Research offers new understanding of complex catalysis, advances catalyst design

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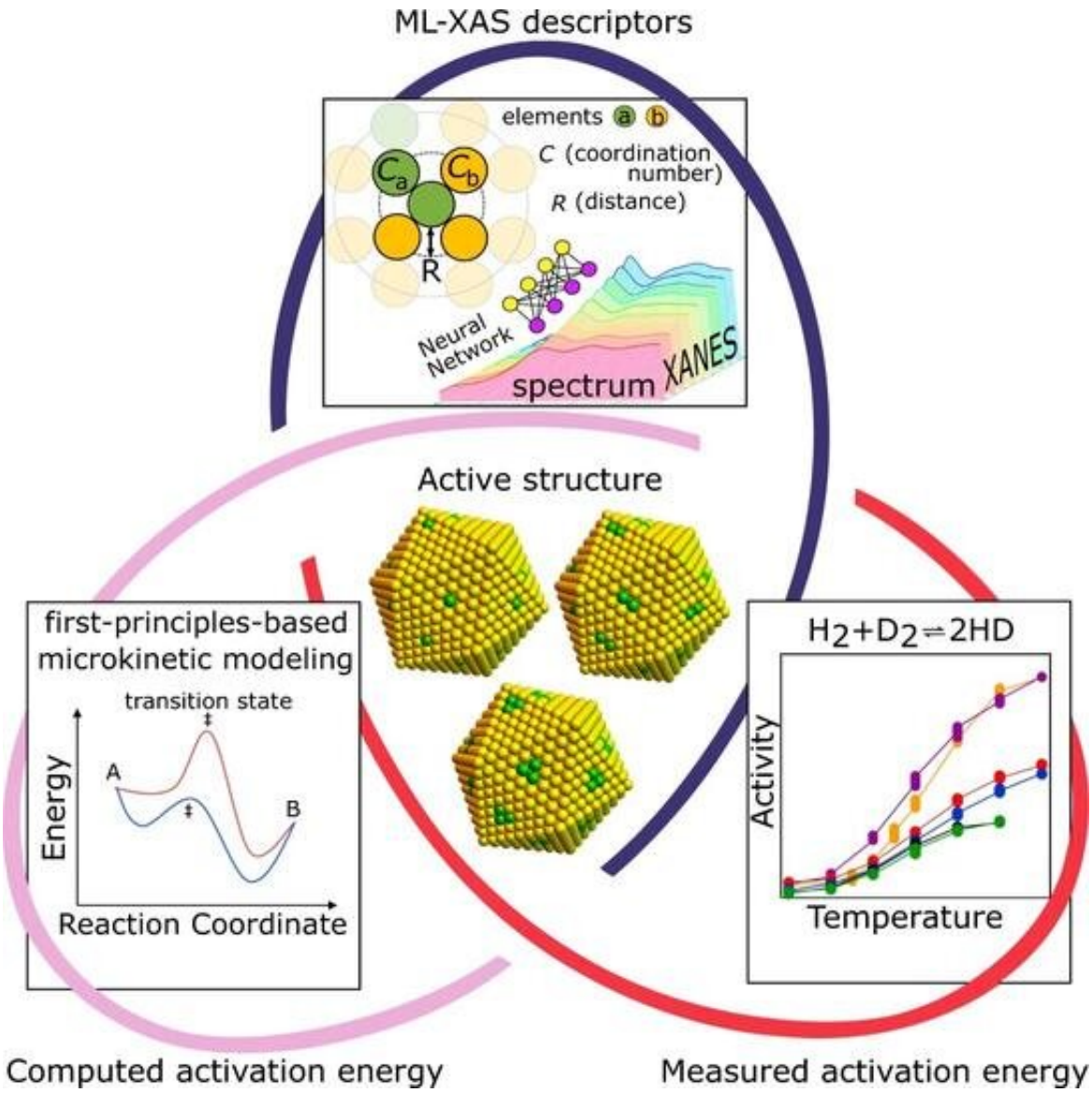

The researcher's multi-pronged strategy uses local structural descriptors extracted from X-ray absorption spectra through machine learning to constrain

the set of candidate active sites, then the corresponding reaction pathways are modeled and apparent activation energies from computations are compared to experimental measurements to further narrow down the dominant active sites. Three possible nanoparticle motifs (center) are shown where the active sites (green) vary between 1 and 3 atoms. Credit: Boris Kozinsky/Harvard SEAS

Many of the catalytic reactions that drive our modern world happen in an atomic black box. Scientists know all the components that go into a reaction, but not how they interact at an atomic level.

Understanding the reaction pathways and kinetics of catalytic reactions at the atomic scale is critical to designing catalysts for more energy-efficient and sustainable chemical production, especially multimaterial catalysts that have ever-changing surface structures.

In a recent paper, researchers from the Harvard John A. Paulson School of Engineering and Applied Sciences (SEAS), in collaboration with researchers from Stony Brook University, University of Pennsylvania, University of California, Los Angeles, Columbia University, and University of Florida, have peered into the black box to understand, for the first time, the evolving structures in a multimaterial catalyst at the atomic scale.

The research was done as part of the Integrated Mesoscale Architectures for Sustainable Catalysis (IMASC), an Energy Frontier Research Center funded by the Department of Energy, headquartered at Harvard. It was published in *Nature Communications*.

"Our multipronged strategy combines reactivity measurements, machine learning-enabled spectroscopic analysis, and kinetic modeling to resolve a long-standing challenge in the field of catalysis—how do we

understand the reactive structures in complex and dynamic alloy catalysts at the atomic level," said Boris Kozinsky, the Thomas D. Cabot Associate Professor of Computational Materials Science at SEAS and co-corresponding author of the paper. "This research allows us to advance catalyst design beyond the trial-and-error approach."

The team used a multimaterial catalyst containing small clusters of palladium atoms mixed with larger concentrations of gold atoms in particles approximately five nanometers in diameter. In these catalysts, the chemical reaction takes place on the surface of tiny islands of palladium. This class of catalyst is promising because it is highly active and selective for many chemical reactions but it's difficult to observe because the clusters of palladium consist of only a few atoms.

"Three-dimensional structure and composition of the active palladium clusters cannot be determined directly by imaging because the experimental tools available to us do not provide sufficient resolution," said Anatoly Frenkel, professor of Materials Science and Chemical Engineering at Stony Brook and co-corresponding author of the paper. "Instead, we trained an artificial neural network to find the attributes of such a structure, such as the number of bonds and their types, from the X-ray spectrum that is sensitive to them."

The researchers used X-ray spectroscopy and machine learning analysis to narrow down potential atomic structures, then used first principles calculations to model reactions based on those structures, finding the atomic structures that would result in the observed catalytic reaction.

"We found a way to co-refine a structure model with input from experimental characterization and theoretical reaction modeling, where both riff off each other in a feedback loop," said Nicholas Marcella, a recent Ph.D. from Stony Brook's Department of Materials Science and Chemical Engineering, a postdoc at University of Illinois, and the first

author of the paper.

"Our multidisciplinary approach considerably narrows down the large configurational space to enable precise identification of the active site and can be applied to more complex reactions," said Kozinsky. "It brings us one step closer to achieving more energy-efficient and sustainable catalytic processes for a range of applications, from manufacturing of materials to environmental protection to the pharmaceutical industry."

More information: Nicholas Marcella et al, Decoding reactive structures in dilute alloy catalysts, *Nature Communications* (2022). DOI: 10.1038/s41467-022-28366-w

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