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Metal-Organic Framework Nodes Support Single-Site Nickel(II)-Hydride Catalysts for the Hydrogenolysis of Aryl Ethers

Yang Song,^{†,1} Zhe Li,^{†1,2} Pengfei Ji,¹ Michael Kaufmann,¹ Xuanyu Feng,¹ Justin S. Chen,¹ Cheng Wang,² and Wenbin Lin^{*,1}

¹Department of Chemistry, The University of Chicago, 929 E 57th St, Chicago, IL 60637, USA

²College of Chemistry and Chemical Engineering, iCHEM, State Key Laboratory of Physical Chemistry of Solid Surface Xiamen University, Xiamen 361005, China

ABSTRACT: Herein we report that the Ti₈-BDC (MIL-125) metal-organic framework (MOF) supports single-site solid Ni^{II}hydride catalyst for the hydrogenolysis of aryl ethers containing α -O-4, β -O-4, and 4-O-5 linkages to exclusively afford hydrocarbons under mild condition without the addition of a base. The catalytic activity of Ti₈-BDC-NiH is highly dependent on the reduction of Ti₈(μ_2 -O)₈(μ_2 -OH)₄ nodes. DFT calculations revealed two key steps of σ -bond metathesis in the catalytic cycle of Ti₈-BDC-NiH catalyzed hydrogenolysis. This work highlights the potential of MOF supported single-site catalysts in aryl-ether bond scission and other processes for the efficient production of biofuels and chemical feedstocks.

KEYWORDS: metal-organic frameworks, hydrogenolysis, single-site catalysts, nickel-hydride catalysts, reduction of titanium, C-O cleavage

Lignin, comprising 15-30 wt % lignocellulosic biomass and storing 40% of its energy,¹ has the potential to supplement or replace non-renewable fossil carbon as a source of aromatic compounds.² However, selectively depolymerizing lignin into small molecules is still a great challenge due to the high strength of its aryl ether bonds.³ Hydrogenolysis has been examined as one route to depolymerize lignin,⁴ but most lignin hydrogenolysis reactions require nonsustainable catalysts based on Pd, Ru, Rh and Pt and harsh reaction conditions.⁵ It would be highly desirable to replace precious metal catalysts with Earthabundant Ni-based catalysts in these hydrogenolysis reactions. Hartwig and coworkers recently reported the reductive cleavage of aryl ethers by homogenous Ni catalysts under mild conditions.⁶ Heterogeneous catalysts with Ni nanoparticles stabilized on various supports have also been examined for reductive cleavage of aryl ethers.⁷ Whereas incomplete utilization of all Ni centers in nanoparticles diminishes overall catalytic efficiency, the non-uniform distribution of catalytic sites on the solid supports complicates the delineation of active catalysts and reaction mechanisms. Thus, it is highly desirable to design single-site solid catalysts to improve the catalytic efficiency of lignin depolymerization and to understand C-O cleavage mechanisms.

Metal-organic frameworks (MOFs) have recently attracted great attention as single-site solid catalysts.⁸ Earlier MOF catalysts were mostly prepared via organic linker functionalization⁹ or through entrapment of catalytically active nanoparticles or metal clusters in channels.¹⁰ Inorganic nodes of MOFs have recently been functionalized to provide structurally unique single-site solid catalysts that do not have homogeneous counterparts.¹¹ We previously showed that the Tioxo/hydroxo node of Ti₈-BDC (BDC is 1,4benzenecarboxylate) supports a novel Co^{II}-H catalyst for highly effective hydrogenation of arenes and heteroarenes.^{11c} We report here the use of the Tioxo/hydroxo node of Ti₈-BDC to support the Ni^{II}-H catalyst for highly effective and selective hydrogenolysis of aryl ethers commonly found in lignin (Scheme 1). We further demonstrate the tuning of hydrogenolysis activity by reducing the Ti₈ node of Ti₈-BDC.

Scheme 1. Ti_8 node-supported Ni^{II}-H catalyzes hydrogenolysis of lignin model compounds. Titanium, nickel, oxygen, carbon and hydrogen atoms are shown in blue, green, red, gray and white, respectively.



