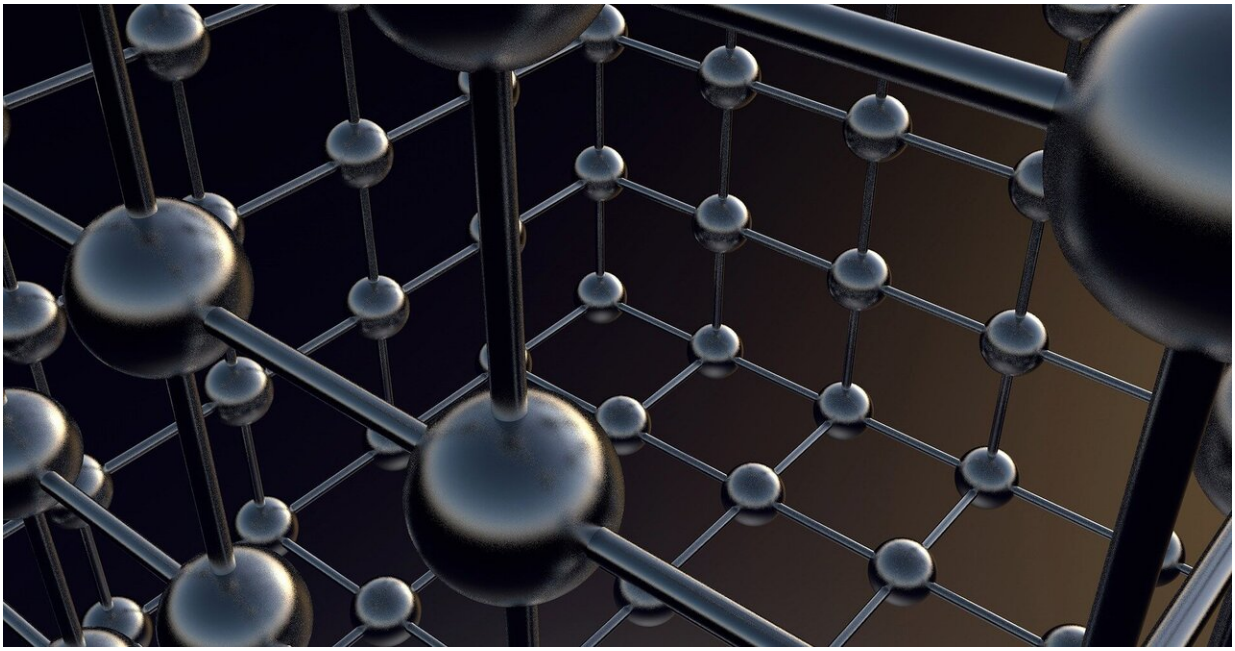
New atomic-scale understanding of catalysis could unlock massive energy savings

April 6 2023, by Jason Daley



Credit: Pixabay/CC0 Public Domain

In an advance they consider a breakthrough in computational chemistry research, University of Wisconsin–Madison chemical engineers have developed model of how catalytic reactions work at the atomic scale. This understanding could allow engineers and chemists to develop more efficient catalysts and tune industrial processes—potentially with enormous energy savings, given that 90% of the products we encounter in our lives are produced, at least partially, via catalysis.

Catalyst materials accelerate chemical reactions without undergoing changes themselves. They are critical for refining petroleum products and for manufacturing pharmaceuticals, plastics, food additives, fertilizers, green fuels, industrial chemicals and much more.

Scientists and engineers have spent decades fine-tuning catalytic reactions—yet because it's currently impossible to directly observe those reactions at the extreme temperatures and pressures often involved in industrial-scale catalysis, they haven't known exactly what is taking place on the nano and atomic scales. This new research helps unravel that mystery with potentially major ramifications for industry.

In fact, just three catalytic reactions—steam-methane reforming to produce hydrogen, ammonia synthesis to produce fertilizer, and methanol synthesis—use close to 10% of the world's energy.

"If you decrease the temperatures at which you have to run these reactions by only a few degrees, there will be an enormous decrease in the energy demand that we face as humanity today," says Manos Mavrikakis, a professor of chemical and biological engineering at UW–Madison who led the research. "By decreasing the energy needs to run all these processes, you are also decreasing their environmental footprint."

Mavrikakis and postdoctoral researchers Lang Xu and Konstantinos G. Papanikolaou along with graduate student Lisa Je published news of their advance in the April 7, 2023 issue of the journal *Science*.

In their research, the UW–Madison engineers develop and use powerful modeling techniques to simulate catalytic reactions at the atomic scale. For this study, they looked at reactions involving transition metal catalysts in nanoparticle form, which include elements like platinum, palladium, rhodium, copper, nickel, and others important in industry and

green energy.

According to the current rigid-surface model of catalysis, the tightly packed atoms of transition metal catalysts provide a 2D surface that chemical reactants adhere to and participate in reactions. When enough pressure and heat or electricity is applied, the bonds between atoms in the chemical reactants break, allowing the fragments to recombine into new chemical products.

"The prevailing assumption is that these metal atoms are strongly bonded to each other and simply provide 'landing spots' for reactants. What everybody has assumed is that metal-metal bonds remain intact during the reactions they catalyze," says Mavrikakis. "So here, for the first time, we asked the question, 'Could the energy to break bonds in reactants be of similar amounts to the energy needed to disrupt bonds within the catalyst?'"

According to Mavrikakis's modeling, the answer is yes. The energy provided for many catalytic processes to take place is enough to break bonds and allow single metal atoms (known as adatoms) to pop loose and start traveling on the surface of the catalyst. These adatoms combine into clusters, which serve as sites on the catalyst where chemical reactions can take place much easier than the original rigid surface of the catalyst.

Using a set of special calculations, the team looked at industrially important interactions of eight transition metal catalysts and 18 reactants, identifying energy levels and temperatures likely to form such small metal clusters, as well as the number of atoms in each cluster, which can also dramatically affect reaction rates.

Their experimental collaborators at the University of California, Berkeley, used atomically-resolved scanning tunneling microscopy to look at carbon monoxide adsorption on nickel (111), a stable, crystalline

form of nickel useful in catalysis. Their experiments confirmed models that showed various defects in the structure of the catalyst can also influence how single metal atoms pop loose, as well as how reaction sites form.

Mavrikakis says the new framework is challenging the foundation of how researchers understand catalysis and how it takes place. It may apply to other non-metal catalysts as well, which he will investigate in future work. It is also relevant to understanding other important phenomena, including corrosion and tribology, or the interaction of surfaces in motion.

"We're revisiting some very well-established assumptions in understanding how catalysts work and, more generally, how molecules interact with solids," Mavrikakis says.

Manos Mavrikakis is Ernest Micek Distinguished Chair, James A. Dumesic Professor, and Vilas Distinguished Achievement Professor in Chemical and Biological Engineering at the University of Wisconsin–Madison. Other authors include Barbara A.J. Lechner of the Technical University of Munich, and Gabor A. Somorjai and Miquel Salmeron of Lawrence Berkeley National Laboratory and the University of California, Berkeley.

More information: Lang Xu et al, Formation of active sites on transition metals through reaction-driven migration of surface atoms, *Science* (2023). DOI: 10.1126/science.add0089. www.science.org/doi/10.1126/science.add0089

Provided by University of Wisconsin-Madison