Ultrafast laser experiments pave way to better industrial catalysts

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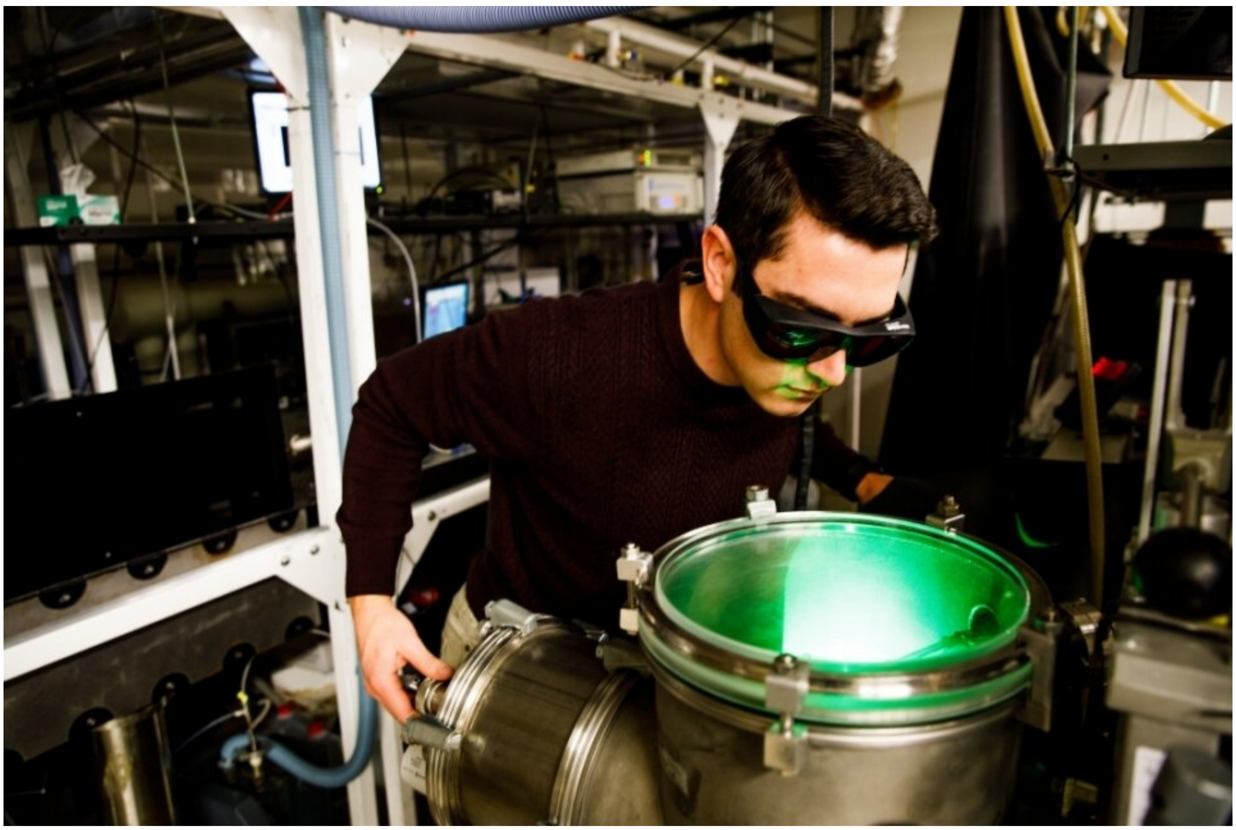

Jake Garcia works in the lab. Credit: Arizona State University

Arizona State University's Scott Sayres and his team have recently published an ultrafast laser study on uncharged iron oxide clusters, which could ultimately lead to the development of new and less-expensive industrial catalysts. It might also contribute to a better understanding of the universe since iron oxides are observed in the emission spectra of stars.

Sayres is an assistant professor in ASU's School of Molecular Sciences and a faculty member in the Biodesign Institute's Center for Applied Structural Discovery.

Most chemical industries utilize catalysts to enhance the rate of reaction and selectivity in obtaining their desired products. For example, catalytic converters in the exhausts of our vehicles commonly use platinum, palladium and rhodium to help break down pollutants.

All three of these metals are significantly more expensive than gold, which is in turn a lot more costly than iron. On average a catalytic converter costs $1,000 but can be as high as $3,000 per vehicle.

"Transition metal oxides are widely used as heterogeneous catalysts in the chemical industry," Sayres said. "The photocatalytic process proceeds through a series of complex reactions, and a fundamental understanding of these catalytic mechanisms is still lacking. Gas-phase studies on molecular scale clusters allow us to probe chemical activities and mechanisms in an unperturbed environment. The atomic precision of clusters can be utilized to identify preferred adsorption sites, geometries or oxidation sites that enable chemical transformations."

The FenOm clusters under investigation here have different compositions: n and m vary but are less than 16. Fe is the chemical symbol for iron and O refers to oxygen.

"This research has not only revealed the stable fragments of bulk iron oxide materials but has shown how the change in atomic composition may affect stability and reactivity of these fragments," said Jake Garcia, graduate student and first author of this paper.

"By resolving the excited state dynamics of atomically precise materials such as iron oxides, we move one step closer to creating more directed molecular catalysts and understanding the reactions which may take place in interstellar media."

Garcia continues that he has found a passion for building experimental instruments in Sayres' lab, and loves studying materials relevant to planetary and earth science.

Ryan Shaffer, who was an undergraduate student working in Sayres' lab, is the second author of the current work.

Detecting iron oxide clusters

Experiments with electrically charged clusters have been common because they can be mass selected with electric or magnetic forces and subsequently reacted individually. Cluster ions are clearly much more reactive than their condensed-phase analogues and neutrals because of their net charge.

Far less work has been done with neutral clusters reported here, which are even better mimics of the true active sites of condensed phases and their surface chemistry. The net charge significantly affects cluster reactivity, and the influence becomes more important as the cluster size decreases due to charge localization.

"The timeframe of electron transitions following excitation is of fundamental interest to the understanding of reaction dynamics. Clusters are atomically precise collections of atoms, where the addition or subtraction of a single atom may drastically change the reactivity of the cluster," Sayres said. "In this work we apply ultrafast pump-probe spectroscopy to study the speed at which energy moves through small iron oxide clusters."

The laser pulses are extremely short: one thousandth of a billionth of a second.

Sayres concludes that the excited state lifetime is strongly affected by atomically precise changes to the cluster composition. Specifically, the higher the oxidation states of the metal, the faster the photoexcitation energy is converted into vibrations. They have found that the excited state lifetimes rely heavily on size and oxidation state.

Catalysts are also extensively used to minimize the harmful byproduct pollutants in environmental applications. Enhanced reaction rates translate to higher production volumes at lower temperatures with smaller reactors and simpler materials of construction.

When a highly selective catalyst is used, large volumes of desired products are produced with virtually no undesirable byproducts. Gasoline, diesel, home heating oil and aviation fuels owe their performance quality to catalytic processing used to upgrade crude oil.

Intermediate chemicals in the production of pharmaceutical products utilize catalysts, as does the food industry in the production of every day edible products. Catalysts are playing a key role in developing new sources of energy and a variety of approaches in mitigating climate change and controlling atmospheric carbon dioxide.

More information: Jacob M. Garcia et al. Ultrafast pump–probe spectroscopy of neutral FenOm clusters (n, m Physical Chemistry Chemical Physics (2020). DOI: 10.1039/D0CP03889J

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