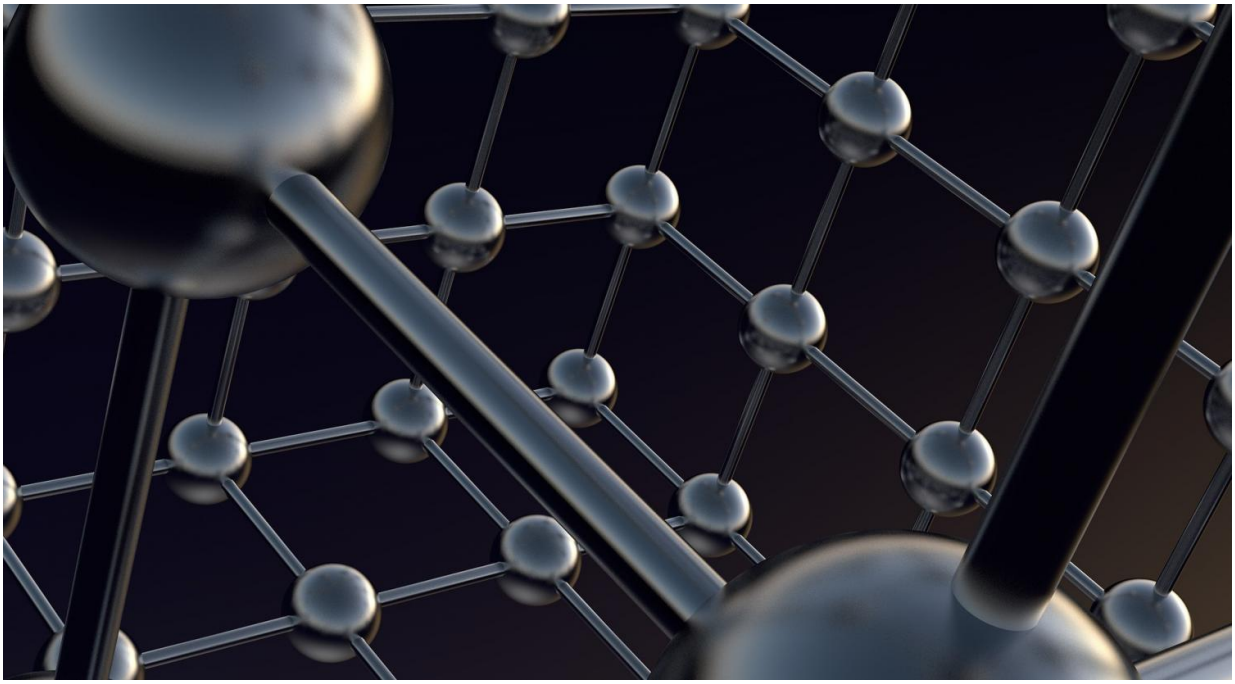
Solid-state catalysis: Fluctuations clear the way

February 18 2019



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The use of efficient catalytic agents is what makes many technical procedures feasible in the first place. Indeed, synthesis of more than 80 percent of the products generated in the chemical industry requires the input of specific catalysts. Most of these are solid-state catalysts, and the reactions they make possible take place between molecules that adsorb to their surfaces.

The specific properties of the catalyst permit the starting molecules to interact and accelerate the reaction between them, without consuming or altering the catalyst itself. However, efficient catalysis also requires efficient mixing, so reactants must be able to diffuse laterally on the surface of the catalyst to maximize the chance of undergoing the desired reaction. Under the conditions employed in industrial processes, however, the surface of the catalyst is generally so densely packed with adsorbed particles that it has been unclear how molecules could effectively diffuse at all. Researchers led by Professor Joost Wintterlin at the Department of Chemistry at Ludwig-Maximilian-Universitaet (LMU) have now shown that, although reactants indeed spend time virtually trapped on the surface of the catalyst, local fluctuations in occupancy frequently provide opportunities to change positions. The new findings appear in the leading journal *Science*.

In order to gain insight into the molecular processes that take place on a solid-state catalyst, Wintterlin and colleagues used scanning tunneling microscopy (STM) to monitor the mobility of individual oxygen atoms on a ruthenium (Ru) catalyst that was densely packed with adsorbed carbon monoxide (CO) molecules. "We chose this system because the oxidation of CO to CO2 on metals belonging to the platinum group is a well-studied model for solid-state catalysis generally," Wintterlin explains. However, conventional scanning tunneling microscopy would have been unable to capture the surface dynamics of this reaction system. But the team succeeded in enhancing the rate of data acquisition, finally attaining rates of up to 50 images per second—high enough to make videos of the dynamics of the particles on the catalyst.

The STM images revealed that the oxygen atoms are completely hemmed in by triangular cages formed by CO molecules adsorbed to the surface of the Ru catalyst. Analysis of the videos showed that single oxygen atoms can only hop between three positions formed by the interstices of the Ru atoms. "But, to our surprise, we also observed that

an atom can escape from its cage, and suddenly begins to diffuse through the carbon monoxide matrix at a rate that is almost as high as if it were on a completely empty surface," says Ann-Kathrin Henß, first author of the research paper. In collaboration with Professor Axel Groß of the Institute of Theoretical Chemistry at Ulm University, the Munich researchers were able to link this phenomenon with fluctuations in the local density of the CO on the surface, which give rise to regions in which the molecules are more or less closely packed together. When such a fluctuation occurs in the vicinity of an oxygen atom, the latter can escape from its cage, and make its way to a new position. In fact, this 'door-opening mechanism' opens up diffusion pathways so rapidly that the movement of the oxygen atoms through the matrix is not significantly impeded. This explains why they can almost always find a new binding partner for the reaction facilitated by the catalyst.

More information: Ann-Kathrin Henß et al, Density fluctuations as door-opener for diffusion on crowded surfaces, *Science* (2019). DOI: 10.1126/science.aav4143

Provided by Ludwig Maximilian University of Munich