



# Computational screening of MOF-supported transition metal catalysts for activity and selectivity in ethylene dimerization



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## ABSTRACT

Deposition of small metal-oxide clusters on the Zr-based nodes of a metal-organic framework has been demonstrated to provide access to a variety of single-site catalysts. Well-defined catalytic active sites are amenable to detailed computational studies of potential catalytic pathways, and they invite screening a wide range of metals to assess their expected activity. Here we report the application of density functional theory to a variety of transition metals (in particular Ti<sup>IV</sup>, V<sup>II</sup>, V<sup>IV</sup>, Cr<sup>II</sup>, Cr<sup>III</sup>, Mn<sup>II</sup>, Mn<sup>IV</sup>, Fe<sup>II</sup>, Fe<sup>III</sup>, Ni<sup>II</sup>, Co<sup>II</sup>, Co<sup>III</sup>, Cu<sup>I</sup>, Cu<sup>II</sup>, Pd<sup>II</sup>, Mo<sup>II</sup>, and W<sup>II</sup>) supported on NU-1000 inorganometallic nodes to evaluate their activity for ethylene dimerization. We found that the rate-determining step varies between different catalysts, which illustrates the importance of considering more than a single step when comparing catalytic cycles across a variety of metals. Our calculations are consistent with the known good activity of supported Ni<sup>II</sup> for ethylene dimerization, and they predict that Cr<sup>II</sup> and Pd<sup>II</sup> are also potentially useful catalysts for this process. We also screen modifications to the organic linker of Ni<sup>II</sup>-NU-1000 by considering the addition of Me, *i*Pr, *t*Bu, CF<sub>3</sub> and NH<sub>2</sub> groups to study the influence of sterically demanding and, the case of CF<sub>3</sub> and NH<sub>2</sub>, respectively, electron-donating and -withdrawing, substituents on the activity for ethylene dimerization; we predict no improvements in activity or selectivity (for 1-butene) with such substitutions.

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## 1. Introduction

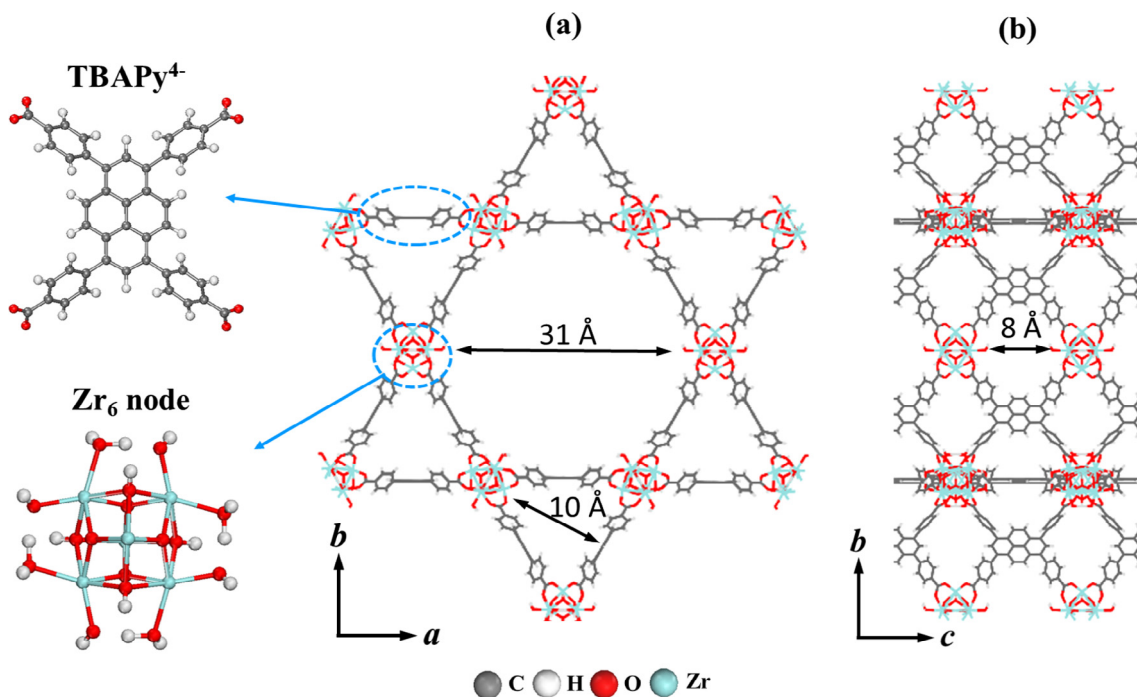
Supported metal catalysts are commonly used in the chemical industry, with very large scale examples including the Fischer-Tropsch [1] and Haber-Bosch processes [2]. The discovery of economical catalysts that exhibit high activity and selectivity can have a decisive impact on reducing manufacturing costs, both financial and energetic. However, characterization of active catalysts *in operando*, especially at the atomic level of detail, is challenging because of the changes of morphology, composition, and structure that may be induced or dynamically operative under working reaction conditions, and this makes it difficult to rationally improve existing catalytic systems or to identify governing rules leading to the design of new ones [3]. Recently, metal-organic frameworks (MOFs) have emerged as promising supports for transition-metal catalysts [4–7]. In contrast to traditional supports (e.g., zeolites or activated carbons), MOFs combine ultrahigh porosity and large surface area [4,6,8–11] with well-defined 3D architectures that offer a remarkable degree of structural and functional tunability.