The Ti₈-BDC MOF was prepared solvothermally by heating a mixture of Ti(OⁱPr)₄, H₂BDC, dimethylformamide (DMF), and methanol based on the literature procedure.¹² The formula was revealed as Ti₈O₈(OH)₄(BDC)₆. The μ_2 -OH groups in Ti₈-BDC were first treated with LiCH₂SiMe₃ to form the Ti₈O₈(OLi)₄(BDC)₆ intermediate, followed by the addition of 1 equiv. of NiBr₂ to afford Ti₈-BDC-NiBr as a light-yellow solid (Figure 1a). Inductively coupled plasma-mass spectroscopy (ICP-MS) analysis indicated that the Ni

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loading in Ti_8 -BDC-NiBr was 0.37 Ni per Ti_8 cluster. Ti_8 -BDC-NiBr maintained the crystallinity of pristine Ti_8 -BDC as shown by powder X-ray diffraction (PXRD) patterns (Figure 1d) and kept the plate-like morphology of Ti_8 -BDC as shown by transmission electron microscopy (TEM) imaging (Figure S2, SI). Nitrogen sorption isotherms of Ti_8 -BDC-NiBr showed a BET surface area of 1280 m²/g, indicating a highly porous structure (Figure 1c). Density functional theory (DFT) calculation was used to optimize the Ni local structure of Ti_8 -BDC-NiBr (Figure S9, SI).¹³ Structure optimization showed an octahedral Ni ion located in the Ti_8 octagonal plane. Fitting of Ni extended X-ray fine structure (EXAFS) result further confirmed the calculated Ni coordination structure in Ti_8 -BDC-NiBr (Figure 1e).



Figure 1. (a) Structure of Ti_8 -BDC and its metalation with $NiBr_2$ to form Ti_8 -BDC-NiBr. (b) TEM of Ti_8 -BDC-NiH. (c) Nitrogen sorption isotherms (77K) for Ti_8 -BDC-NiBr. (d) PXRD patterns of Ni metalated Ti_8 -BDC in comparison to the simulated PXRD pattern of Ti-BDC. (e) EXAFS spectra and fitting results for Ni K-edge adsorption of Ti_8 -BDC-NiBr.

Treatment of Ti_8 -BDC-NiBr with NaBEt₃H led to a drastic color change from light yellow to black with vigorous H₂ bubbling, suggesting electron transfer from the hydride to the Ti_8 -Ni system through reductive elimination of H₂. The similar plate-like morphology was maintained in Ti_8 -BDC-NiH (Figure 1b). PXRD studies indicated that Ti_8 -BDC-NiH maintained the same structure as Ti_8 .BDC (Figure 1d). In order to determine the oxidation states of both Ni and Ti centers, electron paramagnetic spectroscopy (EPR) and Xray absorption near-edge spectroscopy (XANES) were used to study Ti_8 -BDC-NiH. The EPR spectra of Ti_8 -BDC-NiH in toluene displayed one set of intense isotropic signal with a g-value of 1.93 (Figure 2a), which is consistent with the EPR signals of reported Ti^{III} species in the literature.¹⁴ This assignment is supported by the disappearance of the isotropic EPR signal when Ti₈-BDC-NiH was oxidized by ferrocenium hexafluorophosphate (FcPF₆) to afford Ti^{IV}₈-BDC-NiH (see below). The lack of any other signals in the EPR spectrum is consistent with the EPR silent nature of Ni^{II} species.¹⁵ The Ni K-edge XANES spectra indicated that the pre-edges of Ti₈-BDC-NiBr, Ti^{III}₂Ti^{IV}₆-BDC-NiH, and Ti^{IV}₈-BDC-NiH were aligned well to that of the Ni(NO₃)₂·6H₂O standard, indicating the Ni centers are divalent in all three MOFs (Figure 2b). Thus, based on EPR and XANES results, only the Ti^{IV} centers, rather than Ni^{II} centers were reduced through the treatment with NaBEt₃H.

To determine the amount of Ti^{III} after reduction in Ti₈-BDC-NiH, the reduced Ti₈-BDC-NiH was titrated with FcPF₆.¹⁶ In this titration, each Ti^{III} ion can reduce one FcPF₆ molecule to form a neutral ferrocene. 2.13 ± 0.08 equiv. of ferrocene was generated with respect to Ni as determined by gas chromatography (GC) (Figure S6-7, SI). Since the Ni centers maintained the Ni^{II} oxidation state in both reduced and oxidized MOFs shown by Ni K-edge XANES analysis (Figure 2b) and the hydrides of first-row metals (Co, Ni, etc) are poorly reducing agents through electron transfer reactions,¹⁷ Fc⁺ ions must be reduced by the Ti^{III} centers. This analysis indicates the Ti^{III}₂Ti^{IV}₆ composition in each reduced Ti₈-BDC-NiH cluster.

