

(43) Xiao, D. J.; Bloch, E. D.; Mason, J. A.; Queen, W. L.; Hudson, M. R.; Planas, N.; Borycz, J.; Dzubak, A. L.; Verma, P.; Lee, K.; Bonino, F.; Crocellà, V.; Yano, J.; Bordiga, S.; Truhlar, D. G.; Gagliardi, L.; Brown, C. M.; Long, J. R. Oxidation of ethane to ethanol by N_2O in a metal–organic framework with coordinatively unsaturated iron(II) sites. *Nat. Chem.* **2014**, *6*, 590–595.

(44) Zhao, M.; Ou, S.; Wu, C.-D. Porous Metal–Organic Frameworks for Heterogeneous Biomimetic Catalysis. *Acc. Chem. Res.* **2014**, *47*, 1199–1207.

(45) Zhang, T.; Manna, K.; Lin, W. Metal–Organic Frameworks Stabilize Solution-Inaccessible Cobalt Catalysts for Highly Efficient Broad-Scope Organic Transformations. J. Am. Chem. Soc. **2016**, 138, 3241–3249.

(46) Bai, Y.; Dou, Y.; Xie, L.-H.; Rutledge, W.; Li, J.-R.; Zhou, H.-C. Zr-based metal–organic frameworks: design, synthesis, structure, and applications. *Chem. Soc. Rev.* **2016**, *45*, 2327–2367.

(47) Metzger, E. D.; Comito, R. J.; Hendon, C. H.; Dincă, M. Mechanism of Single-Site Molecule-Like Catalytic Ethylene Dimerization in Ni-MFU-4l. J. Am. Chem. Soc. **2017**, 139, 757–762.

(48) Zhang, Y.; Li, J.; Yang, X.; Zhang, P.; Pang, J.; Li, B.; Zhou, H.-C. A mesoporous NNN-pincer-based metal-organic framework scaffold for the preparation of noble-metal-free catalysts. *Chem. Commun.* **2019**, *55*, 2023–2026.

(49) Feng, X.; Ji, P.; Li, Z.; Drake, T.; Oliveres, P.; Chen, E. Y.; Song, Y.; Wang, C.; Lin, W. Aluminum Hydroxide Secondary Building Units in a Metal–Organic Framework Support Earth-Abundant Metal Catalysts for Broad-Scope Organic Transformations. *ACS Catal.* **2019**, *9*, 3327–3337.

(50) Song, Y.; Li, Z.; Ji, P.; Kaufmann, M.; Feng, X.; Chen, J. S.; Wang, C.; Lin, W. Metal–Organic Framework Nodes Support Single-Site Nickel(II) Hydride Catalysts for the Hydrogenolysis of Aryl Ethers. *ACS Catal.* **2019**, *9*, 1578–1583.

(51) Cohen, S. M. Postsynthetic Methods for the Functionalization of Metal–Organic Frameworks. *Chem. Rev.* **2012**, *112*, 970–1000.

(52) Genna, D. T.; Wong-Foy, A. G.; Matzger, A. J.; Sanford, M. S. Heterogenization of Homogeneous Catalysts in Metal–Organic Frameworks via Cation Exchange. J. Am. Chem. Soc. 2013, 135, 10586–10589.

(53) Gascon, J.; Corma, A.; Kapteijn, F.; Llabrés i Xamena, F. X. Metal Organic Framework Catalysis: Quo vadis? *ACS Catal.* **2014**, *4*, 361–378.

(54) Rimoldi, M.; Howarth, A. J.; DeStefano, M. R.; Lin, L.; Goswami, S.; Li, P.; Hupp, J. T.; Farha, O. K. Catalytic Zirconium/ Hafnium-Based Metal–Organic Frameworks. *ACS Catal.* **2017**, *7*, 997–1014.

(55) Newar, R.; Begum, W.; Antil, N.; Shukla, S.; Kumar, A.; Akhtar, N.; Balendra; Manna, K. Single-Site Cobalt-Catalyst Ligated with Pyridylimine-Functionalized Metal–Organic Frameworks for Arene and Benzylic Borylation. *Inorg. Chem.* **2020**, *59*, 10473–10481.

(56) Downing, R. S.; Kunkeler, P. J.; van Bekkum, H. Catalytic syntheses of aromatic amines. *Catal. Today* **1997**, *37*, 121–136.

