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MOF-Based Catalysts for Selective Hydrogenolysis of Carbon-Oxygen Ether Bonds

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ABSTRACT: We demonstrate that metal-organic frameworks (MOFs) can catalyze hydrogenolysis of aryl ether bonds under mild conditions. Mg-IRMOF-74(I) and Mg-IRMOF-74(II) are stable under reducing conditions and can cleave phenyl ethers containing β -O-4, α -O-4, and 4-O-5 linkages to the corresponding hydrocarbons and phenols. Reaction occurs at 10 bar H₂ and 120 °C without added base. DFT-optimized structures and charge transfer analysis suggest that the MOF orients the substrate near Mg²⁺ ions on the pore walls. Ti and Ni doping further increases conversions to as high as 82% with 96% selectivity for hydrogenolysis vs. ring hydrogenation. Repeated cycling induces no loss of activity.

KEYWORDS : Metal-Organic Frameworks, Catalysis, C-O Bond Cleavage, Hydrogenolysis, Aromatic Ethers

The catalytic properties of nanoporous materials known as Metal-Organic Frameworks (MOFs) are attracting considerable attention as a result of their exceptional chemical and structural versatility.^{1,2} MOFs are crystalline materials consisting of metal ions coordinated to bridging organic linkers, forming a micro- or mesoporous structure. These materials offer an exceptionally high degree of synthetic versatility, enabling rational design of pore dimensions and chemistry to achieve product selectivity with high turnover rates. MOFs have remarkably high thermal and chemical stability (some are stable to temperatures as high as 500 °C).^{3,4} Water stability, an issue with some frameworks, is no longer a limiting factor; a large number of water-stable MOFs are now known, some of which are unaffected by boiling in acidic or basic solution, and strategies for improving water stability in those that are not are now available.⁵ MOFs can also serve as hosts for metal nanoparticles (NPs) known to catalyze hydrogenation reactions.⁶⁻⁸ Finally, compared with catalysts supported on amorphous substrates, MOFs possess uniform cavities and a high density of reactive centers, which should contribute to increased turnover rates and selectivities.^{9,10} As a result of these attractive properties, many types of MOF-

catalyzed reactions are known, including oxidation, silylation, sulfurization, epoxidation, cycloaddition, and condensation, to name just a few.^{1-3,9,11} Notably absent from this list are simple bond cleavage reactions, in particular hydrogenolysis, which is used extensively industrially to remove sulfur from hydrocarbons¹² and has gained attention for production of value-added chemicals from biomass.¹³ To our knowledge, there is only one report of MOF-catalyzed hydrogenation of an organic molecule (as opposed to organometallic precursors of metal nanoparticles); in this case, the catalytic reaction occurs in the presence of a sacrificial base.¹⁴ Here, we describe experiments and modeling supporting the notion that MOFs can be effective catalysts for the hydrogenolysis of C–O aromatic ether bonds, which are common linkages in biomass.

MOF-74 was selected as a starting point for catalyst development because this topology has several advantages. First, the recently reported isoreticular IRMOF-74(n) series¹⁵ provides hexagonal 1-D channels with diameters between 1.2 nm and 9.8 nm that can accommodate a range of substrate sizes. Second, the density of open metal sites (OMS) in these MOFs, which can behave as Lewis acids to activate C-O bonds, is the highest known for this class of materials. Third, IRMOF-74(n) can be synthesized with a wide range of metals, (Mg, Mn, Fe, Co, Ni, Cu, and Zn), as well as mixedmetal compounds of up to ten different metals,¹⁶ allowing the reactivity of the OMS to be readily tuned. Finally, we recently demonstrated that Mg-MOF-74 has exceptional thermal and chemical stability, withstanding melt-infiltration with the highly reactive metal hydride NaAlH₄.¹⁰ Moreover, when doped with a titanium halide, this MOF reversibly catalyzes the rehydrogenation of the NaH and Al products into NaAlH₄, possibly by activating hydrogen or generating mobile reactive species. The detailed reaction data, catalyst characterization, and mechanism discussion presented here follow a limited and preliminary report by our team.¹⁷

We selected phenylethylphenyl ether (PPE), benzylphenyl ether (BPE), and diphenyl ether (DPE) (Scheme 1) as representative substrates which incorporate the β -O-4, α -O-4, and