EAXFS fitting revealed that the Ni coordination environment in $Ti^{IV}{}_8$ -BDC-NiH is similar to that of $Ti^{III}{}_2 Ti^{IV}{}_6$ -BDC-Ni^{II}H (Figure S8, SI). The Ti K-edge XANES of $Ti^{IV}{}_8$ -BDC-NiBr and $Ti^{IV}{}_8$ -BDC-NiH were also compared. The pre-edge of $Ti^{III}{}_2 Ti^{IV}{}_6$ -BDC-NiH showed an overall 0.45 eV shift to lower energy, because filling one electron to the d orbital lowers its energy and decreases the energy of the $1s \rightarrow 3d$ transition (Figure 2c). Additionally, the intensity of Ti^{III} pre-edge feature is much higher than that of Ti^{IV} centers, likely because the $[Ti^{IIIO}_6]$ octahedron in $Ti^{III}{}_2 Ti^{IV}{}_6$ is more distorted from O_h symmetry which facilitates the formally forbidden 1s-3d transition in the O_h ligand field. (Figure 2c).¹⁸

The coordination environment and electronic structure of Ti₈-BDC-NiH were optimized by DFT calculations (Figure S11, SI) The coordination geometry of Ni center in $Ti^{III}_2Ti^{IV}_6$ -BDC-NiH was similar to that in Ti₈-BDC-NiBr. EXAFS fits of the Ni K-edge EXAFS data matched DFT-derived structural model well (Figure 2d).



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Figure 2. (a) EPR spectra of Ti^{III}₂Ti^{IV}₆-BDC-NiH and Ti^{IV}₈-BDC-NiH. (b) Ni K-edge XANES spectra of Ti₈-BDC-NiBr, Ti^{III}₂Ti^{IV}₆-BDC-NiH, and Ti^{IV}₈-BDC-NiH compared with the Ni(NO₃)₂·6H₂O standard. (c) Ti K-edge XANES spectra of Ti₈-BDC-NiBr, Ti^{III}₂Ti^{IV}₆-BDC-NiH, and Ti^{IV}₈-BDC-NiH. (d) EXAFS spectra (black circles) and fits (gray solid line) in R-space at the Ni K-edge adsorption of Ti^{III}₂Ti^{IV}₆-BDC-NiH.

We examined the catalytic activity of Ti^{III}₂Ti^{IV}₆-BDC-NiH in hydrogenolysis of model molecules that are commonly found in lignin linkage structures.4 Hydrogenolysis of benzyl phenyl ether as a model compound for the α -O-4 linkage was first studied to optimize the reaction conditions. At 140 °C and 1 bar of H_2 and in the absence of any base, 1 mol % loading of Ti^{III}₂Ti^{IV}₆-BDC-NiH (based on Ni) completely cleaved benzyl phenyl ether in 6 h, affording toluene and cyclohexanol as the only products (Table 1, entry 2). Decreasing the temperature to 120 °C lowered the conversion to 86%, giving toluene (86% yield) and cyclohexanol (82% yield) as major products. While phenol was nearly completely hydrogenated to afford cyclohexanol, no competing hydrogenation of toluene was observed under these conditions (Table1, entry 4). The robustness and recyclability of Ti^{III}₂Ti^{IV}₆-BDC-NiH were demonstrated by the recycle experiments (Figure S21, SI). In contrast, Ni nanoparticles generated from treating NiBr₂ with 10 equiv. NaHBEt₃ gave no reactivity towards the hydrogenolysis of benzyl phenyl ether, ruling out the possibility of Ni nanoparticle catalysis in the Ti^{III}₂Ti^{IV}₆-BDC-NiH system (Table 1, entry 5). Ti^{IV}₈-BDC-NiBr was inactive towards hydrogenolysis reactions (Table 1, entry 6). We also investigated the impact of Ti oxidation states of the Ti₈ cluster on the catalytic performance of Ni^{II}-H. Ti^{IV}₈-BDC-NiH displayed no catalytic activity under the same conditions (Table 1, entry 7). It showed that the reduction of the Ti_8 cluster to Ti^{III}₂Ti^{IV}₆ is essential to the MOF catalytic activity, likely as a result of the fact that Ti^{III}₂Ti^{IV}₆ provides a more electron-rich Ni^{II} centers to facilitate the activation of H₂ for hydrogenolysis of benzyl phenyl ether.

