SANDIA REPORT
SAND2014-18259
Unlimited Release
Printed September 2014

Bio-inspired MOF-based Catalysts for Lignin Valorization

Mark D. Allendorf (PI), Vitalie Stavila, Partha Ramakrishnan, Ryan Davis

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Sandia National Laboratories

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

Available to DOE and DOE contractors from
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Telephone: (865) 576-8401
Facsimile: (865) 576-5728
E-Mail: reports@adonis.osti.gov
Online ordering: http://www.osti.gov/bridge

Available to the public from
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Rd.
Springfield, VA 22161

Telephone: (800) 553-6847
Facsimile: (703) 605-6900
E-Mail: orders@ntis.fedworld.gov
Online order: http://www.ntis.gov/help/ordermethods.asp?loc=7-4-0#online

SAND2014-18259
Unlimited Release
September 2014

Bio-inspired MOF-based Catalysts for Lignin Valorization

Mark D. Allendorf (PI), Vitalie Stavila, Partha Ramakrishnan, Ryan Davis
Sandia National Laboratories
Livermore, California, 94551

Partha Ramakrishnan
Joint BioEnergy Institute, Emeryville, California, 94608

Abstract

Lignin is a potentially plentiful source of renewable organics, with ~50Mtons/yr produced by the pulp/paper industry and 200-300 Mtons/yr projected production by a US biofuels industry. This industry must process approximately 1 billion tons of biomass to meet the US Renewable Fuel goals. However, there are currently no efficient processes for converting lignin to value-added chemicals and drop-in fuels. Lignin is therefore an opportunity for production of valuable renewable chemicals, but presents staggering technical and economic challenges due to the quantities of material involved and the strong chemical bonds comprising this polymer. Aggressive chemistries and high temperatures are required to degrade lignin without catalysts. Moreover, chemical non-uniformity among lignins leads to complex product mixtures that tend to repolymerize. Conventional petrochemical approaches (pyrolysis, catalytic cracking, gasification) are energy intensive (400-800 °C), require complicated separations, and remove valuable chemical functionality. Low-temperature (25-200 °C) alternatives are clearly desirable, but enzymes are thermally fragile and incompatible with liquid organic compounds, making them impractical for large-scale biorefining. Alternatively, homogeneous catalysts, such as recently developed vanadium complexes, must be separated from product mixtures, while many heterogenous catalysts involve costly noble metals.

The objective of this project is to demonstrate proof of concept that an entirely new class of biomimetic, efficient, and industrially robust synthetic catalysts based on nanoporous Metal-Organic Frameworks (MOFs) can be developed. Although catalytic MOFs are known, catalysis of bond cleavage reactions needed for lignin degradation is completely unexplored. Thus, fundamental research is required that industry and most sponsoring agencies are currently unwilling to undertake. We introduce MOFs infiltrated with titanium and nickel species as catalysts for the C-O bond hydrogenolysis in model compounds, which mimic the β-O-4, α-O-4, and 4-O-5 linkages of natural lignin. The versatile IRMOF-74(n) series is proposed as a platform for creating efficient hydrogenolysis catalysts as it not only displays tunable pore sizes, but also

has the required thermal and chemical stability. The catalytic C-O bond cleavage occurs at 10 bar hydrogen pressure and temperatures as low as 120 °C. The conversion efficiency of the aromatic ether substrates into the corresponding hydrocarbons and phenols varies as $PhCH_2CH_2OPh$ > $PhCH_2OPh$ > PhOPh (Ph = phenyl), while the catalytic activity generally follows the following trend Ni@IRMOF-74>Ti@IRMOF-74>IRMOF-74. Conversions as high as 80%, coupled with good selectivity for hydrogenolysis vs. hydrogenation, highlight the potential of MOF-based catalysts for the selective cleavage of recalcitrant aryl-ether bonds found in lignin and other biopolymers.

This project supports the DOE Integrated Biorefinery Program goals, the objective of which is to convert biomass to fuels and high-value chemicals, by addressing an important technology gap: the lack of low-temperature catalysts suitable for industrial lignin degradation. Biomass, which is ~30 wt% lignin, constitutes a potentially major source of platform chemicals that could improve overall profitability and productivity of all energy-related products, thereby benefiting consumers and reducing national dependence on imported oil. Additionally, DoD has a strong interest in low-cost drop-in fuels (Navy Biofuel Initiative) and has signed a Memorandum of Understanding with DOE and USDA to develop a sustainable biofuels industry.

CONTENTS

FIGURES

TABLES

1. INTRODUCTION

Lignin is one of the most abundant biomass sources with potential to become a sustainable source of value-added chemicals and fuels. However, this goal remains challenging because of the recalcitrance and diverse structure of polymeric lignin with multiple C-O ether and carbon–carbon linkages characterized by high energies and chemical inertness.[1, 2] Lignin is a complex mixture of oxygenated polyaromatics with cross-linked C9 phenol units, which may contain ortho-methoxy groups and other substituents (see Scheme 1). The most common linkages present in softwood lignin are β-O-4 (45-50%), 5-5 (18-25%), β-5 (9-12%), β-1 (7-10%), α-O-4 (6-8%), and 4-O-5 bonds (4-8%).[3, 4] To address the expected shortages of these important chemicals, new, dedicated routes for their on-purpose production are highly desired.

The conventional pyrolysis approaches to depolymerize lignin are energy intensive, produce complex mixtures, and remove valuable chemical functionality.[2, 5, 6] Low-temperature routes are desirable, but homogeneous catalysts suffer from catalyst recovery issues, while enzymes that cleave lignin bonds in nature are thermally fragile and incompatible with organic solvents needed for large-scale manufacturing.[1] Catalytic hydrogenolysis is an attractive approach towards lignin degradation; however, existing methods require harsh conditions (>200 °C and >30 bar hydrogen pressure) and/or expensive catalysts based on rare metals, such as Au, Ru, Ir, Rh, Pd, Pt.[2] In addition, the use of platinic metals often leads to complex mixtures of arenes and cycloalkanes, which makes the isolation of individual compounds rather challenging. Nickel- [7-11] or mixed nickel-titanium[12] catalysts represent promising alternatives with good conversion efficiencies reported.