Through functionalization of the organic linker or modification of the inorganic nodes, many highly dispersed single-site catalysts have been synthesized and studied [12–25]. Such well-defined structures are amenable to detailed theoretical studies of their catalytic reaction mechanisms.

NU-1000 is a MOF composed of [Zr<sub>6</sub>(μ<sub>3</sub>-O)<sub>4</sub>(μ<sub>3</sub>-OH)<sub>4</sub>(OH)<sub>4</sub>(OH<sub>2</sub>)<sub>4</sub>]<sup>8+</sup> nodes and tetratopic 1,3,6,8-(*p*-benzoate)pyrene (TBAPy<sup>4-</sup>) linkers; it has uniform hexagonal and triangular channels with diameters of 31 and 10 Å, respectively, that penetrate layers separated by smaller pores (of diameter 8 Å) along the crystallographic *c* direction, as shown in Fig. 1. NU-1000 is a particularly interesting MOF because OH and H<sub>2</sub>O groups coordinated on the Zr<sub>6</sub> node make it an excellent potential platform for metal anchoring at each node face through atomic layer deposition [26–28], solvothermal deposition [13,28], or metal exchange [7]. In this fashion, a uniformly distributed Ni single-site catalyst (Ni-NU-1000) has been synthesized [12], the structure of which has been determined from experimental and theoretical characterization to involve Ni hydroxo clusters bridging Zr nodes at either side of the small *c* pore [29]. The oxidation state of Ni in Ni-NU-1000 catalyst was characterized by X-ray photoelectron spectroscopy (XPS), and a peak at 856.5 eV was clearly observed that is due to the 2p<sub>3/2</sub> electrons of Ni(II) [12]. In addition, the Ni

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**Fig. 1.** Structure of NU-1000: (a) the hexagonal and triangular channels, viewed along the *c* direction, and (b) the small pore bridging the *ab* layers, viewed along the *a* direction.

K-edge EXAFS data for Ni-NU-1000 suggested the Ni species in Ni-NU-1000 catalyst has features between those for the bulk reference compounds  $\alpha$ -Ni(OH)<sub>2</sub> and NiO. Therefore, the catalytic active site of Ni-NU-1000 was identified as nickel in oxidation state +2 [12,29]. A computational comparison of the catalytic activity of a single Ni atom vs the experimentally dominant Ni<sub>4</sub> cluster in the NU-1000 *c* pore found negligible variations in predicted activity for ethylene dimerization [30], which suggests no role for cooperativity in the catalytic mechanism, and no differentiation of Ni atoms with respect to position in the *c* pore. Ethylene dimerization activity was, however, found to be sensitive to the spin state of the individual Ni<sup>II</sup> atom serving as the catalyst [30]. These observations suggest that there is good potential for a single-atom catalyst model to be an efficient and simple means to screen an array of transition metals for their activity toward ethylene dimerization when sited in NU-1000.

