

## Metal–Organic Frameworks as Potential Catalysts for Industrial 1-Butene Production

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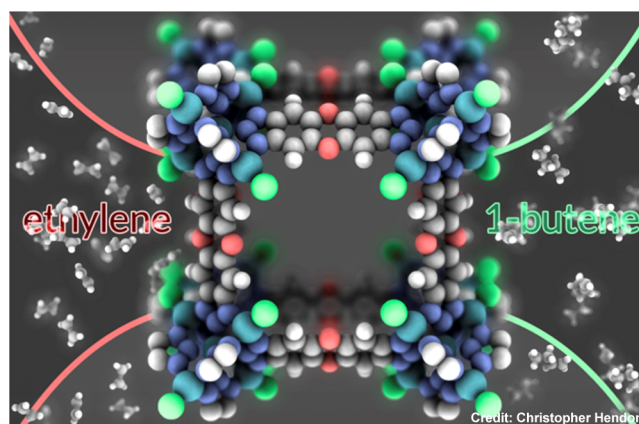
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Since its accidental discovery in 1933, polyethylene has become one of the most common plastics in our daily life. As a member of the polyethylene family, linear low-density polyethylene (LLDPE) is produced by copolymerizing ethylene with alpha olefins. LLDPE features a linear backbone with short alkyl branches capable of sliding against each other without becoming entangled upon stretching, imbuing LLDPE with excellent tensile strength. These features render it an ideal material for food wraps and other stretchable films. A key comonomer for LLDPE, 1-butene, can be produced from cracking higher alkanes, but ethylene dimerization (ED) produces the higher purity 1-butene required for LLDPE production. Consequently, the ED reaction is responsible for half of the 1-butene used industrially in LLDPE production, a staggering 700,000 t annually.<sup>1</sup> Given a choice, industry would prefer to employ heterogeneous catalysts for this process, due to their ease of recycling, separation, and typically longer lifetimes. Yet, decades of efforts in developing solid catalysts that would be competitive with the homogeneous nickel or titanium ED catalysts that are currently used industrially have been met with significant challenges, stemming largely from the accumulation of polyethylene that fouls the reactors, leaching of metal species from immobilized catalysts, or simply poor activity and/or selectivity.<sup>2</sup>

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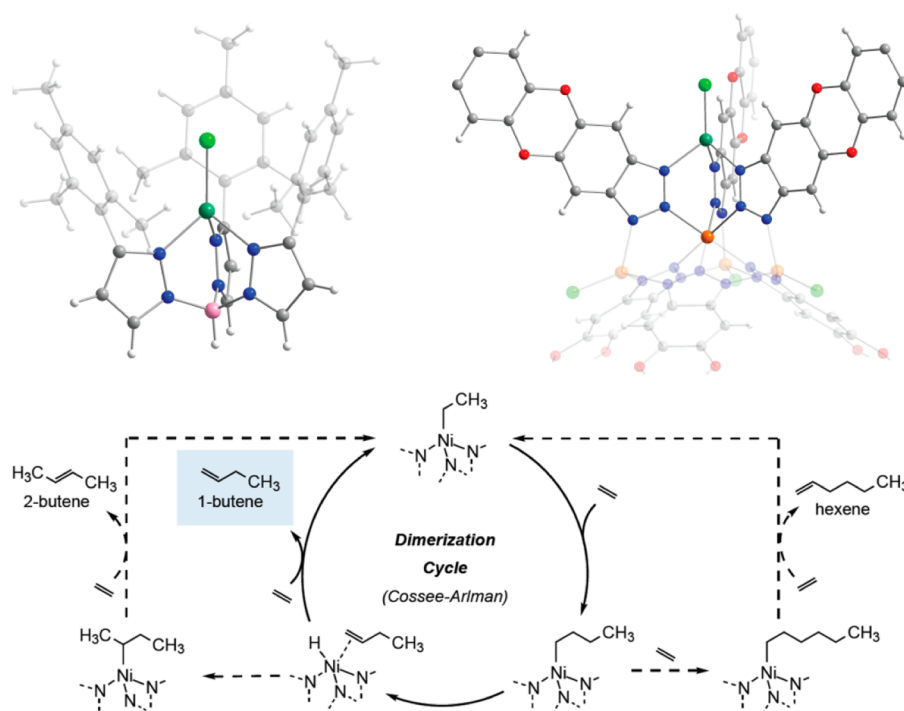
Dincă and co-workers have introduced a metal–organic framework catalyst that could help move industrial 1-butene production into the gas phase.



