

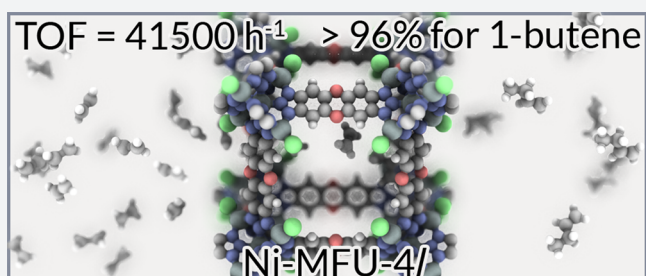
Selective Dimerization of Ethylene to 1-Butene with a Porous Catalyst

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Supporting Information

ABSTRACT: Current heterogeneous catalysts lack the fine steric and electronic tuning required for catalyzing the selective dimerization of ethylene to 1-butene, which remains one of the largest industrial processes still catalyzed by homogeneous catalysts. Here, we report that a metal–organic framework catalyzes ethylene dimerization with a combination of activity and selectivity for 1-butene that is premier among heterogeneous catalysts. The capacity for mild cation exchange in the material MFU-4l (MFU-4l = $Zn_5Cl_4(BTDD)_3$, $H_2BTDD = \text{bis}(1H\text{-}1,2,3\text{-triazolo}[4,5\text{-}b],[4',5'\text{-}i])\text{dibenzo}[1,4]\text{dioxin}$) was leveraged to create a well-defined and site-isolated Ni(II) active site bearing close structural homology to molecular tris-pyrazolylborate complexes. In the presence of ethylene and methylaluminoxane, the material consumes ethylene at a rate of 41,500 mol per mole of Ni per hour with a selectivity for 1-butene of up to 96.2%, exceeding the selectivity reported for the current industrial dimerization process.



INTRODUCTION

The process advantages afforded by continuous throughput and the ready separation of products have made heterogeneous catalysis an enabling technology for the large-scale manufacture of chemical commodities. However, conventional solid catalysts lack the capacity for precise structural design inherent in molecular catalysts that allows fine-tuning of reactivity and selectivity. The multiplicity and intractability of active sites often observed in heterogeneous catalysts complicate structure/activity-based control over reactivity. Consequently, many chemical processes requiring high selectivity rely on homogeneous molecular catalysis. The AlphaButol process, which produces 1-butene through the dimerization of ethylene on a 700,000 t scale annually,^{1,2} remains one of the largest applications of homogeneous catalysis, exceeded industrially by only a few others.³ Despite substantial academic and industrial efforts, new heterogeneous catalysts for ethylene dimerization have suffered from either a lack of activity or poor selectivity.^{4–8} Controlling the selectivity remains a paramount challenge because the product 1-butene is required in high purity for application as a comonomer in polyolefin synthesis^{2,9} and because the accumulation of higher molecular weight byproducts leads to reactor fouling.¹ The product distribution is defined by the relative rates of ethylene insertion versus chain termination, which can be profoundly influenced by variations in the ligand sphere or electronic structure of the active metal.^{10,11} However, fine-tuning of ligand design to control this reactivity has traditionally not been available to heterogeneous systems.

Metal–organic frameworks (MOFs) are a class of materials that offer tunability in the solid state at the molecular level. These

materials are built from metal clusters bridged by organic ligands, which define highly porous three-dimensional structures. Because both the metal clusters and the organic ligands can be modified, MOFs provide the level of control necessary to develop effective heterogeneous catalysts.^{12–15} A growing number of examples utilize these materials for catalysis, with the majority of work installing well-known homogeneous catalysts into the organic ligand.^{16–18} In contrast, the metal clusters, also known as secondary building units (SBUs), provide unique platforms to establish chemical reactivity without decreasing the surface area of the material.^{19–22} The SBUs behave like site-isolated molecules suspended throughout a heterogeneous matrix, a structural configuration which may extend the lifetime of the catalyst by eliminating bimolecular decomposition pathways and which potentially provides additional selectivity by pore shape and size. Furthermore, reactive transition metals may be incorporated into these SBUs by mild cation exchange,²² offering a rational strategy for installing well-defined active sites based on a crystallographically characterized coordination environment. In this work, we demonstrate that the SBUs in nickel-substituted MFU-4l (Ni-MFU-4l) catalyze the selective dimerization of ethylene with a combination of activity and selectivity that is premier among all heterogeneous catalysts.