 Table 1. Ti^{III}₂Ti^{IV}₆-BDC-NiH Catalyzed Hydrogenolysis of

 Benzyl Phenyl Ether^a

\bigcirc	hep	Cat., H ₂ tane, 140º	c) + (→ ОН	•	ОН
Ý			1		2	3	4
Entry	Cat /	Conv.	TOF	GC Yield			
	(Ni loading)	(%)	(h-1)	1 %	2 %	3 %	4 %
1 ^b	Ti ^Ⅲ 2Ti ^Ⅳ 6-NiH	55	9.2	55	0	0	55
	(1 mol %)	55					
2	Ti ^Ⅲ 2Ti ^Ⅳ 6-NiH	100	16.7	100	0	0	100
	(1 mol %)	100					100
3	Ti ^Ⅲ 2Ti ^Ⅳ 6-NiH	34	11.3	34	22	0	12
	(0.5 mol %)	01					
4 ^c	Ti ^Ⅲ 2Ti ^Ⅳ 6-NiH	86	14.3	86	4	0	82
	(1 mol %)	00					
5	Ni NPs	0	0	0	0	0	0
	(2 mol %)	÷					
6	Ti ^{IV} 8-NiBr	0	0	0	0	0	0
	(1 mol %)						
7	Ti [™] 8-NiH	0	0	0	0	0	0
	(1 mol %)						

^aReaction conditions: freshly prepared catalyst (0.5-2 mol %), benzyl phenyl ether, 1 bar H_2 , 140 °C unless specified, heptane, 6 h unless specified. ^bThe reaction time was 1 h. ^cThe reaction temperature was 120 °C.

We then tested the hydrogenolysis of other benzyl ethers including benzyl aryl and benzyl methyl ethers, which are also present in lignin linkages. Benzyl (p-hydroxylphenyl) converted toluene ether was to and 1.4dihydroxylcyclohexane in quantitative yields (Table 2, entry 1). At 1 bar H₂ and 140 °C, 1 mol % catalyst only gave 11% conversion for the hydrogenolysis of benzyl methyl ether. Increasing the temperature to 160 °C gave almost complete conversion without hydrogenating toluene (Table 2, entries 2 and 3). Under the same condition, benzyl acetate underwent complete hydrogenolysis to give toluene and acetic acid in quantitative yields (Table 2, entry 4).

Table 2. Hydrogenolysis of Various Benzyl Ethers^a

 $\bigcirc OR + H_2 \xrightarrow{\text{Ti}^{III}_2 \text{Ti}^{IV}_6 \text{-NiH (1 mol \%)}}_{\text{heptane, 6h}} \bigcirc + \text{ROH}$

Entry	Benzyl Ether	T (°C)	Conv. (%)	TOF (h ⁻¹)	tolue ne (%)	ROH ^b (%)
1	C OH	140	100	16.7	99	99
2		140	11	1.8	9	9
3		160	99	16.5	98	93
4		160	100	16.7	100	96°

^aReaction conditions: freshly prepared $Ti^{III}_{2}Ti^{IV}_{6}$ -BDC-NiH (1 mol %), benzyl ethers, 1 bar H₂, heptane, 6 h. ^bROH represents 1,4-cyclohexanediol for entry 1, methanol for entries 2 and 3, and acetic acid for entry 4. ^cThe yield was determined by HPLC.

further tested Ti^{III}₂Ti^{IV}₆-BDC-NiH in We the hydrogenolysis of more challenging lignin model compounds, including phenylethyl phenyl ether for β -0-4 linkage and diphenyl ether for 4-0-5 linkage in lignin (Table 3). At 160 °C and 1 bar H₂, 1 mol % catalyst converted phenylethyl phenyl ether to give cyclohexanol in 100% yield, ethyl benzene in 92% yield, and ethylcyclohexane in 8% yield (Table 3, entry 1). In order to improve the selectivity, we lowered the catalyst loading (Table 3, entry 2) and the reaction temperature (Table 3, entry 3) to avoid the hydrogenation of ethyl benzene generated from the hydrogenolysis process. At 140 $^{\circ}$ C, 1 bar H₂, and 1 mol % catalyst loading, phenylethyl ether was selectively cleaved to give the cyclohexanol and ethylbenzene as the sole products. The 4-0-5 linkage is considered as one of the strongest C-O bonds in lignin.¹⁹ At 140 °C and 1 bar H₂, 1 mol % catalyst converted only 19% diphenyl ether to form cyclohexanol and benzene. Increasing the temperature to 160 °C achieved 97% conversion and produced benzene in 80% yield and cyclohexanol 84% yield. We also observed 4% of cyclohexane resulting from hydrogenation of diphenyl ether under this condition. In general, Ti^{III}₂Ti^{IV}₆-BDC-NiH showed high reactivity and excellent selectivity in cleaving

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aryl ethers to give saturated hydrocarbons and hydrogenated phenols. Furthermore, $Ti^{III}_2 Ti^{IV}_6$ -BDC-NiH catalytic activity towards the three model linkages in lignin agrees with the trend of bond dissociation energies: 4-0-5 (314 kJ/mol) > β -0-4 (289 kJ/mol) > α -0-4 (218 kJ/mol).^{7b}