Metal–organic frameworks (MOFs), also known as porous coordination networks (PCNs), are a class of hybrid inorganic–organic porous crystalline materials, which consist of metal ions and bridging organic linkers to form a 3D structure. The permanent nanoscale porosity, high surface area, good thermal and chemical stability makes MOFs and guest@MOFs materials promising for various catalytic processes.[13, 14] For instance, metal nanoparticles (NPs) immobilized inside MOF pores are known to catalyze various chemical processes, including hydrogenation reactions and C-O bond cleavage.[15-17] One potential advantage of MOFs over other classes of catalysts is their uniform cavities coupled with the high density of active catalytic centers, such as open metal sites. Furthermore, the channels of MOFs provide confined pockets, effectively acting as “nanoreactors”.[13, 18]

2. RESULTS AND IMPACT

We performed calculations and experiments to demonstrate the C-O bond hydrogenolysis using molecular hydrogen in the presence of MOFs-based catalysts. The starting MOF catalyst candidate was MOF-74 ((or Mg_2(DOBDC), where DODBC=2,5-dioxibenzene-1,4-dicarboxylate)), which was previously shown to be stable under hydrogen atmosphere upon mild heating.[18] The discovery of the isoreticular IRMOF-74(n) series[19] having honeycomb-like hexagonal pores systematically varied between 1.2 nm and 9.8 nm by expanding the linkers from one to eleven phenylene rings makes it possible to encapsulate rather large molecules, including proteins. The pore size is believed to be important for designing MOF catalysts for lignin valorization, as natural lignin even after the depolymerization treatment can be still composed of large oligomers of at least several nm in diameter.[20] In addition, the isostructural IRMOF-74 topology can be achieved with a wide range of earth-abundant metals, such as Mg, Mn, Fe, Co, Ni, Cu, Zn, as well as mixed-metal compounds of up to ten different metals.[21]

We selected phenylethylphenyl ether, benzylphenyl ether, and diphenyl ether as model compounds for β-O-4, α-O-4, and 4-O-5 (or 4,4') linkages of lignin. We choose the magnesium versions of IRMOF-74(I) and IRMOF-74(II), with pore diameters of 1.2 and 2.0 nm, which are sufficiently large to accommodate all three lignin model compounds. In addition to pure MOFs, we also prepared IRMOF-74(I) and IRMOF-74(II) materials infiltrated with Ti and Ni species. Both of these metals are earth-abundant and have been previously shown to act as catalysts for aryl diether hydrogenolysis.[9, 11, 12] The infiltration of Ti species was performed using a previously described procedure by vapor infiltration of $TiCl_4$ into the pores of activated IRMOF-74(I)[18] and IRMOF-74(II), followed by treatment with gaseous hydrogen at 90 °C. Nickel infiltration in IRMOF-74(I) and IRMOF-74(II) was achieved using a strategy pioneered by Fischer's group[22] which involves loading an organometallic precursor and subsequent reduction and removal of the volatile organic compounds to generate metal clusters or nanoparticles (NPs). Bis(cyclopentadienyl) nickel was used a recursor MOF pores, followed by reduction under hydrogen at 90 °C. Both IRMOF-74(I) and IRMOF-74(II) maintain their crystallinity as confirmed by XRD analysis (Figure 1).

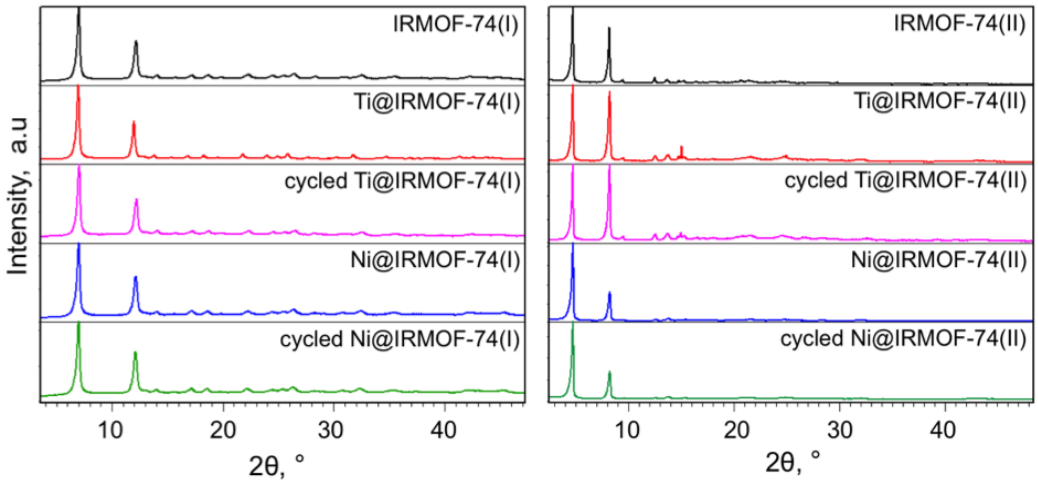


Figure 1. XRD patterns of the as-synthesized and cycled IRMOF-74(I,II)-based catalysts.

The overall atomic composition of the infiltrated samples is confirmed by elemental analysis, showing 1.52 wt% Ti and 2.91 wt% Ni loading in IRMOF-74(I). Similar loadings were found for the metal@IRMOF-74(II) samples, with a Ti content of 1.75 wt% and a Ni fraction of 3.07 wt%. The metal distribution in the as-synthesized powders was determined through scanning electron microscopy (SEM) measurements using energy-dispersive spectroscopy (EDS). The elemental maps confirm that both Ti and Ni species are homogeneously distributed within the MOF particles (Figure 2).