In developing new heterogeneous catalysts for ethylene dimerization, we sought to employ SBUs that are structurally homologous to promising homogeneous catalysts which could benefit from site isolation. Molecular $[\text{Tp}^{\text{Mes}}\text{Ni}]^+$ ($\text{Tp}^{\text{Mes}} =$

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HB(3-mesitylpyrazolyl)₃ complexes are particularly attractive candidates in this sense: they display turnover frequencies of ~30,000 mol of ethylene converted per mole of nickel per hour, with butenes accounting for up to 87% of the products,²³ but suffer from inactivation by catalyst aggregation. We thus surmised that isolating Tp-like moieties in a MOF would offer a more robust environment for catalytic ethylene dimerization. Four of the five Zn²⁺ ions in each SBU of MFU-4l are coordinated in such a manner: the SBUs contain a central Zn atom that is octahedrally coordinated by six nitrogen atoms, and four tetrahedral Zn²⁺ ions coordinated by three nitrogen atoms and a chloride (Figure 1). These tetrahedral Zn²⁺ ions are

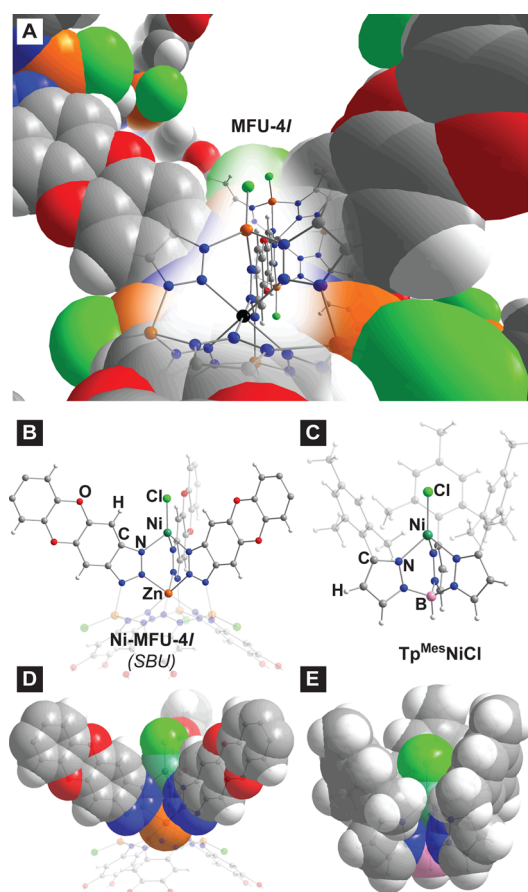


Figure 1. Structure of Ni-MFU-4l and Tp^{Mes}NiCl. (A) A representation of the three-dimensional structure of Ni-MFU-4l highlighting the exposure of the SBUs to the pores. (B) Ball-and-stick model of the inorganic secondary building unit in Ni-MFU-4l. (C) Ball-and-stick model of Tp^{Mes}NiCl. (D) A space-filling model of the inorganic cluster of Ni-MFU-4l. (E) A space-filling model of Tp^{Mes}NiCl.

exposed to the MOF's cubic pores (Figure S1), which display apertures between 1.1 and 2.0 nm.²⁴ Because the bond angles and lengths surrounding these pore-accessible Zn²⁺ ions are almost identical to those found in Tp complexes,²⁵ we reasoned that Ni-MFU-4l could indeed serve as a very proficient heterogeneous catalyst for ethylene dimerization.