(57) Marquez, J.; Pletcher, D. A study of the electrochemical reduction of nitrobenzene to p-aminophenol. *J. Appl. Electrochem.* **1980**, *10*, 567–573.

(58) Cyr, A.; Huot, P.; Marcoux, J.-F.; Belot, G.; Laviron, E.; Lessard, J. The electrochemical reduction of nitrobenzene and azoxybenzene in neutral and basic aqueous methanolic solutions at polycrystalline copper and nickel electrodes. *Electrochim. Acta* **1989**, *34*, 439–445.

(59) Formenti, D.; Ferretti, F.; Scharnagl, F. K.; Beller, M. Reduction of Nitro Compounds Using 3d-Non-Noble Metal Catalysts. *Chem. Rev.* **2019**, *119*, 2611–2680.

(60) Kukula, P.; Gabova, V.; Koprivova, K.; Trtik, P. Selective hydrogenation of unsaturated nitriles to unsaturated amines over amorphous CoB and NiB alloys doped with chromium. *Catal. Today* **2007**, *121*, 27–38.

(61) Jagadeesh, R. V.; Surkus, A.-E.; Junge, H.; Pohl, M.-M.; Radnik, J.; Rabeah, J.; Huan, H.; Schünemann, V.; Brückner, A.; Beller, M. Nanoscale Fe₂O₃-Based Catalysts for Selective Hydrogenation of Nitroarenes to Anilines. *Science* **2013**, *342*, 1073.

(62) Bornschein, C.; Werkmeister, S.; Wendt, B.; Jiao, H.; Alberico, E.; Baumann, W.; Junge, H.; Junge, K.; Beller, M. Mild and selective hydrogenation of aromatic and aliphatic (di)nitriles with a well-defined iron pincer complex. *Nat. Commun.* **2014**, *5*, No. 4111.

(63) Mukherjee, A.; Srimani, D.; Chakraborty, S.; Ben-David, Y.; Milstein, D. Selective Hydrogenation of Nitriles to Primary Amines Catalyzed by a Cobalt Pincer Complex. *J. Am. Chem. Soc.* **2015**, *137*, 8888–8891.

(64) Chakraborty, S.; Leitus, G.; Milstein, D. Selective hydrogenation of nitriles to primary amines catalyzed by a novel iron complex. *Chem. Commun.* **2016**, *52*, 1812–1815.

(65) Tokmic, K.; Jackson, B. J.; Salazar, A.; Woods, T. J.; Fout, A. R. Cobalt-Catalyzed and Lewis Acid-Assisted Nitrile Hydrogenation to Primary Amines: A Combined Effort. J. Am. Chem. Soc. 2017, 139, 13554–13561.

(66) Sorribes, I.; Liu, L.; Corma, A. Nanolayered Co–Mo–S Catalysts for the Chemoselective Hydrogenation of Nitroarenes. *ACS Catal.* **2017**, *7*, 2698–2708.

(67) Tang, B.; Song, W.-C.; Yang, E.-C.; Zhao, X.-J. MOF-derived Ni-based nanocomposites as robust catalysts for chemoselective hydrogenation of functionalized nitro compounds. *RSC Adv.* **2017**, *7*, 1531–1539.

(68) Li, W.; Artz, J.; Broicher, C.; Junge, K.; Hartmann, H.; Besmehn, A.; Palkovits, R.; Beller, M. Superior activity and selectivity of heterogenized cobalt catalysts for hydrogenation of nitroarenes. *Catal. Sci. Technol.* **2019**, *9*, 157–162.

(69) Cossar, P. J.; Hizartzidis, L.; Simone, M. I.; McCluskey, A.; Gordon, C. P. The expanding utility of continuous flow hydrogenation. *Org. Biomol. Chem.* **2015**, *13*, 7119–7130.

(70) Zhou, P.; Jiang, L.; Wang, F.; Deng, K.; Lv, K.; Zhang, Z. High performance of a cobalt–nitrogen complex for the reduction and reductive coupling of nitro compounds into amines and their derivatives. *Sci. Adv.* **2017**, *3*, No. e1601945.