A well-known commercial process for ethylene dimerization is the IFP Alphabutol process, which involves homogenous catalysis using Ti(OR)<sub>4</sub>/AlR<sub>3</sub> as catalyst [31–34]. In contrast to the IFP Alphabutol process, Ni-NU-1000 is a solid catalyst with the reactant in the gas phase, which is preferable because it is a solvent-free process that allows for easy catalyst recycling and easy separation of reaction products from the catalyst. The TOF for Ni-NU-1000 catalyst is 252 h<sup>-1</sup>, which is higher than that for most Ni catalysts supported on zeolites, silica, or metal oxides (NiO/B<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>: 23.1 h<sup>-1</sup>, Ni-NaY: 15 h<sup>-1</sup>, Ni-Y: 11.2 h<sup>-1</sup>, Ni-Beta (Si/Al = 12): 70 h<sup>-1</sup>, Ni-SBA-15: 42 h<sup>-1</sup>) [35], even though the reaction conditions for Ni-NU-1000 are much milder (45 °C, 2 bar) [12] than those reported for Ni supported catalysts (*T* > 100 °C, *P* > 10 bar) [35]. Although Ni<sup>II</sup>-NU-1000 shows good activity for ethylene dimerization at low temperature (~50 °C), the selectivity for 1-butene is modest at 46% [12]. A higher selectivity that would reduce or eliminate costly steps required to obtain 1-butene pure enough for polymerization applications would represent a significant catalytic advance [15,36,37]. Our goal in this work is to employ density functional theory to calculate catalytic oligomerization reaction pathways

for an array of transition metals in various oxidation states including Ti<sup>IV</sup>, V<sup>II</sup>, V<sup>IV</sup>, Cr<sup>III</sup>, Cr<sup>III</sup>, Mn<sup>II</sup>, Mn<sup>IV</sup>, Fe<sup>II</sup>, Fe<sup>III</sup>, Co<sup>II</sup>, Co<sup>III</sup>, Ni<sup>II</sup>, Cu<sup>II</sup>, Cu<sup>III</sup>, Pd<sup>II</sup>, Mo<sup>II</sup> and W<sup>II</sup> by using a single-atom catalyst model to search for potential catalyst candidates that may combine activity competitive with Ni<sup>II</sup> together with improved selectivity for 1-butene production. We also assess whether functionalization of the TBAPy organic linker with sterically demanding, electron-withdrawing, and/or electron-donating groups (Me, *i*-Pr, *t*-Bu, CF<sub>3</sub> and NH<sub>2</sub>) has an influence on the activity and selectivity of the Ni<sup>II</sup>-NU-1000 single-atom catalyst model.

## 2. Computational Models and Methods

### 2.1. NU-1000 cluster model

The Zr<sub>6</sub> node of NU-1000 was truncated from an optimized periodic unit cell of NU-1000 and the organic linkers reduced to capping formate groups ([Zr<sub>6</sub>(μ<sub>3</sub>-O)<sub>4</sub>(μ<sub>3</sub>-OH)<sub>4</sub>(OH)<sub>4</sub>(OH<sub>2</sub>)<sub>4</sub>]<sup>8+</sup>8HCO<sub>2</sub><sup>-</sup>, 70-atom cluster, Fig. 2b) for screening the different supported transition metal catalysts. A truncated model with substituted benzoate groups and formate groups ([Zr<sub>6</sub>(μ<sub>3</sub>-O)<sub>4</sub>(μ<sub>3</sub>-OH)<sub>4</sub>(OH)<sub>4</sub>(OH<sub>2</sub>)<sub>4</sub>]<sup>8+</sup>4RC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub><sup>-</sup>4HCO<sub>2</sub><sup>-</sup>), with R = H, Me, *i*Pr, *t*Bu, CF<sub>3</sub> or NH<sub>2</sub> (see Fig. 3; the cluster has 110 atoms when R is H), was used for studying the effects of linker substitution on the Ni<sup>II</sup>-NU-1000 single-atom catalyst.

### 2.2. Activated M-NU-1000 cluster models

To activate it for ethylene dimerization, Ni<sup>II</sup>-NU-1000 as deposited by ALD is first treated with Et<sub>2</sub>AlCl, as described in prior experimental and theoretical work (Fig. 2a) [12,38]. For an activated M<sup>II</sup>-NU-1000 cluster involving a metal in oxidation state II, the ethyl-substituted M<sup>II</sup> atom bridges two oxygen atoms from the original terminal -OH<sub>2</sub> and -OH groups, with one proton removed from the former to maintain charge neutrality. The same

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