RESULTS AND DISCUSSION

Direct solvothermal synthesis of a nickel-doped MFU-4l from mixtures of Ni²⁺ and Zn²⁺ starting materials was unsuccessful, producing only amorphous solids. However, simple exchange of the parent zinc framework by soaking in an *N,N*-dimethylforma-

mid (DMF) solution of Ni(NO₃)₂·6H₂O, under conditions mimicking those reported previously,^{26,27} afforded nickel-substituted materials with a Ni content that could be tuned by varying the soaking time and temperature. Exchanging Zn²⁺ ions for Ni²⁺ does not affect the structural integrity or the porosity of the MOF, as verified by comparisons of the exchanged materials with the parent Zn materials using powder X-ray diffraction and N₂ gas sorption analysis (Figure S2, Figure S3).

Ni-MFU-4l displays excellent activity for ethylene dimerization, whereas the parent Zn analogue remains inactive. A typical catalytic protocol consisted of the addition of methylalumoxane (MAO) to a rapidly stirred suspension of Ni-MFU-4l in toluene, with subsequent pressurization with ethylene gas. Upon completion, the reactor was rapidly cooled with a dry ice/acetone bath to condense the oligomerized products, and the reaction was quenched with ice-cold water. After a 60 min reaction at 25 °C, 30 bar of ethylene, and in the presence of 100 equiv of MAO, a Ni-MFU-4l sample with a Ni:Zn ratio of ~1:9 (Ni(10%)-MFU-4l) shows a turnover frequency of 21,000 mol of ethylene consumed per mole of Ni per hour. The products contain 94.9% butenes, 4.8% hexenes, and no other detectable higher oligomers, with only trace polyethylene (0.3% by weight). Leaching experiments indicate that the observed activity is not attributable to homogeneous decomposition products (Figure S8). Further optimization of the reaction conditions showed that temperature has a dramatic effect on the catalytic performance of Ni-MFU-4l. For a given ethylene pressure, the dimerization activity is comparable at 0 and 25 °C, although no polymeric residues are isolable at 0 °C. There is, however, a marked drop-off in oligomerization activity when the reaction temperature is increased to 50 °C, with a concomitant decrease in the selectivity for 1-butene in favor of the isomerized, less desirable product 2-butene (Table 1, entries 5–13).

The reaction pressure also plays a key role in the catalytic performance of Ni-MFU-4l. Two distinct reactivity regimes are present for Ni(10%)-MFU-4l when the ethylene pressure is varied between 5 and 50 bar at 25 °C in the presence of 100 equiv of MAO (Figure 2B). The activity of Ni(10%)-MFU-4l has a first order dependence on ethylene at pressures below 25 bar, which is consistent with the Cossee–Arlman mechanism that is commonly proposed for ethylene oligomerization with homogeneous nickel complexes (Figure 2A).¹⁰ The activity of Ni(10%)-MFU-4l plateaus at pressures higher than 25 bar, although the selectivity for 1-butene continues to increase at higher pressures of ethylene (Figure 2C). This trend suggests that higher ethylene pressure suppresses the competitive reinsertion of 1-butene, which would contribute to the 2-butene and hexene byproduct formation.²⁸

Activation of Ni-MFU-4l by an alkyl aluminum reagent is essential for catalysis, and reactivity is strongly influenced by the identity and relative loading of this activator. No catalytic activity is observed in the absence of an aluminum activator, and the replacement of MAO with diethylaluminum chloride (Et₂AlCl) or triethylaluminum (Et₃Al) leads to a greatly diminished activity. For instance, replacement of MAO with an equivalent amount of Et₂AlCl retards the turnover frequency of Ni(10%)-MFU-4l at 50 bar and 25 °C from 21,000 h⁻¹ to 4,700 h⁻¹. The amount of MAO also correlates positively with the observed catalytic activity. This is most obvious when the quantity of MAO is doubled from 50 to 100 equiv (Table 1, entries 3 and 4). Increasing the amount of MAO beyond 100 equiv nevertheless leads to incremental improvements in activity, which reaches 27,000 mol of ethylene consumed per mole of nickel per hour in

