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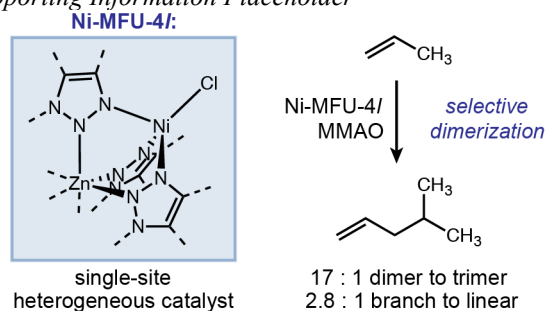## Selective Dimerization of Propylene with Ni-MFU-4

Selective Dimerization of Propylene with Ni-MFU-4*l*

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Supporting Information Placeholder

single-site heterogeneous catalyst

17 : 1 dimer to trimer
2.8 : 1 branch to linear

ABSTRACT: We report the selective dimerization of propylene to branched hexenes using Ni-MFU-4*l*, a solid catalyst prepared by cation exchange. Analysis of the resulting product distribution demonstrates that the selectivity arises from 2,1-insertion and slow product reinsertion, mechanistic features reproduced by a molecular nickel *tris*-pyrazolylborate catalyst. Characterization of Ni-MFU-4*l* by X-ray absorption spectroscopy provides evidence for discrete, *tris*-pyrazolylborate-like coordination of nickel, underscoring the small-molecule analogy that can be made at metal-organic framework nodes.

BODY

The nodes of metal-organic frameworks (MOFs) represent promising targets for industrially significant single-site heterogeneous catalysis. These secondary building units (SBUs) are often capable of cation exchange with preservation of their local coordination structure,[1,2] offering a predictable strategy for installing a discrete active site in a solid, high-surface area medium. Along these lines, we recently reported the selective dimerization of ethylene to 1-butene using Ni-MFU-4*l* (**1**),[3] prepared by replacing Zn^{2+} ions with Ni^{2+} in $Zn_5Cl_4(BTDD)_3$ (MFU-4*l*, $H_2BTDD =$ bis(1H-1,2,3-triazolo[4,5-b],[4',5'-i])dibenzo[1,4]dioxin)).[4] The cation exchange, performed by soaking MFU-4*l* in a Ni^{2+} solution at room temperature, preserves the crystallinity and high surface area of of the parent material, suggesting that Ni^{2+} has been incorporated into an SBU with an otherwise preserved structure.[4]

Here, we evaluate **1** as a heterogeneous catalyst for the selective dimerization of propylene, a reaction for which molecular complexes provide the best chain- and

regioselectivity.[5–7] Industrially, this process continues to rely on soluble nickel catalysts, despite the large reactor volumes and challenging catalyst recovery associated with homogeneous catalysis.[8–11] We reasoned that Ni-MFU-4*l* would be a selective catalyst for this reaction based on the proposed structural analogy between **1** and molecular *tris*-pyrazolylborate (Tp) complexes, given the selective olefin dimerization activity of catalysts such as $Tp^{Mes}NiCl$ (**2**).[12] Because MFU-4*l* coordinates Zn^{2+} tetrahedrally with three azolate nitrogens, it serves as a good template for scorpionate-like coordination of Ni^{2+} ions, installed through cation exchange (Figure 1).[13] Indeed, computational modeling of Ni-MFU-4*l* within the Kohn-Sham DFT construct (DFT-**1**, Figure 1) and comparison of the model with the reported crystal structure of scorpionate **2** confirmed a close structural analogy between **1** and **2** (Table S3.1): both feature a pseudotetrahedral arrangement of three nitrogen atoms and one chloride. The most

Figure 1. The structural analogy between Ni-MFU-4*l* and $Tp^{Mes}NiCl$ (structures abbreviated for clarity).
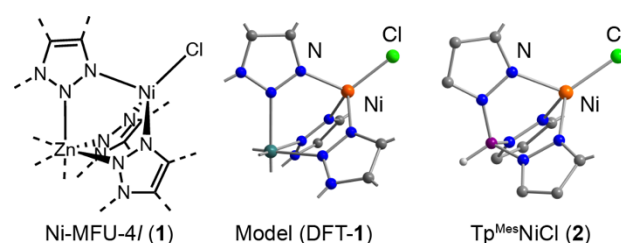

Ni-MFU-4*l* (**1**)   Model (DFT-**1**) $Tp^{Mes}NiCl$ (**2**)

Table 1. Fitting results of the EXAFS spectra. The average error in bond length is 0.01 Å and in σ^2 is 0.002 Å^2. The fitting ranges for Tp_2Ni and Ni-MFU-4*l* are $\Delta k = 3.0$-11.0 Å^{-1} and $\Delta R = 1.0$-2.0 Å. For $NiCl_2$, the ranges are $\Delta k = 3.0$-10.0 Å^{-1} and $\Delta R = 1.4$-2.4 Å