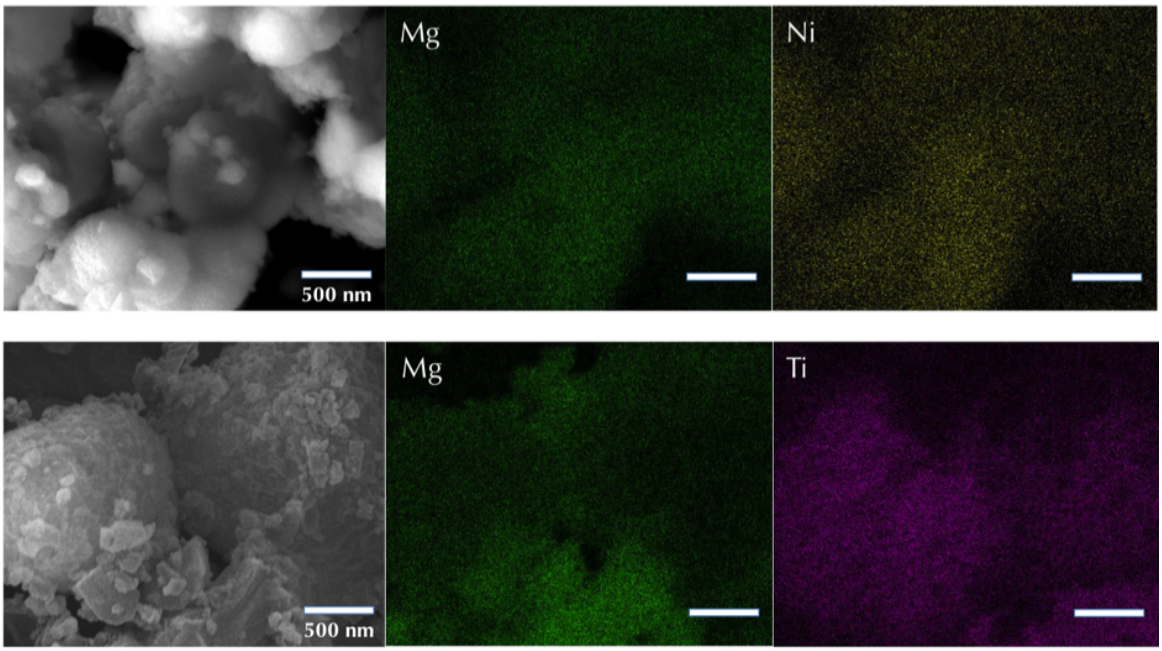


Figure 2. SEM and EDS analysis of Ti@IRMOF-74(I) and Ni@IRMOF-74(I) samples. The scale bar in all EDS maps is 500 nm.

The as-synthesized MOF-based catalysts were evaluated in hydrogenolysis reactions of phenylethylphenyl ether (β-O-4 lignin linkage), benzylphenyl ether (α-O-4 lignin linkage), and diphenyl ether (4-O-5 lignin linkage). Table 1 summarizes the results of the hydrogenolysis tests under 10 bar hydrogen pressure with IRMOF-74(I) and IRMOF-74(II) catalysts at various temperatures and reaction times. Such H_2 gas pressures are commonly used in industrial hydrogenation reactions, including heterogeneous catalysis.[23] The catalytic tests were performed in stainless steel reactors loaded with solutions of the lignin model compounds in p-xylene and the MOF catalyst. The mixtures were pressurized with hydrogen and heated to 90-120 ºC for a fixed amount of time.

Table 1. Catalytic effect of MOF-based catalysts on hydrogenolysis of lignin model molecules.

Entry	Catalyst	Substrate	T, ºC	Time, hours	**Conversion, %**
1	IRMOF-74(I)	1 (β-O-4)	120	16	**13**
2	Ti@IRMOF-74(I)	1 (β-O-4)	120	16	**56**
3	Ni@IRMOF-74(I)	1 (β-O-4)	120	16	**70**
4	IRMOF-74(II)	1 (β-O-4)	120	16	**40**
5	Ti@IRMOF-74(II)	1 (β-O-4)	120	16	**63**
6	Ni@IRMOF-74(II)	1 (β-O-4)	120	16	**82**
7	IRMOF-74(I)	2 (α-O-4)	120	16	**10**
8	Ti@IRMOF-74(I)	2 (α-O-4)	120	16	**33**
9	Ni@IRMOF-74(I)	2 (α-O-4)	120	16	**57**
10	IRMOF-74(II)	2 (α-O-4)	120	16	**17**
11	Ti@IRMOF-74(II)	2 (α-O-4)	120	16	**49**
12	Ni@IRMOF-74(II)	2 (α-O-4)	120	16	**76**
13	IRMOF-74(I)	3 (□-O-5)	120	16	**4**
14	Ti@IRMOF-74(I)	3 (□-O-5)	120	16	**19**
15	Ni@IRMOF-74(I)	3 (□-O-5)	120	16	**29**
16	IRMOF-74(II)	3 (□-O-5)	120	16	**9**
17	Ti@IRMOF-74(II)	3 (□-O-5)	120	16	**20**
18	Ni@IRMOF-74(II)	3 (□-O-5)	120	16	**34**
19	Ni@IRMOF-74(II)	1 (β-O-4)	90	16	**50**
20	Ni@IRMOF-74(II)	1 (β-O-4)	100	16	**57**
21	Ni@IRMOF-74(II)	1 (β-O-4)	110	16	**64**
22	Ni@IRMOF-74(II)	1 (β-O-4)	120	1	**38**
23	Ni@IRMOF-74(II)	1 (β-O-4)	120	2	**45**
24	Ni@IRMOF-74(II)	1 (β-O-4)	120	4	**54**

Initial tests with undoped IRMOF-74(I) and IRMOF-74(II) powders revealed that all three ethers partially react with molecular hydrogen to generate small amounts of phenol and the corresponding aromatic hydrocarbons. The yield is higher when the MOFs are infiltrated with Ti, and significantly higher in the case of Ni-doped samples. For both IRMOF-74(I) and IRMOF-74(II)-based catalysts the C-O bond conversion efficiency varies in the following order: $PhCH_2CH_2OPh$ > $PhCH_2OPh$ > PhOPh. For all three substrates the catalytic activity generally follows the following trend Ni@IRMOF-74>Ti@IRMOF-74>IRMOF-74. The best catalytic conversions were found for substrates bearing the β-O-4 and α-O-4 linkages, with conversions as high as 82 and 76%, respectively (Table 1). The hydrogenolysis reaction of phenylethylphenyl ether occurs as low as 90 ºC, although the conversion efficiency is significantly lower. Our experiments indicate that at 120 ºC the conversion efficiency after 1, 2 and 4 hours is 38, 45 and 54%, respectively. This indicates that reaction time plays a crucial role in determining the conversion efficiency.

Functionalization of MOF pores with Ni or Ti species resulted in better conversion efficiencies for all 3 substrates, as supported by GCMS and NMR data. **Figure 3** shows the GCMS and ^{1}H NMR results of catalytic hydrogenolysis of benzylphenylether (BPE) to form toluene and phenol. GCMS data clearly indicate the occurrence of new peaks in the GC chromatogram assigned to reaction products. No reaction occurs when no catalyst is used (see inset in **Figure 3**). The ^{1}H NMR spectra clearly show the reaction products, alongside residual starting material. The NMR and GCMS results indicate that no ring hydrogenation occurs and the main reaction products of benzylphenylether (BPE) hydrogenolysis are the corresponding arene (toluene) and alcohol (phenol). Our results indicate that the MOF structure remains unchanged after hydrogenolysis, as confirmed by powder X-ray diffraction (**Figure 1**).