Table 1. Ethylene Dimerization with Ni-MFU-4l^a

entry	pressure (bar)	T (°C)	MAO equivalents	TOF (h ⁻¹) ^f	selectivity (wt %)			
					C ₄ ^g	C ₆ ^h	α -C ₄ ⁱ	overall 1-butene ^j
1 ^b	50	25	500	27,000	96.5	3.5	92.3	89.1
2 ^b	50	25	250	26,700	97.4	2.6	93.7	91.3
3 ^b	50	25	100	21,000	97.2	2.8	94.6	92.0
4 ^b	50	25	50	5,900	95.8	4.2	84.7	81.1
5 ^b	50	0	100	22,600	98.4	1.6	97.8	96.2
6 ^b	50	25	100	21,000	97.2	2.8	94.6	92.0
7 ^b	50	50	100	1,700	87.5	12.5	80.5	70.4
8 ^b	30	0	100	21,600	97.4	2.6	95.5	93.0
9 ^b	30	25	100	21,000	95.2	4.8	86.9	82.7
10 ^b	30	50	100	1,600	89.3	10.7	83.1	74.2
11 ^b	15	0	100	6,300	94.2	5.8	93.5	88.1
12 ^b	15	25	100	11,100	94.8	5.2	80.7	76.5
13 ^b	15	50	100	600	85.2	14.8	79.3	67.6
14 ^b	5	25	100	3,600	92.9	7.1	72.8	67.6
15 ^b	10	25	100	7,000	94.4	5.6	80.8	76.3
16 ^b	15	25	100	11,100	94.8	5.2	80.7	76.5
17 ^b	20	25	100	16,400	94.9	5.1	81.9	77.7
18 ^b	25	25	100	19,800	95.7	4.3	86.8	83.1
19 ^b	30	25	100	21,000	95.2	4.8	86.9	82.7
20 ^b	40	25	100	20,000	96.6	3.4	94.3	91.1
21 ^b	50	25	100	21,000	97.2	2.8	94.6	92.0
22 ^c	50	25	500	9,100	97.3	2.7	93.0	90.5
23 ^b	50	25	500	27,000	96.5	3.5	92.3	89.1
24 ^d	50	25	500	39,600	97.3	2.7	94.7	92.1
25 ^e	50	25	500	41,500	97.4	2.6	94.5	92.0

^aAs determined by GC analysis. ^bCatalyst is Ni(10%)-MFU-4l ^cCatalyst is Ni(30%)-MFU-4l ^dCatalyst is Ni(3%)-MFU-4l ^eCatalyst is Ni(1%)-MFU-4l. ^fMoles of ethylene converted per mole of nickel per hour, determined by GC analysis. ^gPercent oligomeric products that are C₄ olefins. ^hPercent oligomeric products that are C₆ olefins. ⁱPercent 1-butene relative to all C₄ products. ^jThe overall selectivity for 1-butene among all products.