Indeed, this new MOF catalyst outperforms all existing heterogeneous catalysts and even beats the industrial homogeneous catalyst in terms of selectivity for 1-butene.<sup>3</sup>

Inspired by the high-performance molecular catalyst  $(\text{Tp}^{\text{Mes}})\text{NiCl}$  ( $\text{Tp}^{\text{Me}} = \text{hydrotris}(3\text{-mesitylpyrazolyl})\text{borate}$ ),<sup>4</sup> Dincă and co-workers designed these MOF catalysts to feature a  $\text{Ni}^{\text{II}}$  ion with a coordination environment very similar to  $(\text{Tp}^{\text{Mes}})\text{NiCl}$  through postsynthetic metal exchange<sup>5</sup> of the metal nodes in the known MOF MFU-4l (see Figure 1).<sup>6</sup> Microporous catalysts such as MOFs provide several key advantages over their molecular counterparts: (1) the high porosity enables a high density of active sites per mass/volume of catalyst; (2) the monodisperse, nanometer-sized pores can provide size and shape selectivity, thereby avoiding longer oligomers and polymer products that cannot fit within MOF pores; (3) well-defined active sites act as single-site catalysts, thereby affording similar tunability to homogeneous catalysts; and (4) spatial isolation of the active

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**Figure 1.** Top: Structures of the molecular catalyst  $(\text{Tp}^{\text{Mes}})\text{NiCl}$  (left) and the MOF catalyst Ni-MFU-4l (right). Orange, green, light green, red, blue, gray, pink, and white spheres represent Zn, Ni, Cl, O, N, C, B, and H atoms, respectively. Bottom: Proposed catalytic cycle for ethylene dimerization in Ni-MFU-4l. Graphics from ref 3 used by permission. Copyright 2016 American Chemical Society.

sites in a robust framework eliminates bimolecular decomposition pathways of the catalysts, enhancing the catalyst lifetime and reusability.

This study shows that at room temperature, the Ni-MFU-4l catalysts exhibit strikingly high activity, with turnover frequencies of up to 41,500 per hour. Record-high selectivities of up to 98.4% for butenes is achieved under optimized conditions, 97.8% of which is 1-butene. Notably, the polymeric products that typically foul reactors for ED and deactivate catalysts, especially on the industrial scale,<sup>7,8</sup> were not detected. Increasing selectivity has long been considered a key challenge for industrial catalyst design, because ED is essentially an arrested polymerization that relies upon selective chain termination after the catalyst stitches exactly two ethylene molecules, eliminating 1-butene and turning over (see Figure 1). Chain propagation, where additional ethylene molecules insert sequentially at the metal center to produce higher oligomers and polymers, and chain isomerization, which can move the terminal double bond to an internal one to yield less valuable 2-butene, both compete with chain termination and are notoriously difficult to control.<sup>9</sup> By decreasing the steric crowding around the Ni atom and by pinning it inside the MOF in a scorpionate-like environment, Dincă and co-workers successfully minimized these two undesirable catalytic pathways, increased the activity of their catalyst relative to the homogeneous  $(\text{Tp}^{\text{Mes}})\text{Ni}$  analogue, and enabled the catalytic production of

Dincă and co-workers successfully minimized these two undesirable catalytic pathways, increased the activity of their catalyst relative to the homogeneous  $(\text{Tp}^{\text{Mes}})\text{Ni}$  analogue, and enabled the catalytic production of high purity 1-butene with high activity and excellent cyclability.

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The fact that Ni-exchanged MFU-4l outperforms the molecular species  $(\text{Tp}^{\text{Mes}})\text{NiCl}$  in nearly all aspects, together with its excellent reusability, promises a real, practical solution for industrial use in ED. The catalysis here is still in the solution-phase, both because this allowed direct comparison with the homogeneous industrial catalyst and other heterogeneous catalysts, and because the reaction requires an aluminum alkyl initiator, methyl-aluminoxane. Nevertheless, the development of this competitive heterogeneous catalyst brings the intriguing goal of turning ED into a continuous, gas-phase process in a flow reactor ever so closer to reality.<sup>8</sup> By designing a reactor with external thermal management, and coupling the outlet with a purification system that can feed unreacted ethylene back to the reactor, one can imagine

a transformative change in the industrial process for 1-butene production. Perhaps most importantly, the report by Dincă and co-workers provides an significant demonstration of MOF-based heterogeneous catalysis, by offering a palpable solution to a real, existing industrial challenge that no other classical heterogeneous catalysts, such as ceramics, metals, or zeolites, have been able to solve.

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