

BRIDGING THE GAP IN DUAL METAL NANOWIRES

Catalysts are a cornerstone of industrial chemistry, efficiently transforming feedstocks into chemicals that permeate the modern world. Discovery of new catalysts with improved catalytic activity and chemical selectivity drive increases in productivity, efficiency, and cost-savings. An emerging class of nanoscale catalysts supported by metal-organic frameworks (MOFs) provides a new route to improving catalyst selectivity due to the well-defined atomic structure of the catalyst. To resolve the atomic structure of nanocatalysts made using atomic layer deposition (ALD) on MOFs, researchers combined complementary structural and computational analyses to build the complete picture of catalytic Ni-Hydroxo clusters on a zirconia-based MOF. Critical structural tools for this research included x-ray scattering and spectroscopy measurements at the APS. They discovered a heterobimetallic nanowire structure formed within the MOF, offering a new general approach for the construction of nanowires with specific structures using ALD on MOFs.

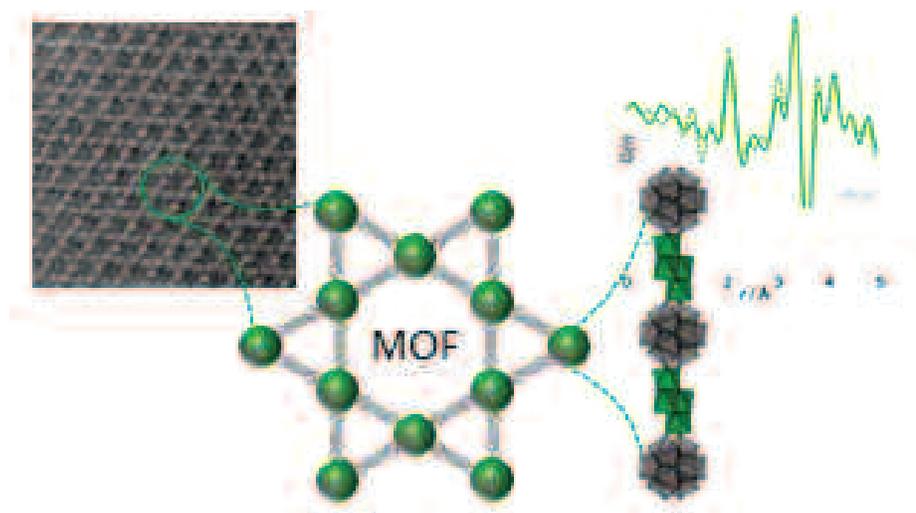


Fig. 1. A scanning transmission electron micrograph (left) of a zirconium-based metal-organic framework (MOF, center), NU-1000, containing Zr₆-based nodes (grey clusters) with hexagonal and triangular pores shown. The MOF was functionalized with nickel-hydroxo clusters (green clusters, right) to generate heterobimetallic nanowires (right). A representative differential pair distribution function (green line, upper right) is shown, derived from x-ray total scattering experiments at beamline 11-ID-B of the APS and helped resolve the structure of the nanowires.

10-ID-B • MR-CAT • Materials science, environmental science, chemistry • X-ray absorption fine structure, time-resolved x-ray absorption fine structure, microfluorescence (hard x-ray) • 4.3-27 keV, 4.8-32 keV, 15-65 keV • On-site • Accepting general users •

11-ID-B • XSD • Chemistry, environmental science, materials science • Pair distribution function, high-energy x-ray diffraction • 58.66 keV, 86.7 keV • On-site • Accepting general users •

17-BM-B • XSD • Chemistry, materials science • Powder diffraction, pair distribution function • 27-51 keV • On-site • Accepting general users •

20-BM-B • XSD • Materials science, environmental science, chemistry • X-ray absorption fine structure, microfluorescence (hard x-ray) • 2.7-32 keV, 2.7-35 keV • On-site • Accepting general users •

MOFs are structurally regular, with an open crystalline lattice defining a regular network of internal pores with high surface area of well-defined surface chemistry. Atomic layer deposition of catalysts onto MOFs can produce well-defined structures with intriguing catalytic function; but local disorder within the structure makes it difficult to resolve the structure of emerging MOF-based catalysts, hindering efforts to understand, and improve, their reactivity.

The team from the Inorganometallic Catalyst Design Center, an Energy Frontier Research Center funded by the U.S. Department of Energy involving partners from Argonne, the University of Minnesota, the Pacific Northwest National Laboratory (PNNL), and Northwestern University focused on NU-1000, a zirconium-based MOF with large pores, strong zirconium-oxygen bonds, and high chemical and thermal stability. Using a two-step ALD process, the researchers deposited catalytic nickel clusters onto the MOF, replacing hydroxyl groups. To work out the details of deposition, the researchers analyzed the catalyst's structure via multiple complementary methods.

As a first step, the researchers performed synchrotron x-ray scattering on NU-1000 before and after nickel functionalization: powder x-ray diffraction on XSD beamline 17-BM-B and total scattering data for pair distribution function (PDF) analysis on XSD beamline 11-ID-B, both at the APS (Fig. 1). Based on the relatively broad diffraction data of

"Bridging" cont'd. on page 162

proach to nanowire synthesis. Because ALD can work with a variety of chemicals, such an approach may produce a rich menagerie of bimetallic nanowires.

— Erika Gebel Berg

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“Bridging” cont’d. from page 161

functionalized NU-1000, the researchers concluded it had increased distortions compared to NU-1000. The diffraction data provided a low-resolution map of where the nickel was deposited, indicating localization within the small pores of the NU-1000 framework, while the PDF data provided precise information on the Ni–O and Ni...Ni atom distances. Next, the team performed x-ray absorption spectroscopy (XANES and EXAFS), collecting transmission geometry XAS measurements at the MR-CAT 10-ID-B and the XSD 20-BM-B beamlines, also at the APS. These data demonstrated that on average, the nickel atoms were 6-coordinated (NiO₆) with a slightly distorted octahedral geometry.

Using structural information from the x-ray data, the researchers were able to distinguish the computational models that best matched the experimental observations. Adjacent zirconia nodes appeared to be bridged by the nickel clusters, creating bimetallic nanowires. The tight binding and separation between clusters may be key to catalytic function, and appears to mitigate deactivation of the catalyst during the hydrogenation of light olefins.

The researchers suggest it may be possible to dissolve the MOF to isolate the nanowires and develop a novel ap-