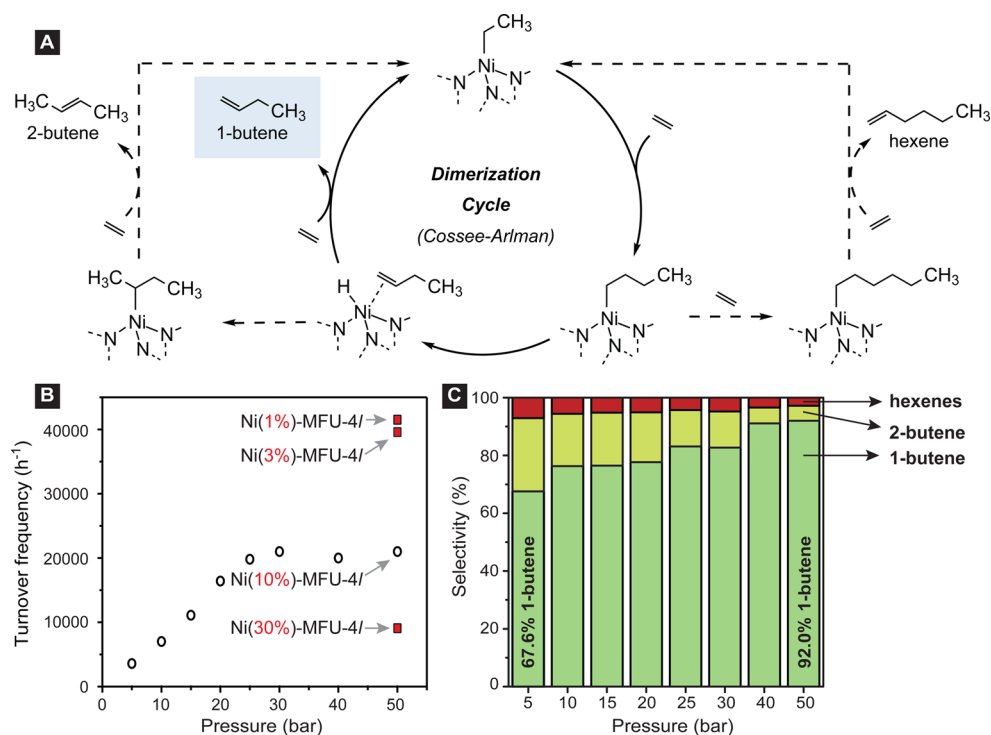


Figure 2. Mechanism, activity, and product distribution of ethylene dimerization with Ni-MFU-4l. (A) Proposed catalytic cycle for ethylene dimerization in Ni-MFU-4l. (B) The pressure and Ni content dependence of ethylene dimerization in Ni-MFU-4l. (C) The product distribution at various ethylene pressures for Ni(10%)-MFU-4l at 25 °C with 100 equiv of MAO.

Table 2. Heterogeneous Catalysts for Ethylene Dimerization

catalyst	pressure (bar)	T (°C)	TOF (h ⁻¹) ^a	selectivity (wt %)			reference
				C ₄ ^b	C ₆ ^c	α -C ₄ ^d	
Ni(1%)-MFU-4l	50	25	41,500	97.4	2.6	94.5	this work
Ni(10%)-MFU-4l	50	0	22,600	98.4	1.6	97.8	this work
Ni-MCM-48	35	150	47,400	42	37	N.R.	6
Ni-MCM-41 (3.4 Å)	35	150	26,800	41	15	N.R.	6
Ni-MCM-41 (8.5 Å)	35	150	40,700	48	33	N.R.	6
NiO/Al ₂ O ₃	27.5	150	190	85.4	9.6	100	8
Ni-Y	40	50	10,482	67	10	N.R.	4, 5
Ni-MCM-36	40	150	16,000	45	25	35	7
Ni-MCM-36	40	70	4,200	81	8	55	7
MixMOF-Ni-b	20	40	16,400	92.7	6.1	N.R.	17
MixMOF-Ni-b	20	20	2,500	79.5	6.9	N.R.	17
IRMOF-3-Ni-a	20	20	2,200	35.0	9.3	N.R.	17
Ni@(Fe)MIL-101	30	25	20,900	N.R.	N.R.	N.R.	16
Ni@(Fe)MIL-101	15	20	9,400	89.3	9.5	N.R.	16
Ni@(Fe)MIL-101	15	10	6,300	95	4.5	N.R.	16
Ni@(Fe)MIL-101	15	0	10	N.R.	N.R.	N.R.	16
Ni@(Fe)MIL-101	15	30	3,600	93	6.5	N.R.	16
Ni@(Fe)MIL-101	50	25	17,700	89.6	3.6	94.5	this work, SI
Ti(OEt) ₄ /AlPO ₄	38	85	28,700	N.R.	N.R.	N.R.	34
Ti(OEt) ₄ /AlPO ₄	38	85	22,500	N.R.	N.R.	N.R.	34
Ti(OEt) ₄ /Silica	38	85	25,400	N.R.	N.R.	N.R.	34
Ti(OEt) ₄ /Silica	38	85	18,400	N.R.	N.R.	N.R.	34

