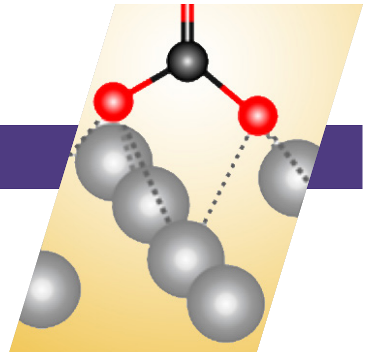
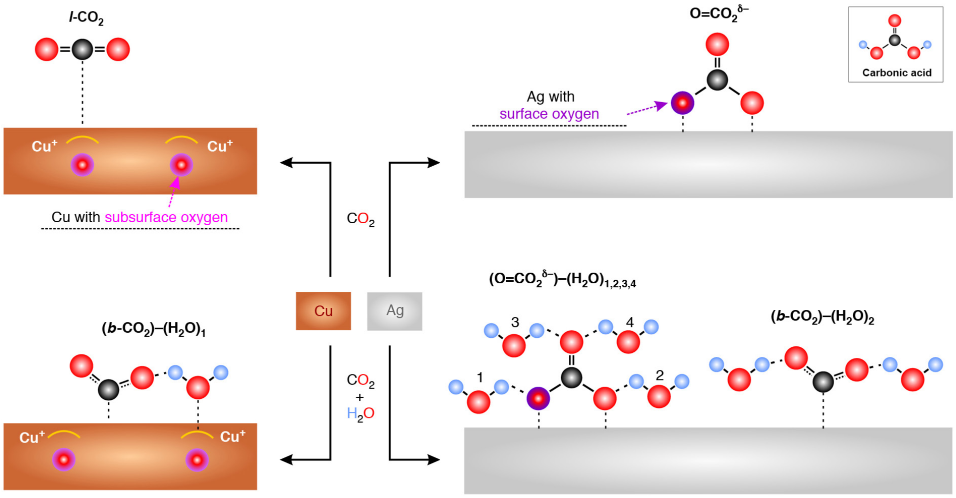
ADVANCED LIGHT SOURCE

CHEMICAL SCIENCES

A New Path to Carbon Dioxide Transformation





CO_2 adsorption on copper (top left), silver (top right) and in the presence of H_2O (bottom left and right). The depictions of CO_2 on copper (from a previous study) show that linear and bent forms of CO_2 (*l*-CO_2 and *b*-CO_2, respectively) are formed with CO_2 adsorption alone and in the presence of H_2O, aided by subsurface oxygen and surface H_2O. In this study, the researchers found that CO_2 on silver forms a completely new molecule ($O{=}CO_2^{2\delta-}$), similar in structure to carbonic acid (inset).

Scientific Achievement

Combining experiments at the Advanced Light Source (ALS) with quantum-mechanical calculations, scientists found dramatic differences in how carbon dioxide (CO_2) reactions begin on silver as opposed to copper

Significance and Impact

Both metals help transform CO_2—a greenhouse gas—into more useful forms, and this new atomic-level data could help make the process more efficient.

Rebalancing the carbon cycle

Fossil fuels are the lifeblood of modern societies, but their increased use releases carbon dioxide (CO_2)—a greenhouse gas—into the atmosphere faster than plants can recycle it through photosynthesis. One way to address this is to reprocess CO_2 into syngas, a feedstock for generating other useful chemicals. However, because CO_2 is highly nonreactive, catalysts such as copper and silver are needed to facilitate the transformation ("reduction") of CO_2 into carbon monoxide (CO), a major component of syngas.

In searching for more efficient catalysts, scientists have computationally screened and lab-tested many materials. These approaches, however, have been based on preconceived notions about the relevant reaction mechanisms and have not produced dramatic successes. An atomic-level understanding of CO_2 catalysis is essential to designing optimally performing materials.

Collaboration on copper

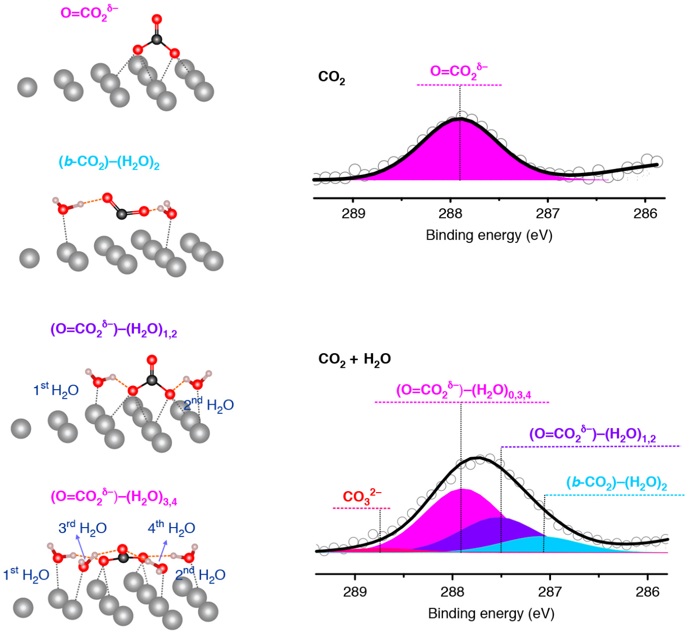
The Joint Center for Artificial Photosynthesis (JCAP) is a Department of Energy (DOE) Research Hub that aims to mimic photosynthesis—to produce renewable fuel using sunlight, and water, and CO_2. In a previous collaboration, JCAP brought together theorists from Caltech and experimentalists from the ALS to study in detail what happens to CO_2 at a copper surface.