Table 3. Hydrogenolysis of Other Lignin ModelCompoundsa

1 : R = -0 2 : R = -6	$\begin{array}{c} & & & \\ & & & \\ & & & \\ \hline & & \\ & & \\ & & \\ \hline & & \\ &$								
Fatas	Substr	T (0C)	Conv.	TOF	GC Yield				
Entry	ate	T (°C)	(%)	(h-1)	3 %	4 %	5 %	6 %	
1	1	160	100	16.7	92	-	0	100	
2 ^b	1	160	88	29.3	88	-	8	80	
3	1	140	96	16.0	96	-	0	96	
4	2	140	19	3.2	-	19	0	19	
5	2	160	97	16.2	-	80	0	84	

^aReaction conditions: freshly prepared $Ti^{III}_{2}Ti^{IV}_{6}$ -BDC-NiH (1 mol %), aryl ether, 1 bar H₂, heptane, 6 h. ^b $Ti^{III}_{2}Ti^{IV}_{6}$ -BDC-NiH (0.5 mol %).

We performed DFT calculations to determine the energetics for the plausible reaction pathways for Ti^{III}₂Ti^{IV}₆-BDC-NiH catalyzed hydrogenolysis of benzyl phenyl ether $(\alpha$ -O-4) (Figure 3). The [Ni]-H catalyst first reacts with benzyl phenyl ether via four-centered transition state involving a $[2\sigma - 2\sigma]$ cycloaddition of the [Ni]-H bond with the 'PhO-CH₂Ph' bond to furnish [Ni]-OPh and toluene. [Ni]-OPh then undergoes σ -bond metathesis with H₂ through four-centered transition state to afford phenol while regenerating the [Ni]-H to finish the catalytic cycle. The transition states of four-centered Ni-H/substrate (TS1) and four-centered H₂/[Ni]-OPh (TS2) have activation energies of Ea₁= 21.28 kJ·mol⁻¹ and Ea₂= 58.01 kJ·mol⁻¹, respectively. DFT calculations thus show that σ -bond metathesis between [Ni]-OPh and H₂ to form [Ni]-H and phenol is the rate-determining step (RDS). The corresponding energy profiles are shown in Figure 3b. We also performed DFT calculations on two alternative pathways involving oxidative addition/reductive elimination steps using the same functional and found either chemically unreasonable intermediates or very high energy barriers (Figure S14-S17, SI). This result supports our proposed mechanism involving key steps of σ -bond metathesis.



Reaction Coordinate

Figure 3. (a) Proposed mechanism for the hydrogenolysis of benzyl phenyl ether (α -O-4) by the Ti^{III}₂Ti^{IV}₆-BDC-NiH. The activation energies for key σ -bond metathesis are shown. (b) DFT-computed minimum-energy reaction path diagram for the catalytic hydrogenolysis on the Ni-H site.

In summary, the $Ti_8(\mu_2-O)_8(\mu_2-OH)_4$ SBU of MIL-125 served as an excellent support for single-site Ni-H catalysts that are highly active for aryl ether hydrogenolysis. Lignin model compounds containing α -0-4, β -0-4, and 4-0-5 linkages were all selectively cleaved by the Ni-H catalyst to produce aromatic molecules under mild conditions. Our MOF-based catalysts do not need any base (such as NaO^tBu) as additive.^{6, 7e} Interestingly, upon treating with NaBEt₃H, the Ti-oxo node of Ti₈-BDC-NiBr was partially reduced via reductive elimination of H₂ and the electron spillover from Ni to Ti. The resultant Ti^{III}₂Ti^{IV}₆-BDC-Ni^{II}-H is highly reactive towards the hydrogenolysis reaction, while the oxidized Ti^{IV}₈-BDC-Ni^{II}-H is completely inactive, demonstrating the essential role of the reduction of Ti₈ node on the catalytic activity of the supported Ni^{II}-H moieties. We believe that MOF node supported single site solid catalysts are promising candidates for the sustainable synthesis of biofuels and chemical feedstocks owing to their low price, high stability and exceptional reactivity.

ASSOCIATED CONTENT

SUPPORTING INFORMATION.

Experimental procedures, detailed synthesis and characterization of catalysts, X-ray absorption spectroscopic analysis, evaluation of catalytic performances, DFT calculations and catalysis procedures are included in 1

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AUTHOR INFORMATION

Corresponding Author

wenbinlin@uchicago.edu

Author Contributions

[†]These authors contributed equally.

Notes

These authors declare no competing financial interest.

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