Sample	Scattering Pair	Coordination Number	Bond Length (Å)	σ^2 (Å^2)
Tp_2Ni	Ni–N	6	2.06	0.006
$NiCl_2$	Ni–Cl	6	2.40	0.009
Ni-MFU-4*l*	Ni–N	3	1.99	0.006
	Ni–Cl	1	2.14	0.003
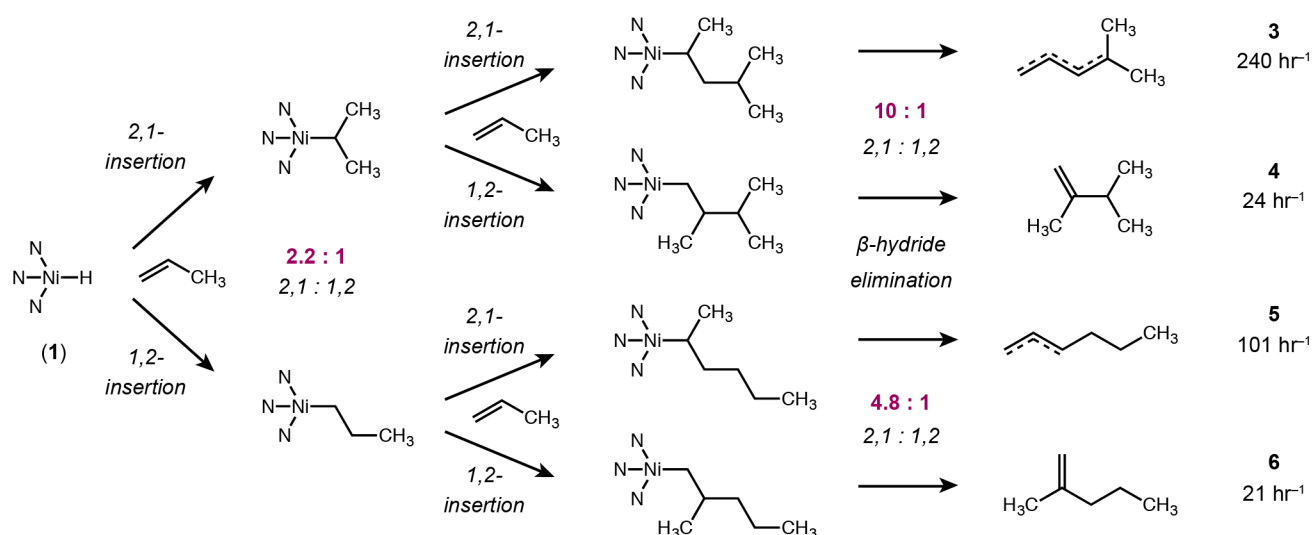
Scheme 1. Product distribution and insertion tree for the dimerization of propylene by **1** (yields by NMR).

significant difference is a slightly wider bite angle for DFT-**1**, with ∡N-Ni-N = 97.06° versus 92.88° for **2**. Notably, the porous structure of MFU-4*l* is well preserved in DFT-**1** (Figure S3.1).

To verify the Ni^{2+} coordination environment, **1** was examined by X-ray absorption spectroscopy (XAS). The XAS spectra of Tp_2Ni and anhydrous $NiCl_2$ were also collected for comparison. The edge energy obtained for Ni-MFU-4*l* agrees well with both of these standards (Table S2), consistent with a Ni(II) oxidation state in **1**. Furthermore, Ni-MFU-4*l* displays a more intense pre-edge feature than either $NiCl_2$ or Tp_2Ni, consistent with a lower-symmetry, pseudo-tetrahedral coordination environment (Figure S4.2). Fitting the X-ray absorption fine structure (EXAFS) data resulted in three Ni–N bonds (1.99 Å, Table S4.2) and one Ni–Cl bond (2.14 Å), similar in length to those of DFT-**1** (1.95 Å and 2.12 Å respectively). Fitting a different coordination number and a different combination of scattering atoms both gave significantly worse fits, allowing us to rule out other potential coordination modes for Ni^{2+} in **1**.

The competence of **1** and **2** as propylene dimerization catalysts was evaluated in the presence of modified methylaluminoxane-12 (MMAO-12) and 6 bar of applied propylene pressure, under slurry-phase and semi-batch conditions as in the ethylene dimerization with **1**.[3] On a total Ni basis, **1** is less active than **2** (490 moles of product per mole Ni per hour, versus 2,000 hr^{-1} respectively), and both catalysts are considerably less active toward propylene than toward ethylene.[12,14] These differences in reactivity can be explained based on the greater steric hindrance of propylene compared to ethylene, and the differences in the steric environment of the active sites in **1** and **2**. Nevertheless, the dimer to trimer ratios (C6:C9) are high and nearly identical for the two catalysts (17:1). Neither MFU-4*l* nor MMAO-12 show oligomerization activity in the absence of nickel.

To gain insight into the C6 regioselectivity, propylene dimerization was repeated using C_6D_6 as solvent, so that the resulting product distribution could be analyzed by quantitative ^{13}C-NMR. This analysis reveals a modest selectivity for branched products, which are valuable as anti-knock additives for gasoline,[8–11] with a 2.8 : 1 ratio of dimers **3**, **4**, and **6** to **5** (Scheme 1). The low overall concentration of chain-walking products suggests that reinsertion of the products is slow, also consistent with the high C6:C9 selectivity. Consequently, the resulting product distribution can be analyzed as a product of primary insertion selectivity.[15–17] Indeed, we recently showed that ethylene dimerization with **1** proceeds through such a coordination-insertion mechanism.[14] Parsing the product distribution into an insertion tree indicates a mechanistic preference for 2,1- over 1,2-insertion of propylene (Scheme 1). In this analysis, regioselectivity increases with the steric size of the alkyl group on nickel (H < 1-propyl < 2-propyl). Significantly, this branch distribution is well reproduced by **2** under analogous conditions, including a comparable step-specific 2,1-insertion selectivity and low isomerization rate (Figure S6.1).

In summary, we have shown that Ni-MFU-4*l* serves as a selective propylene dimerization catalyst whose selectivity can be understood by structural and mechanistic analogy to molecular Ni(II) *tris*-pyrazolylborate complexes. This work underscores the molecule-like reactivity and tunability of MOF nodes that underlie catalyst development and selectivity for α-olefin dimerization, which represents a longstanding goal of heterogeneous catalysis.

ASSOCIATED CONTENT

Supporting Information. The supporting information is available free of charge on the ACS Publication website. Experimental details, gas chromatograms, NMR data, computational methods, XAS data.

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