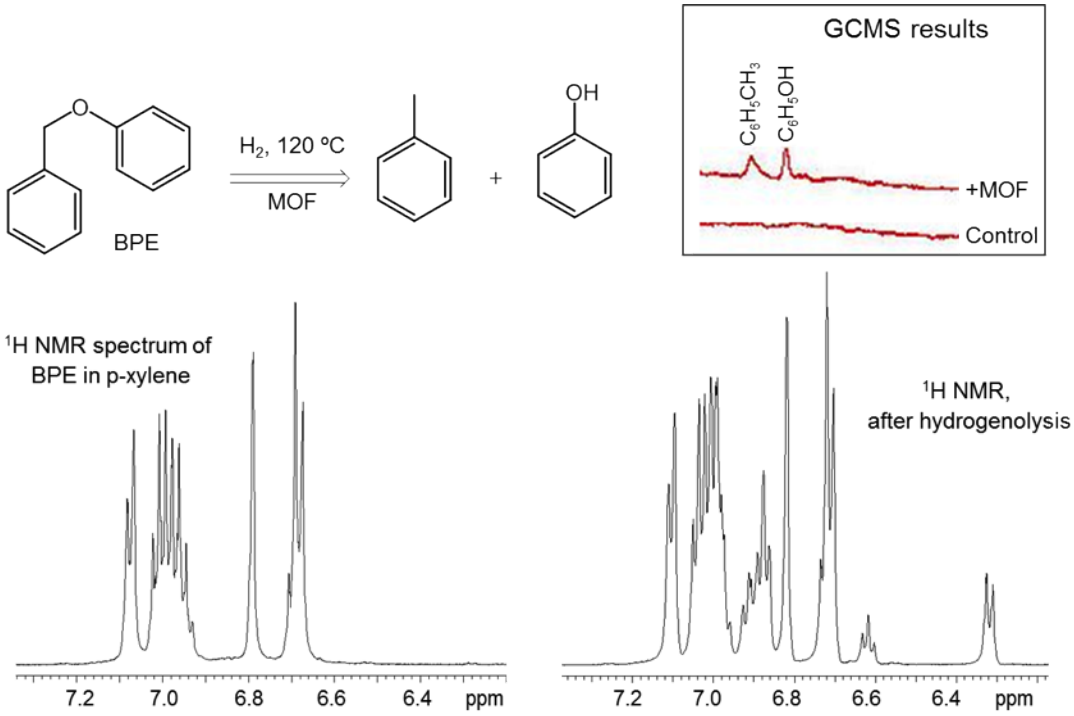


Figure 3 GCMS and 1H NMR results showing partial conversion of benzylphenylether into toluene and phenol at 120 ºC under 10 bar hydrogen.

Sergeev *et al.* reported that Ni NPs are efficient in catalyzing the cleavage of a range of aromatic ethers in the presence of NaO^{t}Bu.[9] The presence of the base is believed to stabilize the Ni NPs, effectively acting as a surfactant. EDS data support this hypothesis and indicate the presence of both sodium and nickel in the catalytically-active nickel NPs. In contrast, the Ni NPs generated in the absence of NaO^{t}Bu display low reactivity and poor selectivity for hydrogenolysis over hydrogenation.[9] Our results indicate that the Ti@IRMOF-74 and Ni@IRMOF-74 catalysts are active and highly selective for hydrogenolysis over hydrogenation without any additional base required. It is likely that the MOF pores provide a stabilizing effect on the Ti and Ni NPs, which circumvents the need for an additional base for the catalysts to be active.

3. COMPUTATIONAL DETAILS

Additional insights into the potential hydrogenation reaction pathways were evaluated using quantum-chemistry methods. We explored the molecular basis of lignin model compounds interactions with MOF catalyst using density functional theory (DFT). The geometry optimizations lignin model compounds such as phenylethylphenyl ether, benzylphenyl ether and diphenyl ether representing β-O-4, α-O-4 , and 4-O-5 linkages, respectively, were performed using the M06-2X hybrid exchange-correlation functional and the 6-31+G(d, p) basis set. Frequency calculations were carried out to verify that the computed structures corresponded to energy minima. Bond dissociation energies (BDEs) for ether bond (C-O) of lignin model compounds were obtained as the difference of the sum of the energies of the dissociated product fragments and the energy of the molecule.

$$BDE = (E_{Frag1} + E_{Frag2}) - E_{Mol} \quad (1)$$

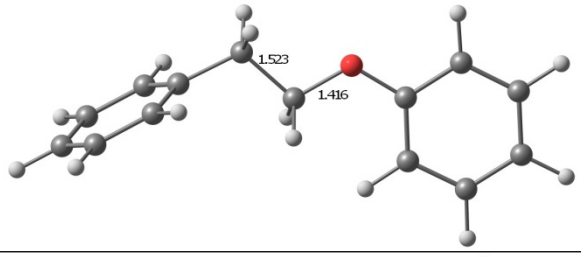
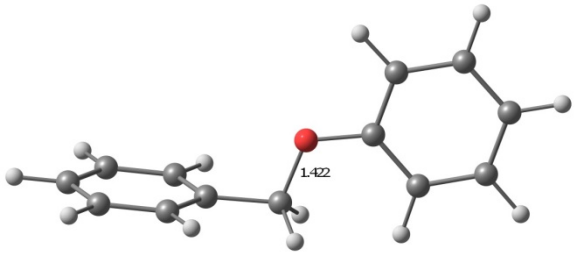
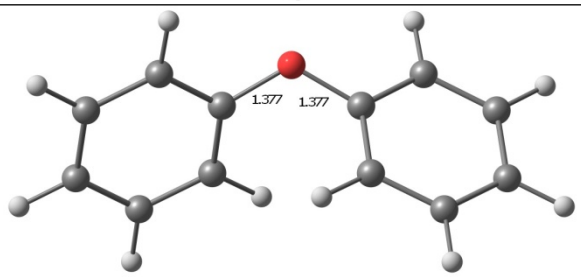
where E_{Mol} is the total energy of the molecule, E_{Frag1} and E_{Frag2} are energies of the dissociated products through the selected C–O linkages. All dissociated fragments were fully optimized. In addition, the energies were corrected by including the zero-point energies (ZPE), the thermal contributions at 393 K.