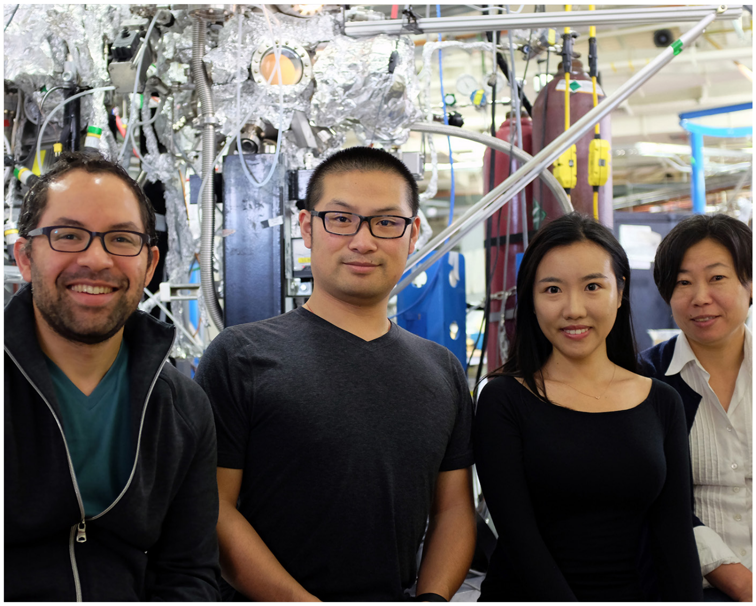
In that study, the researchers found that subsurface oxygen in the copper dramatically boosts the early stages of CO_2 catalysis. Bent CO_2 (*b*-CO_2) was shown to be a stable intermediate species in the presence of water. Such insights are essential to understanding, and eventually driving (using electrochemical processes), the reaction pathways to desired products.

A close-up of the silver lining

Now, a similar JCAP collaboration between the ALS and Caltech has expanded on the earlier work by investigating how CO_2 and water molecules interact with a silver surface. They combined ambient-pressure x-ray photoelectron spectroscopy (APXPS) at ALS Beamline 9.3.2 with quantum-mechanical calculations to obtain a comprehensive understanding of the initial steps of CO_2 adsorption and activation on silver.

Beamline 9.3.2 offers photons with a





Left: Quantum-mechanical predictions and experimental observations of CO_2 adsorption on Ag, in the case of CO_2 alone and in the presence of H_2O. The diagrams show predicted CO_2 adsorption structures on Ag. The spectra show experimental C 1s APXPS data (open circles) and the fit (black line) with the various components having energy separations predicted by theory (colored curves). Right: Ethan Crumlin, Yifan Ye, Jin Qian, and Junko Yano.

soft x-ray energy range that allows surface-sensitive probes, advancing investigations at solid/gas interfaces. The beamline endstation chamber allows excellent control of O_2, CO_2, and H_2O gas pressures and reaction temperatures, important for accurately predicting the stable chemical species on the surface through simulations. A vacuum chamber attached to the analyzer allows in situ sample preparation and direct, pristine-sample measurement.

A new reaction pathway

The results revealed a very different mechanism of CO_2 activation on silver versus copper. A stable intermediate chemical species ($O{=}CO_2^{2\delta-}$) forms on silver when exposed to CO_2 alone. In the presence of CO_2 and water, the intermediate attaches up to four water molecules, and two water molecules stabilize b-CO_2 as well. The new surface-chemisorbed species structurally resembles carbonic acid (H_2CO_3), but processes completely different electric properties. The $(O{=}CO_2^{2\delta-})$–$(H_2O)_n$ clusters on silver represent a significantly more favorable activation mechanism than b-CO_2 on copper.

These unprecedented and surprising results—made possible using a synergistic and systematic experimental and computational approach—raise numerous questions about subsequent steps that will drive many new studies. Overall, the results lay a foundation for understanding the differences between catalysts, with the goal of controlling CO_2 adsorption using additives or alloys and observing the reactions in process as they're being electrochemically driven.

Contact: Ethan Crumlin (ejcrumlin@lbl.gov)

Researchers: Y. Ye and E.J. Crumlin (ALS and Berkeley Lab); H. Yang, J. Qian, T. Cheng, H. Xiao, and W.A. Goddard III (California Institute of Technology); H. Su (ALS and University of Science and Technology of China); K.-J. Lee (ALS and Gwangju Institute of Science and Technology, South Korea); and J. Yano (Berkeley Lab).

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