^aMoles of ethylene converted per mole of nickel per hour. N.R. = not reported. ^bThe percentage of oligomeric products that are C₄ olefins. ^cThe percentage of oligomeric products that are C₆ olefins. ^dThe percentage of 1-butene relative to all C₄ products.

the presence of 500 equiv of MAO at 50 bar and 25 °C (Table 1, entry 1). Under these conditions, Ni(10%)-MFU-4l shows a selectivity of 96.5% for butenes, with an overall selectivity of 89.1% for 1-butene. The selectivity for 1-butene increases even further when catalysis is run with 100 equiv of MAO at 50 bar and 0 °C (Table 1, entry 5). These conditions lead to a turnover frequency of 22,600 mol of ethylene consumed per mole of nickel per hour and an optimized selectivity of 98.4% for butenes, a record among all active heterogeneous catalysts, with 1-butene making up 97.8% of the C₄ fraction. Indeed, the optimized overall selectivity for 1-butene is thus 96.2%, a technologically significant improvement over the industrial process, whose selectivity for 1-butene under operating conditions is 93%.^{2,29–31} Importantly, under these optimized conditions, Ni(10%)-MFU-4l produces C₆ olefins as the sole observable byproducts, with no higher oligomers observed by GC, and no isolable polymers. In an industrial setting, these C₆ byproducts do not foul the reactor, can readily be separated using technology currently employed in the AlphaButol process,² and are valuable themselves as copolymerization monomers.

Having identified optimal reaction conditions for catalysis, we sought to evaluate the role of mass transport on the activity of Ni-MFU-4l by examining the impact of nickel loading on the turnover frequency. Subjecting Ni-MFU-4l samples with molar Ni loadings of 1%, 3%, 10%, and 30% of the total metal content to the optimal catalytic conditions revealed clear differences in turnover frequency. Thus, the turnover frequency decreased from 27,000 mol of ethylene consumed per mole of nickel per hour for Ni(10%)-MFU-4l to 9,100 h⁻¹ for Ni(30%)-MFU-4l. Potential deactivation stemming from the agglomeration of Ni sites on the same or neighboring SBUs notwithstanding, the decreasing turnover frequency with increased nickel loading is consistent with mass transport limitations typical of porous catalysts. Accordingly, decreasing the nickel loading should

improve the activity per nickel site. Indeed, under optimized catalytic conditions Ni(1%)-MFU-4l exhibits a turnover frequency of 41 500 h⁻¹ (Table 1, entries 22–25). This value is commensurate with the activity of homogeneous [Tp^{Mes}Ni]⁺, which has a maximum reported activity of 34,600 h⁻¹ when treated with MAO. Assuming that the intrinsic activities of Ni-exchanged SBUs and [Tp^{Mes}Ni]⁺ are within the same range, these results suggest that the Ni-SBUs act as heterogenized molecular catalysts and are the active species in Ni-MFU-4l, with the majority of nickel sites contributing to catalysis, not just those on the surface.

Surprisingly, although the maximum observed turnover frequency of Ni-MFU-4l is similar to that of the [Tp^{Mes}Ni]⁺, its maximum selectivity for 1-butene, 96.2%, is notably superior to the latter, which only reaches 80.8%. This superior selectivity is not solely attributable to differences in reaction conditions, because Ni-MFU-4l still has a selectivity of 93.0% for 1-butene when operated under the most selective conditions for the molecular [Tp^{Mes}Ni]⁺ complexes. Although shape or size selectivity induced by the pores of Ni-MFU-4l may explain the preference for butenes relative to hexenes, they do not account for the higher 1-butene selectivity observed with the heterogeneous catalyst. An alternative explanation is that the less sterically encumbered active site in Ni-MFU-4l enhances the rate of chain transfer relative to chain propagation or chain isomerization. By analogy, cationic Ni²⁺ α -diimine complexes are well-known catalysts for ethylene oligomerization, but turn into ethylene polymerization catalysts when steric bulk is added in positions axial to the active site.^{32,33} It is thus apparent that the Ni environment within Ni-MFU-4l balances active site accessibility and pore-induced shape/size selectivity, thereby leading to the high selectivity for 1-butene.