IRMOF-74(I) and IRMOF-74(II) geometries were used for the analysis of the MOFs pore size to accommodate the lignin model compounds and we were quantified the binding preference on the reactions catalyzed by MOF. For the cluster calculations, we used the proto type MOF cluster with lignin model compounds to calculate the binding energies and relax the geometries using hybrid QM/QM method without any constrains. For QM/QM calculations, the ONIOM ("Our own *N*-layered Integrated molecular Orbital and Molecular mechanics") approach implemented in Gaussian09 was used.[24] During the optimization of the various MOF-lignin model compound complexes, the lignin were treated at a higher level (MO6-2X/6-31+G(d,p)) quantum mechanical level of theory and the MOF cluster at semi-empirical(PM6) quantum mechanical level of theory. The binding energies were then obtained at the MO6-2X/6-31+G(d,p) level. The basis set superposition errors were deducted for all binding energy calculations using the counterpoise method.[25]

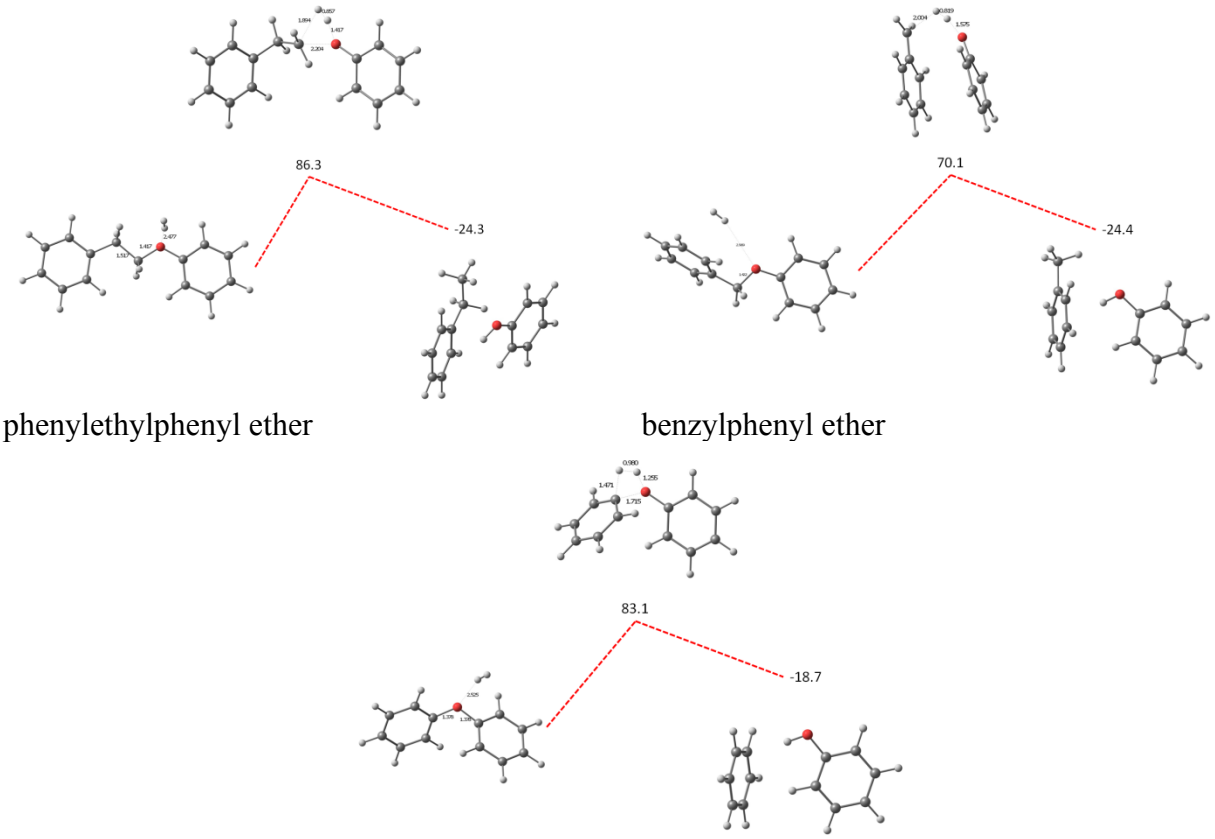
The optimized geometries of phenylethylphenyl ether, benzylphenyl ether and diphenyl ether and calculated ether bond dissociation energies at 393 K for lignin model compounds are reported in Table 2. Within the ether bond linkage types, 4-O-5 compound contain the shorter linkages (1.37 Å) and the β-O-4 (1.41 Å), and α-O-4 (1.42 Å) compounds tend to have longer ether bond lengths. The BDE trend shows that ether linkages of α-O-4 and β-O-4 are found to be weaker than the 4-O-5 linkages. Ether bond in 4-O-5 type linkage is the strongest and also exhibit the shortest bond length, as reported earlier.[3] Mechanistic pathway for hydrogenolysis of lignin model compounds is investigated. The key structures (reactants, products and transfer states) involved in the reaction paths for lignin model compounds with interacting hydrogen atoms complexes are illustrated in Figure 4. Analytical evaluation of force constants and vibrational frequencies were used to verify the nature of the minima and transition states. In particular, all transition states (TS) have one and only one imaginary frequency, and the corresponding normal coordinates were used to confirm the nature of the reactants and products in each step of the reaction mechanism. As can be seen in the proposed reaction pathway, the hydrogenolysis of

ether bonds proceeds with a transition state (TS-1), and is followed by hydrogen atoms transferred to oxygen and carbon of the substrates to facilitate the formation of saturated products. In the initial lignin-dihydrogen complex, the hydrogen atom adsorbed to the ether oxygen bond is a more favorable conformation for 4-O-5 and β-O-4 linkages. The α-O-4 model compound favors the abortion of hydrogen with oxygen of ether bond and is also localized on the π-region of the aromatic ring.

Table 2. Optimized geometries of lignin model compounds and calculated Bond dissociation energies (BDE) of ether linkages.

Lignin model compounds	Optimized structure	BDE in kcal/mol
phenylethylphenyl ether		69.53
benzylphenyl ether		56.83
diphenyl ether		82.53

The reaction complexes and relative energies at 393 K of these reaction paths are also reported in Figure 4. Overall, it can be seen that activation reaction barrier is higher for hydrogenolysis of lignin model compounds reactions presumably due to the absence of catalysts. Calculated activation energy of the hydrogen atom transport path by C-O bond cleavage of phenylethylphenyl ether and diphenyl ether compounds are higher than benzylphenyl ether. It is interesting to note that we could capture the simultaneous hydrogen atom transfer to oxygen and carbon atoms these ether bond cleavage reaction pathway. Conversely, the energy barrier for the hydrogen atom transfer to lignin linkages is much higher without any catalytic environment.



phenylethylphenyl ether benzylphenyl ether

diphenyl ether

Figure 4. The proposed mechanistic pathway for hydrogenolysis reactions of lignin model compounds and relative energies (kcal/mol) calculated using MO6-2X/6-31+G(d,p) level of theory at 393 K.