4-O-5 (or 4,4') linkages. In addition to the pure MOFs, we also prepared IRMOF-74(I) and IRMOF-74(II) samples infiltrated with TiCl_x and Ni NPs, which were previously shown to catalyze aryl ether hydrogenolysis.¹⁸⁻²⁰ The infiltration of Ti species was performed using our previously described procedure,¹⁰ in which TiCl₄ is vapor-infiltrated into the pores of the activated MOF, followed by treatment with gaseous hydrogen at 90 °C. The insertion of Ni was achieved using methods pioneered by Fischer's group to create metal NPs in MOFs.²¹ The as-synthesized MOF-based catalysts were evaluated for their catalytic activity in hydrogenolysis reactions with the PPE, BPE and DPE substrates (Scheme 1), results of which are given in Table 1. The reactions were performed in stainless steel cells loaded with the substrate compound in p-xylene and the MOF catalyst. Mixtures were pressurized with H_2 and heated to 90 – 120 °C, well within the stability range for the IRMOF-74(I,II) materials.¹⁵ In all cases the reactor pressure was 10 bar H₂; such pressures are commonly used in industrial hydrogenation reactions, including many heterogeneous catalysis processes.²²

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59 60 Experiments using pure IRMOF-74(I,II) catalysts revealed that all three ethers react with H_2 to generate small amounts of phenol and the corresponding aromatic hydrocarbon (Scheme 1). In all cases, higher conversions were obtained using the IRMOF-74(II) catalyst. The difference can be quite substantial; for example, the conversion of PPE increased from 12% to 39% by using IRMOF-74(II) as the catalyst instead of IRMOF-74(I) (Table 1). Optimized geometries computed using density functional theory (DFT) indicate that all three substrates will fit within the pores of either MOF (see Supp. Info), suggesting that other factors, such as access to the OMS, the transition state geometry, or the reactant and/or product diffusion rates within the pore, are responsible for this trend.



Scheme 1. Reactions catalyzed by IRMOF-74(I, II).

Performing the hydrogenolysis reactions in the presence of the TiCl_x and Ni-infiltrated MOF catalysts leads to a significant increase in conversion efficiency (Table 1). GCMS and ¹H NMR analysis (Figs. S1 and S2) of the reaction products of all three substrate molecules clearly indicate new peaks corresponding to the monomeric products (1–4). The conversions obtained using both MOFs follow the trend PPE > BPE > DPE (Fig. S3). In all cases (with or without TiCl_x or Ni dopants), it is clear that the MOF-based catalysts facilitate the reaction; no substrate conversion occurred in the

absence of the MOF catalyst (Table S1, Supp. Info). When compared to commercial Ranev Ni and TiCl₃ (entries 25 and 26, Table 1), the Ni@IRMOF and Ti@IRMOF catalysts display similar conversion efficiency, but significantly better selectivity. In addition, the products of the reactions catalyzed by Ni Raney include substantial quantities of cyclohexanol, whereas no products of ring hydrogenation or ring opening were detected in any of the reactions catalyzed by the MOFs. PXRD data (Fig. 1) indicate that the MOF structure is unchanged by the hydrogenolysis reaction. Moreover, elemental analysis of the supernatant following the reaction yielded no evidence of Mg, Ti, or Ni, confirming that the MOF itself is the active catalyst and not a solubilized metalcomponent. Finally, repeated cycling of the catalysts did not affect their performance; for example, the recovered Ni@IRMOF-74(I) catalyst was reused for up to five tests without any significant loss in catalytic activity (Table S1, Supp. Info).

Table 1. Catalytic effect of tested MOFs on hydrogenolysis of aryl-ether compounds.

Entry	Catalyst	Sub-	Т, °С	Time	Conv.,	Selectivity			
		strate		hours	%	1	2	3	4
1	IRMOF-74(I)	PPE	120	16	12	87			91
2	Ti@IRMOF-74(I)	PPE	120	16	51	89			90
3	Ni@IRMOF-74(I)	PPE	120	16	68	91			94
4	IRMOF-74(II)	PPE	120	16	39	83			87
5	Ti@IRMOF-74(II)	PPE	120	16	60	79			83
6	Ni@IRMOF-74(II)	PPE	120	16	82	96			98
7	IRMOF-74(I)	BPE	120	16	10		78		84
8	Ti@IRMOF-74(I)	BPE	120	16	33		75		79
9	Ni@IRMOF-74(I)	BPE	120	16	57		82		85
10	IRMOF-74(II)	BPE	120	16	17		73		78
11	Ti@IRMOF-74(II)	BPE	120	16	42		84		89
12	Ni@IRMOF-74(II)	BPE	120	16	76		91		95
13	IRMOF-74(I)	DPE	120	16	4			79	82
14	Ti@IRMOF-74(I)	DPE	120	16	19			81	85
15	Ni@IRMOF-74(I)	DPE	120	16	29			80	87
16	IRMOF-74(II)	DPE	120	16	9			75	78
17	Ti@IRMOF-74(II)	DPE	120	16	20			77	80
18	Ni@IRMOF-74(II)	DPE	120	16	34			85	87
19	Ni@IRMOF-74(II)	PPE	90	16	51	86			92
20	Ni@IRMOF-74(II)	PPE	100	16	56	76			79
21	Ni@IRMOF-74(II)	PPE	110	16	67	83			82
22	Ni@IRMOF-74(II)	PPE	120	1	39	86			91
23	Ni@IRMOF-74(II)	PPE	120	2	47	92			95
24	Ni@IRMOF-74(II)	PPE	120	4	56	93			97
25	Raney Ni	PPE	120	16	76	81			75
26	TiCl ₃	PPE	120	16	39	74			73