One of the major attractions in heterogenizing homogeneous catalysts stems from the possibility of extending the catalyst

lifetime by eliminating bimolecular decomposition pathways. To study the lifetime of Ni-MFU-4l and the potential for catalyst recycling, we constructed a two-reactor system that allows us to distill the reaction products without exposing the Ni-MFU-4l/MAO slurry to the atmosphere. This experimental setup allows the removal of products by distillation and repressurization of the reactor for evaluating reactivity in consecutive catalytic runs. A reactor charged with Ni(10%)-MFU-4l was thus cycled continuously over 72 h (8 cycles), with only a minor decrease in catalyst activity (Figure S10). In contrast, the activity of the industrially employed homogeneous catalysts for ethylene dimerization decreases by 50% over the course of 1 h.³¹

Ni-MFU-4l compares favorably to other heterogeneous catalysts for ethylene dimerization. A large amount of work has focused on using nickel-exchanged zeolites and mesoporous silica as catalysts for the oligomerization of ethylene, with some degree of success.^{4–7} However, these catalysts are poorly selective for dimerization, with butenes typically comprising only 40–45% of the resulting products. Furthermore, Ni-exchanged zeolites and mesoporous silica are also poorly selective for α -olefins, with overall selectivity for 1-butene of only \sim 15%. Previous efforts to develop MOF catalysts for ethylene dimerization have focused on installing well-known homogeneous catalysts into the organic linkers^{16,17} or onto the inorganic SBUs.¹⁸ Although these catalysts show activities ranging from 6,000 to 20,000 h⁻¹, reasonable selectivities for butenes of at least 90% were associated only with the lower activities. Moreover, some of these catalysts form substantial polymeric deposits that lead to catalyst deactivation.¹⁸ Indeed, even under identical conditions to those optimized for Ni-MFU-4l, a freshly prepared sample of Ni@(Fe)MIL-101 showed an ethylene consumption activity of only 17,700 h⁻¹, with abundant production of polyethylene (Table 2, Table S1, Figure S11). Supported titanium alkoxides come closest to Ni-MFU-4l in terms of activity.³⁴ However, these supported titanium catalysts produce substantial polymeric deposits accounting for as much as 5% of the total products.³⁴ Polymeric byproducts present a more substantial liability for large-scale production due to reactor fouling and are much less desirable as end products than the C₆ olefins observed under optimized conditions with Ni-MFU-4l.

The foregoing results demonstrate the considerable potential for using MOFs to catalyze industrially significant reactions that currently have no viable solutions in heterogeneous catalysis. Under optimized conditions, the selectivity of Ni-MFU-4l for 1-butene surpasses that of the industrial homogeneous catalyst, whereas its activity is on par with the best heterogeneous catalysts and with analogous homogeneous [Tp^{Mes}Ni]⁺ complexes. The outstanding activity and selectivity of Ni-MFU-4l demonstrate the power in utilizing cation exchange in MOFs to develop well-defined heterogeneous catalysts. We anticipate that exploring further reactivity at the metal nodes of MOFs will lead to important new applications for these highly tunable materials in heterogeneous catalysis.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.6b00012.

Experimental methods, control experiments, comparison with alternative MOF catalysts, and Figures S1–S11 (PDF)

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Notes

The authors declare the following competing financial interest(s): The authors and MIT have filed a patent on some of the results herein.

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