The coordinates of the IRMOF-74(I) (VOGTIV) and IRMOF-74(II) (RAVVUH) were taken from the experimentally determined crystal structures.[19] We carried out an initial analysis on the pore sizes of the MOFs to accommodate the model compounds with different lignin linkages. Figure 5 illustrates the pore size diameter of IRMOF-74(I) (14 Å) and IRMOF-74(II) (22 Å). End to end distance (highlighted atoms) of the optimized geometries of phenylethylphenyl ether, benzylphenyl ether and diphenyl ether are shown in Figure 5. The distances of these lignin model compounds are vary between 9-12 Å units. Also, it is worth to compare the length of actual lignin containing H, G, and S type of monomers. We obtained optimized geometry of 4-O-5 (H), β-O-4 (S) and α-O-4(G) lignin dimers at M06-2x/6-311++G(d,p) level and their lengths vary between 10-14 Å units. This evidently shows that the smaller MOFs can accommodate the lignin model compounds chosen in this work and MOFs with the larger pore size can catalyze higher molecular weight lignins. To understand the absorption and hydrogenolysis, we have chosen a cluster model of IRMOF-74 with five coordinated open metal sites at QM/QM method using MO6-2x/6-31G(d,p):PM6 levels of theory. The model cluster structures were taken from the experimental crystal structures. The small cluster was then terminated by –H, $–CH_3$ and Li.

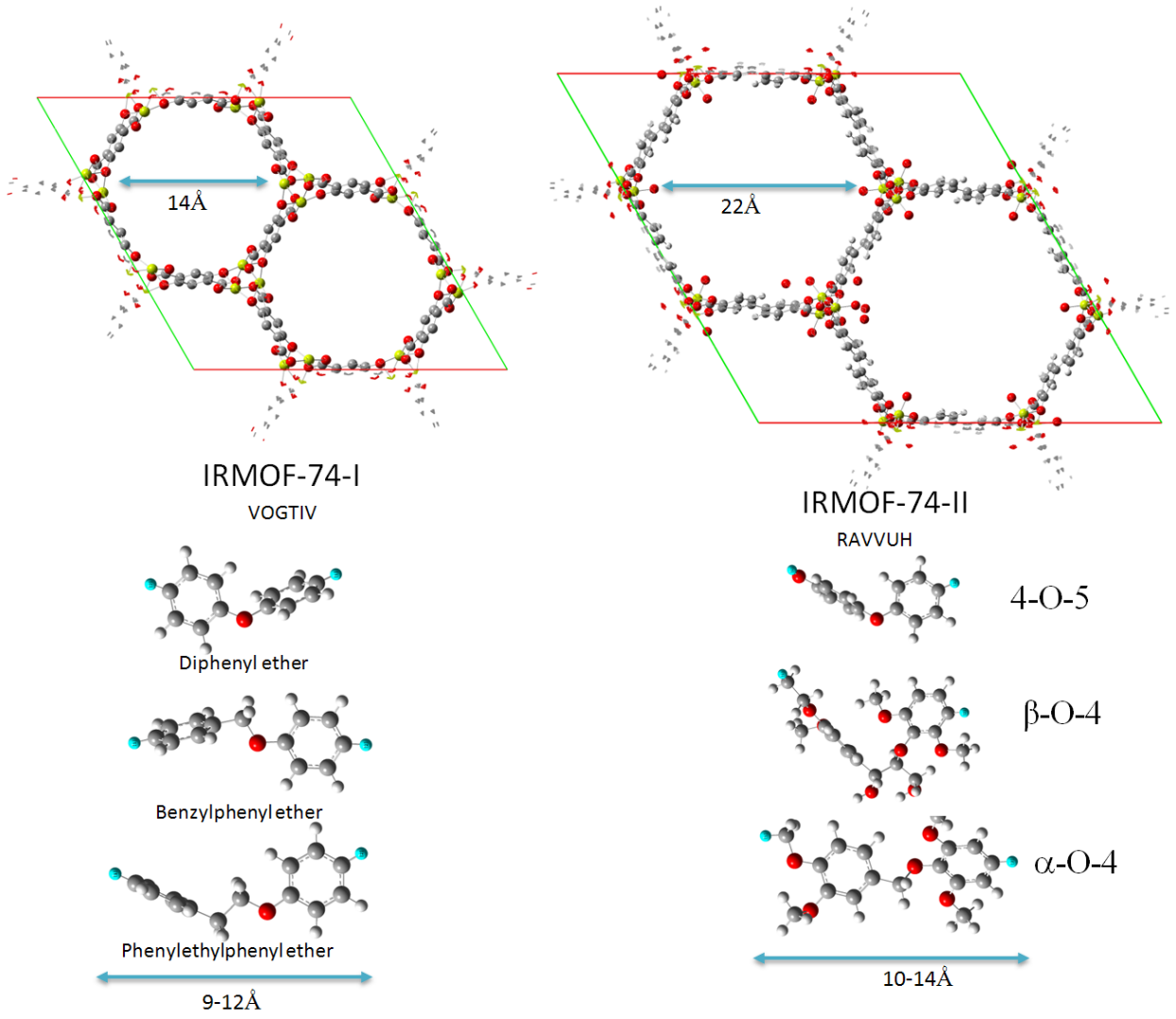


Figure 5. Structure and the pore size of IRMOF-74(I) and IRMOF-74(II) and end to end distance (highlighted atoms) of the optimized geometries of lignin model compounds with different linkages.

In the geometry optimizations, the lignin model compounds placed on cluster model in different starting configurations were allowed to relax. Figure 6 shows the resulting minimum energy configuration of lignin model compound complexes with MOF calculated using the meta hybrid DFT level. Our initial hypothesis was that the oxygen atoms of the ether groups would interact with the MOF open metal sites. Surprisingly, predictions show that aromatic rings of the lignin model compounds oriented toward metal sites and forming metal-π interactions as the preferred mode of interactions (Figure 6). It was found that the calculated absorption energy of binding followed the order phenylethylphenyl ether > benzylphenyl ether > diphenyl ether. Interestingly, the trend is consistent with the observed experimental yield.