Powder XRD indicates that both IRMOF-74(I) and IRMOF-74(II) showed no signs of structural degradation or loss of crystallinity upon infiltration with guest species or after catalytic tests (Fig. 1). The metal loadings, determined by elemental analysis, are 1.52 wt% Ti and 2.91 wt% Ni in IRMOF-74(I) and 1.75 wt% Ti and 3.07 wt% Ni in IRMOF-74(II). The Ti:Cl ratio in the titanium- infiltrated samples annealed under hydrogen is close to 1:3, suggesting that Ti⁺³ species are present in the final product.¹⁰ 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 present and are well dispersed within the MOF particles (Figure 2 and Fig. S4,

Supp. Info). Since the penetration depth of 15 keV electrons used in EDS measurements is about 5 μ m, this method probes the entire catalyst particle and not only its surface.



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



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

XPS measurements (Figure 2, bottom panels) indicate that the Ti(III) is present as TiCl₃, based on its characteristic peaks centered at 457.5 (Ti $2p_{3/2}$) and 463.0 eV (Ti $2p_{1/2}$) (Fig. 2, left bottom panel). In the case of Ni-doped samples, the species detected are 45% Ni⁰ and 55% Ni(OH)₂, as evi-

denced by the Ni $2p_{3/2}$ peaks located at 852.6 and 856.3 eV, respectively (Fig. 2, right bottom panel). The Ni(OH)₂ species likely result from the short exposure to air during the transfer of the sample into the XPS chamber (see Fig. S4, Supp. Info). Nitrogen BET analysis indicates that the surface area of IRMOF-74(I) is reduced from 1627 m^2/g for the activated material to 431 m^2/g and 459 m^2/g upon infiltration with Ti and Ni species, respectively. The surface area reduction is somewhat less for IRMOF-74(II), from 1736 m^2/g for the activated IRMOF-74(II) to 672 and 591 m^2/g for Ti@IRMOF-74(II) and Ni@IRMOF-74(II). As Mg-IRMOF-74 is a robust framework (TGA shows no decomposition below 350 °C²³ and it exhibits a surface area near the theoretical value after degassing under vacuum for 16 hours at 225 $^{\circ}C^{24}$), we believe that partial blockage of the 1D channels by guest species is the likely cause of the decreased surface area. Some pore collapse leading to amorphous domains undetectable by XRD cannot be fully ruled out, but if this occurs, these regions would most likely be inaccessible to guest molecules. The fact that the BET data show accessible pore volume remains after infiltration with Ti and Ni and that, in all cases, conversions are higher for the larger-pore IRMOF-74(II), points to reactions occurring within the MOF pores and not processes on the MOF surface.



Figure 3. Optimized gas-phase geometries for adsorbed PPE, $PPE+H_2$, and the hydrogenolysis products, obtained using the QM/QM method. Substrate compounds and OMS on the MOF are shown as spheres vs. the stick model of the cluster.

The activity of the catalysts follows the trend Ni@IRMOF-74 > Ti@IRMOF-74 > IRMOF-74, regardless of substrate, with the highest conversions obtained for the β -O-4 and α -O-4 linkages (82% and 76%, respectively) using Ni@IRMOF-74(II). More remarkably, all three catalysts display very good selectivity for hydrogenolysis vs. hydrogenation, with selectivity towards ethylbenzene and phenol formation from PPE as high as 98%. Based on the stoichiometry of the reactions in Scheme 1, equal amounts of the two products should be obtained. We find that slightly lower amounts of 1, 2, or 3 are obtained relative to phenol (Table 1). This is likely due to the higher volatility of the compounds, leading to finite concentrations in the head space above the reaction that are not fully recovered when the hydrogen pressure is released. The residual gas analysis (RGA) measurements of the volatiles present in the reaction vessel indicate that, in addition to hydrogen (m/z=2), fragments of aromatic hydrocarbons (m/z=78, 91) (Figure S6, Supp. info) from the solvent and/or reaction products are present as well.

