

Computational Study of MOF-Supported Metal Catalysts for Ethylene Dimerization

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Background

NU-1000

NU-1000 is a MOF composed of $[Zr_6(\mu_3-O)_4(\mu_3-OH)_2(\mu_3-OH)_2(\mu_3-OH)_2]^{8+}$ nodes and tetratopic 1,3,6,8-(p-benzoate)pyrene (TBAPy⁴⁻) linkers. It is a particularly interesting mesoporous material.

Potential Catalyst Support:

- Chemically and Thermally stable
- Large pore size (31 Å) facilitates gas diffusion
- Reactive -OH/H₂O sites provide an excellent platform for metal deposition

Atomic Layer Deposition

Through atomic layer disposition (ALD), a variety of metals have been successfully deposited on the Zr₆ node of NU-1000, resulting in a uniformly dispersed single-site metal catalysts.

Mondloch, J. E. et al. *J. Am. Chem. Soc.*, 2013, 135, 10294.

Ni-NU-1000

High-purity 1-butene is preferred for linear low-density polyethylene production.

Ni-NU-1000 (ALD) catalyst shows good activity for ethylene dimerization (TOF = 252 h⁻¹), but the selectivity for 1-butene production is about 50%.

Li, ZY et al., *J. Am. Chem. Soc.* 2016, 138, 1977.

SEM **XRD** **N₂ isotherm**

Ni-EXAFS spectra **Difference Envelope Density (DED)**

- The c lattice constant shrinks upon Ni deposition.
- The pore volume reduces.
- Ni species are deposited in the small pore.
- Ni species are octahedral NiO₆H₂ clusters.

Platero-Prats, A. E. et al. *J. Am. Chem. Soc.*, 2017, 139, 10410

Goals

- Identify the structure of Ni-NU-1000.
- Determine the reaction mechanism for ethylene dimerization.
- Search for potential catalysts with higher selectivity for 1-butene production by computational screening.

Ni₄-NU-1000

Ni(OH)₂ layer **Ni₃** **Ni₄** **Ni₅**

Periodic Ni_x-NU-1000 Models

NU-1000 Ni₃-NU-1000 Ni₄-NU-1000 Ni₅-NU-1000 Ni_{4,1}-NU-1000

c lattice constant of Ni-NU-1000

Exp. vs Sim.	Ni ₃	Ni ₄	Ni ₅	Ni _{4,1}
cycles	0 1 2	0 3 5 6 3 4	0 4 3 4 3 4	0 5 10 3 5
average number of Ni atoms per node	0.53	1.03	1.53	2.03

Bond distances of nNi_x-NU-1000

Material	Ni-O(Å)	Ni...Ni(Å)
1Ni ₄ -NU1000	2.069	3.060
2Ni ₄ -NU1000	2.075	3.077
3Ni ₄ -NU1000	2.076	3.102
Exp. (1 cycle)	2.046(2)	3.035(9)

The trends of c lattice constant variation for Ni₄ and Ni_{4,1} are in good agreement with XRD results.

Ni K-edge EXAFS Exp. vs Sim.

Aaron League and Varinia Bernales

Different Ni₄ hydroxo cluster models (A, B and C) were optimized and their simulated EXAFS spectra were compared with experimental results.

The Ni₄-hydroxo cluster with an Ni(OH)₂-layer like structure (Model C) agrees well with the EXAFS spectra, which is identified to be the dominant species in Ni-NU-1000 catalyst.

Platero-Prats, A. E. et al. *J. Am. Chem. Soc.*, 2017, 139, 10410

Activity of M-NU-1000

Energetic span model of Kozuch and Shaik

$$TOF = \frac{k_B T}{h} \frac{e^{-\Delta G_r / RT} - 1}{\sum_{i,j=1}^N e^{(E_i - E_j - \Delta G_{ij}) / RT}} = \frac{\Delta}{M}$$

$$\Delta G_{ij} = \begin{cases} \Delta G_r & \text{if } i > j \\ 0 & \text{if } i \leq j \end{cases}$$

Kozuch and Shaik, *Acc. Chem. Res.*, 2011, 40, 101

Log(TOF)

The computational screening indicates Cr²⁺, Ni²⁺ and Pd²⁺ could be potential catalysts for ethylene dimerization.

Computational Details

M06-L functional
def2-SVP basis set: H, C, and O atoms of the Zr₆ node and linkers
def2-TZVP basis set: C and H atoms of the reacting hydrocarbons and the transition metals (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Pd, Mo, W, Zr), including the SDD effective core potential for Pd, Mo, W and Zr atoms

M-NU-1000

4 elementary steps:

- C-C Coupling
- β-H Elimination
- 1-butene desorption
- Ethylene hydrogenation

Cluster model

Energy profile (kcal/mol)

TS_{2,3} 13.2
TS_{3,4} -1.0
TS_{6,7} -2.8
TS_{5,1} -13.7

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Ni-Facac-NU-1000

Facac AIM **Ni AIM**

Et₂AlCl activation

Products Selectivity (%)

Ni-Facac-AIM-NU-1000 exhibited reduced ethylene oligomerization activity (TOF = 12 h⁻¹) as compared to Ni-AIM-NU-1000, while C₄ product selectivity was significantly improved to 100%.

DFT results show that the Gibbs free energy of activation for C₂→C₄ and C₄→C₆ on Ni-Facac-AIM-NU-1000 is higher than that on Ni-AIM-NU-1000, suggesting the lower activity and higher selectivity for ethylene oligomerization of Ni-Facac-AIM-NU-1000 as compared with Ni-AIM-NU-1000.

Energy profile (kcal/mol)

TS_{2,3} 18.3
TS_{3,4} -1.0
TS_{6,7} 7.8
TS_{5,1} -4.3

Conclusions

- We employ periodic density functional calculations to characterize the structure and reactivity of Ni-NU-1000 catalyst. Our results suggest Ni₄-hydroxo clusters in the c pore of NU-1000 are the dominant species in Ni-NU-1000 catalyst.
- We find that both the atomic Ni catalyst and the Ni₄-hydroxo cluster have higher catalytic activity in the singlet state than in the triplet state. We also find that the atomic Ni catalyst and the Ni₄-hydroxo cluster have very similar activity when the Ni is in the singlet state. The catalytic activity of Ni-NU-1000 for ethylene dimerization depends more strongly on the spin state of the Ni atoms than on the Ni cluster size.
- We have used a single-Ni-atom cluster model for screening a variety of transition metals for their catalytic activity toward ethylene dimerization. The computational screening indicates Cr²⁺, Ni²⁺ and Pd²⁺ could be potential catalysts for ethylene dimerization.
- Ni-Facac-AIM-NU-1000 exhibited reduced ethylene oligomerization activity, while the C₄ product selectivity was significantly improved.

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