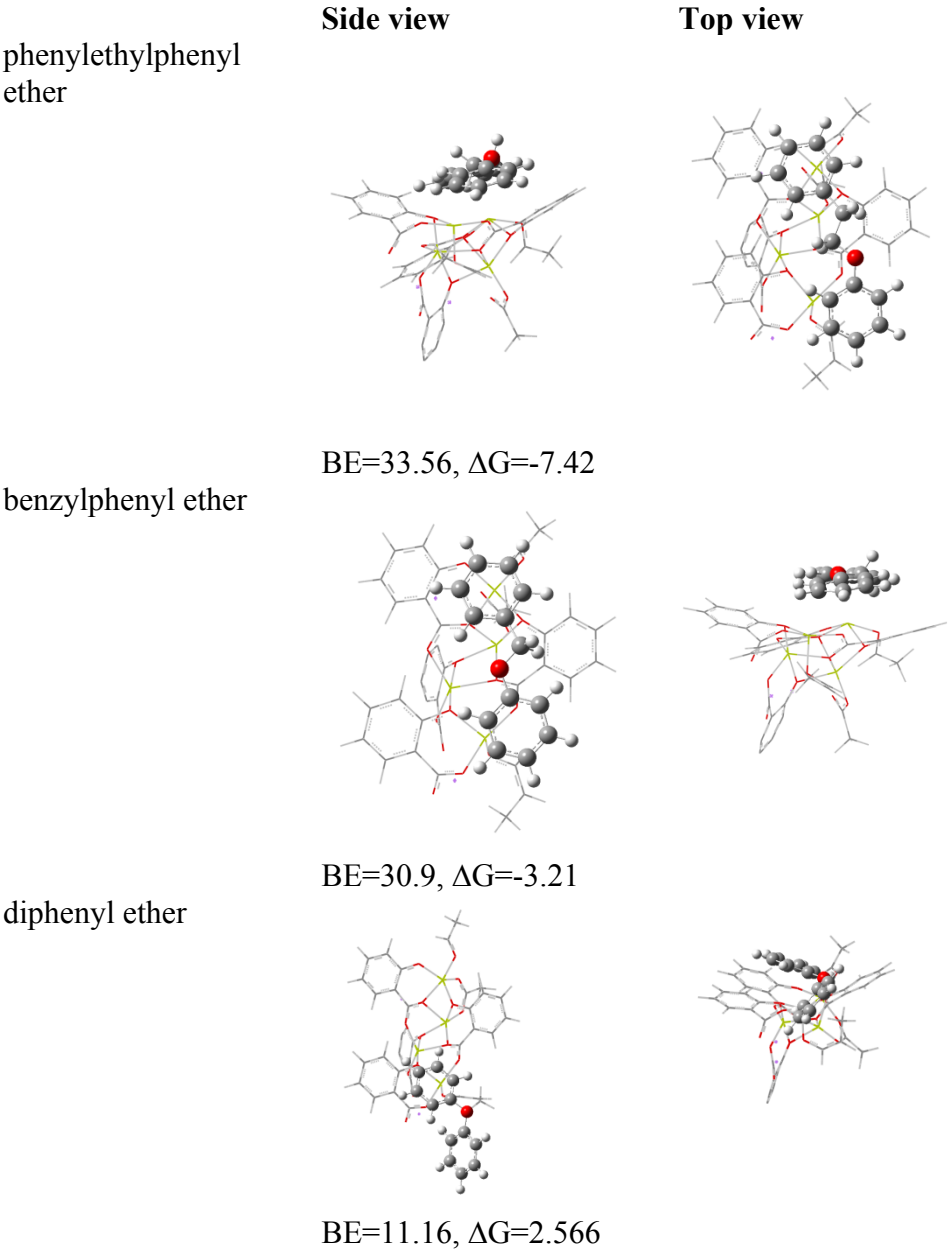


Figure 6. Configuration of lignin model compounds with the cluster model of IRMOF-74 obtained using QM/QM method. Binding energies (kcal/mol) and free energy of product formations are given respectively for the selected lignin model compounds in this work.

In order to explore the of hydrogenolysis catalytic reactions in the presence IRMOF-74, we computed the free energy of the product formation of lignin model compounds interaction with the cluster model of MOF using QM/QM method. The free energy of formation of the products quantified as the difference between in the presence and absence of MOFs. Calculated free energy profile show a similar trend to the absorption energy and experimental yield. The higher binding energy and sign of the free energy profile clearly indicate that hydrogenolysis of

phenylethylphenyl ether, one of the most dominant lignin linkage type is effectively catalyzed by IRMOF-74. Important to note here that, nickel catalyzed hydrogenolysis has been reported to break these strong 4-O-5 ether bond.[10] Computed absorption preference indicates that the influence of metal combinations on the reactions could be tuned for selective catalysis of different lignin linkages.

4. CONCLUSIONS

MOF-based heterogeneous catalysts have been developed for selective hydrogenolysis of lignin model compounds, namely phenylethylphenyl ether (β-O-4 linkage), benzylphenyl ether (α-O-4 linkage), and diphenyl ether (4-O-5 linkage). The conversion efficiency of the aromatic ethers into the corresponding hydrocarbons and phenols varies as $PhCH_2CH_2OPh$ > $PhCH_2OPh$ > PhOPh, while the activity of the catalysts generally follows the following order Ni@IRMOF-74(I,II)>Ti@IRMOF-74(I,II)>IRMOF-74(I,II). In particular, the Ni-doped IRMOF-74(I,II) samples were shown to be the most active in catalyzing the β-O-4 linkage and α-O-4 linkage, with conversions as high as 82 and 76%, respectively. The experimental results agree well with the DFT theory predictions which indicate higher binding energy between the phenylethylphenyl ether and benzylphenyl ether to IRMOF-74(I) and IRMOF-74(II). Recycling experiments indicate that the metal immobilized IRMOF-74(I,II) samples could be used five times with essentially no loss in catalytic activity. The exact reaction mechanism is unknown; however, the modeling and experimental results presented here indicate that both confinement inside the MOF pores and the presence of reactive metal species plays a critical role in determining the catalytic conversion and selectivity. Although additional efforts are needed to improve the conversion efficiencies, the MOF-based catalysts reported in this work demonstrate excellent selectivity for hydrogenolysis over hydrogenation, highlighting the potential of MOFs as platforms for developing efficient heterogeneous catalysts for selective cleavage of C-O aromatic bonds.