(71) Zhou, P.; Jiang, L.; Wang, S.; Hu, X.; Wang, H.; Yuan, Z.; Zhang, Z. Synthesis of Secondary Aldimines from the Hydrogenative Cross-Coupling of Nitriles and Amines over Al₂O₃-Supported Ni Catalysts. ACS Catal **2019**, *9*, 8413–8423.

(72) Wang, J.; Tang, Q.; Jin, S.; Wang, Y.; Yuan, Z.; Chi, Q.; Zhang, Z. Mild and selective hydrogenation of nitriles into primary amines over a supported Ni catalyst. *New J. Chem.* **2020**, *44*, 549–555.

(73) Sergeev, A. G.; Hartwig, J. F. Selective, Nickel-Catalyzed Hydrogenolysis of Aryl Ethers. *Science* **2011**, *332*, 439.

(74) He, J.; Zhao, C.; Lercher, J. A. Ni-Catalyzed Cleavage of Aryl Ethers in the Aqueous Phase. J. Am. Chem. Soc. 2012, 134, 20768–20775.

(75) Molinari, V.; Giordano, C.; Antonietti, M.; Esposito, D. Titanium Nitride-Nickel Nanocomposite as Heterogeneous Catalyst for the Hydrogenolysis of Aryl Ethers. *J. Am. Chem. Soc.* 2014, *136*, 1758–1761.

(76) Gao, F.; Webb, J. D.; Hartwig, J. F. Chemo- and Regioselective Hydrogenolysis of Diaryl Ether C-O Bonds by a Robust Heterogeneous Ni/C Catalyst: Applications to the Cleavage of Complex Lignin-Related Fragments. *Angew. Chem., Int. Ed.* **2016**, *55*, 1474–1478.

(77) Jiang, L.; Guo, H.; Li, C.; Zhou, P.; Zhang, Z. Selective cleavage of lignin and lignin model compounds without external hydrogen, catalyzed by heterogeneous nickel catalysts. *Chem. Sci.* **2019**, *10*, 4458–4468.

(78) Senkovska, I.; Hoffmann, F.; Fröba, M.; Getzschmann, J.; Böhlmann, W.; Kaskel, S. New highly porous aluminium based metalorganic frameworks: Al(OH)(ndc) (ndc = 2,6-naphthalene dicarboxylate) and Al(OH)(bpdc) (bpdc = 4,4'-biphenyl dicarboxylate). *Microporous Mesoporous Mater.* **2009**, *122*, 93–98.

(79) Bloch, E. D.; Britt, D.; Lee, C.; Doonan, C. J.; Uribe-Romo, F. J.; Furukawa, H.; Long, J. R.; Yaghi, O. M. Metal Insertion in a Microporous Metal–Organic Framework Lined with 2,2'-Bipyridine. *J. Am. Chem. Soc.* **2010**, *132*, 14382–14384.

(80) Ji, P.; Manna, K.; Lin, Z.; Urban, A.; Greene, F. X.; Lan, G.; Lin, W. Single-Site Cobalt Catalysts at New $Zr_8(\mu_2-O)_8(\mu_2-OH)_4$ Metal-Organic Framework Nodes for Highly Active Hydrogenation of Alkenes, Imines, Carbonyls, and Heterocycles. *J. Am. Chem. Soc.* **2016**, 138, 12234–12242.

(81) Stöcker, M. Biofuels and Biomass-To-Liquid Fuels in the Biorefinery: Catalytic Conversion of Lignocellulosic Biomass using Porous Materials. *Angew. Chem., Int. Ed.* **2008**, *47*, 9200–9211.

(82) Zakzeski, J.; Bruijnincx, P. C. A.; Jongerius, A. L.; Weckhuysen, B. M. The Catalytic Valorization of Lignin for the Production of Renewable Chemicals. *Chem. Rev.* **2010**, *110*, 3552–3599.

(83) Ren, Y.; Yan, M.; Wang, J.; Zhang, Z. C.; Yao, K. Selective Reductive Cleavage of Inert Aryl C–O Bonds by an Iron Catalyst. *Angew. Chem., Int. Ed.* **2013**, *52*, 12674–12678.

(84) Sergeev, A. G.; Webb, J. D.; Hartwig, J. F. A Heterogeneous Nickel Catalyst for the Hydrogenolysis of Aryl Ethers without Arene Hydrogenation. J. Am. Chem. Soc. **2012**, 134, 20226–20229.