Background

Ni NU-1000

Ni NU-1000 is a MOF composed of \( \text{Zr}_6(μ_3-O)_2(μ_3-OH)_2(μ-OH)_4 \) nodes and tetramethyl 1,3,5,7-tetrazacyclooctane (TTAP4) ligands. It is a particularly interesting mesoporous material.

Potential Catalyst Support:

- Large-pore size (21 Å) facilitates gas diffusion
- Reacts with \( \text{H}_2 \) or \( \text{H}_2 \text{O} \) to form an excellent platform for metal deposition

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

Atomic Layer Deposition

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%.

Ni-NU-1000

Through atomic layer deposition (ALD), a variety of metals have been successfully deposited on the \( \text{Zr}_6 \) node of Ni-NU-1000, resulting in a uniformly dispersed single-site metal catalyst.

Ni4-NU-1000

Ni4-NU-1000 is a MOF composed of \( \text{Zr}_6(μ_3-O)_2(μ_3-OH)_2(μ-OH)_4 \) nodes and tetramethyl 1,3,5,7-tetrazacyclooctane (TTAP4) ligands. It is a particularly interesting mesoporous material.

Periodic Ni4-NU-1000 Models

The lattice constant of Ni4-NU-1000 is 1.5% smaller than that of Ni-NU-1000, which agrees with previous experimental results.

The lattice constant of Na4-NU-1000 is 1.5% smaller than that of Ni4-NU-1000, which agrees with previous experimental results.

Conclusions

- We employ periodic density functional calculations to characterize the structure and reactivity of Ni4-NU-1000 catalyst. Our results suggest Na4-hydride clusters in the c pore of Ni4-NU-1000 are the dominant species in Ni4-NU-1000 catalyst.
- We find that both the atomic Ni catalyst and the Ni4-hydride cluster have higher catalytic activity in the single state than in the triple state. We also find that the atomic Ni catalyst and the Ni4-hydride cluster have very similar activity when the Ni is in the single state.
- The catalytic activity of Ni4-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 Ni4-hydride cluster model for screening a variety of transition metals for their catalytic activity toward ethylene dimerization. The computational screening indicates Cr4+, Mn4+ and Fe4+ could be potential catalysts for ethylene dimerization.

Ni-Facac-NU-1000

Ni-Facac-NU-1000 exhibited reduced ethylene oligomerization activity, while the C4 product selectivity was significantly improved.

4 elementary steps:

1. C-C Coupling
2. H-Dissociation
3. 1-butenel decomposition
4. Ethylene hydrodimerization

We applied density functional theory (DFT) to screen a variety of transition metal supported on Ni4-NU-1000 catalysts (including Fe4+, Cr4+, Mn4+, Ni4+, Mo4+, Rh4+, Pd4+ and Cu4+, Cu3+, PD4, Mo4 and W4) for their activity toward ethylene dimerization.

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