5. REFERENCES

1. Straathof, A.J.J., *Transformation of Biomass into Commodity Chemicals Using Enzymes or Cells.* Chem. Rev., 2013. **114**(3): p. 1871-1908.
2. Zakzeski, J., et al., *The Catalytic Valorization of Lignin for the Production of Renewable Chemicals.* Chem. Rev., 2010. **110**(6): p. 3552-3599.
3. Parthasarathi, R., et al., *Theoretical Study of the Remarkably Diverse Linkages in Lignin.* J. Phys. Chem. Lett., 2011. **2**(20): p. 2660-2666.
4. Chakar, F.S. and A.J. Ragauskas, *Review of current and future softwood kraft lignin process chemistry.* Indu. Crop Prod., 2004. **20**(2): p. 131-141.
5. Morgan, T.J. and R. Kandiyoti, *Pyrolysis of Coals and Biomass: Analysis of Thermal Breakdown and Its Products.* Chem. Rev., 2013. **114**(3): p. 1547-1607.
6. Pandey, M.P. and C.S. Kim, *Lignin Depolymerization and Conversion: A Review of Thermochemical Methods.* Chem. Eng. Technol. , 2011. **34**(1): p. 29-41.
7. Zhang, J., Y. Chen, and M.A. Brook, *Reductive Degradation of Lignin and Model Compounds by Hydrosilanes.* ACS Sustainable Chem. Eng., 2014. **2**(8): p. 1983-1991.
8. Yang, L., Y. Li, and P.E. Savage, *Hydrolytic Cleavage of C–O Linkages in Lignin Model Compounds Catalyzed by Water-Tolerant Lewis Acids.* Ind. Eng. Chem. Res., 2014. **53**(7): p. 2633-2639.
9. Sergeev, A.G., J.D. Webb, and J.F. Hartwig, *A Heterogeneous Nickel Catalyst for the Hydrogenolysis of Aryl Ethers without Arene Hydrogenation.* J. Amer. Chem. Soc., 2012. **134**(50): p. 20226-20229.
10. Sergeev, A.G. and J.F. Hartwig, *Selective, Nickel-Catalyzed Hydrogenolysis of Aryl Ethers.* Science, 2011. **332**(6028): p. 439-443.
11. Wang, X. and R. Rinaldi, *Solvent Effects on the Hydrogenolysis of Diphenyl Ether with Raney Nickel and their Implications for the Conversion of Lignin.* ChemSusChem, 2012. **5**(8): p. 1455-1466.
12. Molinari, V., et al., *Titanium Nitride-Nickel Nanocomposite as Heterogeneous Catalyst for the Hydrogenolysis of Aryl Ethers.* J. Amer. Chem. Soc., 2014. **136**(5): p. 1758-1761.
13. Gascon, J., et al., *Metal Organic Framework Catalysis: Quo vadis?* ACS Catal., 2014. **4**(2): p. 361-378.
14. Corma, A., H. García, and F.X. Llabrés i Xamena, *Engineering Metal Organic Frameworks for Heterogeneous Catalysis.* Chem. Rev., 2010. **110**(8): p. 4606-4655.
15. Aijaz, A. and Q. Xu, *Catalysis with Metal Nanoparticles Immobilized within the Pores of Metal–Organic Frameworks.* J. Phys. Chem. Lett., 2014. **5**(8): p. 1400-1411.
16. Guo, Z., et al., *Pt Nanoclusters Confined within Metal–Organic Framework Cavities for Chemoselective Cinnamaldehyde Hydrogenation.* ACS Catal., 2014. **4**(5): p. 1340-1348.
17. Barta, K. and P.C. Ford, *Catalytic Conversion of Nonfood Woody Biomass Solids to Organic Liquids.* Acc. Chem. Res. , 2014. **47**(5): p. 1503-1512.
18. Stavila, V., et al., *Reversible Hydrogen Storage by NaAlH4 Confined within a Titanium-Functionalized MOF-74(Mg) Nanoreactor.* ACS Nano, 2012. **6**(11): p. 9807-9817.
19. Deng, H., et al., *Large-Pore Apertures in a Series of Metal-Organic Frameworks.* Science, 2012. **336**(6084): p. 1018-1023.
20. Nanayakkara, S., A.F. Patti, and K. Saito, *Chemical depolymerization of lignin involving the redistribution mechanism with phenols and repolymerization of depolymerized products.* Green Chem., 2014. **16**(4): p. 1897-1903.

21. Wang, L.J., et al., *Synthesis and Characterization of Metal–Organic Framework-74 Containing 2, 4, 6, 8, and 10 Different Metals.* Inorg. Chem., 2014. **53**(12): p. 5881-5883.
22. Meilikhov, M., et al., *Metals@MOFs – Loading MOFs with Metal Nanoparticles for Hybrid Functions.* Eur. J. Inorg. Chem. , 2010. **2010**(24): p. 3701-3714.
23. Wang, D.-S., et al., *Asymmetric Hydrogenation of Heteroarenes and Arenes.* Chem. Rev., 2011. **112**(4): p. 2557-2590.
24. Lundberg, M., et al., *Case Studies of ONIOM(DFT:DFTB) and ONIOM(DFT:DFTB:MM) for Enzymes and Enzyme Mimics.* J. Chem. Theory Comput., 2010. **6**(4): p. 1413-1427.
25. Boys, S.F. and F. Bernardi, *Calculation of Small Molecular Interactions by Differences of Separate Total Energies - Some Procedures with Reduced Errors.* Mol. Phys. , 1970. **19**(4): p. 553-&.

APPENDIX A: PRESENTATIONS

M. D. Allendorf, V. Stavila, R. Davis, P. Ramakrishnan "MOF-Based Catalysts for Lignin Degradation," invited presentation, Fall American Chemical Society meeting, Aug. 2014, San Francisco, CA.

V. Stavila, R. W. Davis, P. Ramakrishnan, K. L. Sale, M. D. Allendorf "MOF-Based Catalysts for Lignin Valorization," poster presented at 4th International Conference on Metal-Organic Frameworks and Open Framework Compounds," Sept. 28 – Oct. 1, 2014, Kobe, Japan.

DISTRIBUTION

1	MS1413	Michael Kent	8622
2	MS9161	Mark Allendorf	8600
3	MS9161	Sarah Allendorf	8650
4	MS9161	Vitalie Stavila	8367
5	MS9291	Blake Simmons	8634
6	MS9292	Parthasarathi Ramakrishnan	8634
7	MS9292	Ken Sale	8634
8	MS9292	Ben Wu	8634
9	MS9671	Ryan Davis	8634
1	MS0899	Technical Library	9536 (electronic copy)

For LDRD reports, add:

1	MS0359	D. Chavez, LDRD Office	1911


Sandia National Laboratories