That substrate confinement within the MOF pore plays a key role in establishing the efficiency and selectivity of these catalysts is supported by DFT calculations, which indicate that the OMS in the IRMOF-74 pores bind and orient the substrate within the pore. We used a cluster model (Figs. 3, S7, S8) consisting of four five-coordinate Mg^{2+} ions, each connected to five oxygen donor atoms, approximating one wall of the hexagonal pore. Computed binding energies (see details in the Supp. Info) indicate that all three substrates interact strongly with the cluster, even in the presence of the p-xylene solvent (Tables 2 and S3). These energies follow the trend PPE > BPE > DPE (Table 2), consistent with the experimental conversions. The involvement of the OMS is indicated by the observation that, for all three substrates, the relaxed cluster-substrate geometries position one of the substrate aromatic rings directly over a Mg²⁺ ion (shown in Fig. 3 for PPE and Fig. S9 for BPE and DPE). Global charge transfer analysis¹⁴ (Table S4) indicates that in the MOFsubstrate complex there is charge transfer from the model compound to the MOF, with the MOF acting as an electron acceptor and the aromatic ether molecules as electron donors. In addition, the computed free energies of hydrogenolvsis (ΔG°) on the cluster are more negative than the purely gas-phase reaction (Table 2). Examination of the predicted binding energies ΔH°_{B} for the reactants and products chemisorbed to the cluster indicates that, in addition to orienting the substrate, the cluster facilitates the reaction by stabilizing the products relative to the reactants; product binding energies are higher than those of the reactants (Table S3). (Note that ΔG° (gas phase) represents the overall thermodynamic change for the hydrogenolysis reaction, whether or not the cluster is present). Significantly, ΔH°_{B} is considerably stronger and ΔG° is more negative for PPE and BPE than for DPE. Moreover, the interaction of DPE with the cluster has very little effect on the predicted ΔG° (-81.8 kJ/mol on the cluster vs. -80.3 kJ/mol in the gas phase). These results are consistent with the experiments, which show much higher conversions for PPE and BPE compared to DPE for all catalysts and conditions tested. We also note that the MOF OMS may play a role in activating or at least orienting H₂ in the pores; it is established by both neutron scattering studies²⁵ and DFT calculations²⁶ that the Mg²⁺ OMS in Mg-IRMOF-74(I) are the strongest H_2 binding sites.

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Table 2. Computed substrate binding energies (ΔH°) (to the IRMOF-74 cluster model) and change in Gibbs free energy (ΔG°) upon hydrogenolysis at 393 K.

Substrate	Δi kJ/	Н° _в /mol	ΔG° , kJ/mol Substrate + H ₂ \rightarrow Hydrocarbon + PhOH								
	No	With	Gas	On MOF							
	Solvent	Solvent	phase	cluster							
PPE	135.1	81.9	-103.5	-142.3							
BPE	124.5	75.2	-106.6	-129.1							
DPE	44.9	37.2	-80.3	-81.8							

Clearly, the Ti and Ni dopants have an important, but different, role from the MOF itself, one that is not directly addressed by our DFT calculations. However, a reasonable hypothesis is that the transition metal species inside the MOF pores activate dihydrogen molecules more efficiently than the pure MOFs, reducing the activation energy of the hydrogenolysis reaction and generating higher concentrations of reactive H-species. Both titanium and nickel are well known to activate the dihydrogen molecule²⁷ and it is likely that they perform a similar role here. Our hypothesis suggests an additional, synergistic role for the MOF, namely, to increase the local concentration of active hydrogen, thereby accelerating the reaction. This is consistent with our prior study of Ti-doped Mg-IRMOF-74(I), which showed that the reversibility of NaAlH₄ decomposition in the pores is dramatically increased by the presence of the dopant.¹⁰

In summary, Mg-IRMOF-74(I) and Mg-IRMOF-74(II) selectively catalyze C-O aryl-ether bond cleavage, which is a new reaction category for MOFs. The results indicate that the MOF itself actively participates in the reaction, most likely through the interaction of the OMS with the substrate. Substrate conversion is enhanced by confinement of transition metal dopants within the MOF pores; additional mechanistic studies are required, however, to determine the extent to which these effects are synergistic. Although the observed catalytic activity is slightly lower compared to the best known C-O hydrogenolysis catalysts, ^{18-20,20,28} a significant advantage of these MOF-based catalysts is that their activity is achieved without the addition of a base, such as NaO^tBu.^{20,28} Interestingly, Ni@IRMOF-74 has higher reactivity with PPE than DPE, whereas the ligandless Ni catalyst reacts with these at comparable rates, suggesting the possibility of selective β -O-4 hydrogenolysis using the MOF. The Ni@IRMOF-74 catalysts also exhibit higher stability when recycled than Ni NPs stabilized on MIL-120, which exhibit consistent degradation of activity with reuse.^{9,29} Finally, in a few limited tests in which we suspended these catalysts in an ionic liquid (see Supporting Information), no structural degradation or dissolution was observed after 16 hours, indicating that these MOFs are compatible with some novel biomass pretreatment methods under development.³⁰

ASSOCIATED CONTENT

Supporting Information. Additional details on experiments and calculations. This material is available free of charge via the Internet at <u>http://pubs.acs.org</u>.

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TOC Figure

