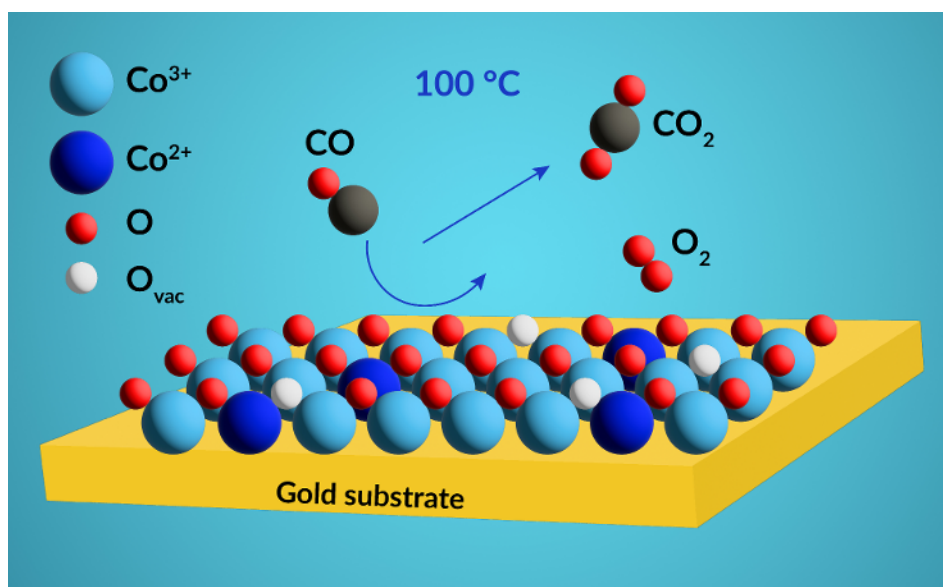# Probing Active-Site Chemical States in a Co-Based Catalyst

Carbon monoxide (CO) is converted to carbon dioxide (CO_2) by a thin layer of cobalt oxide on a gold substrate. Under oxygen-rich conditions, a phase containing trivalent cobalt (Co^{3+}) is formed that catalyzes the reaction effectively over a wide range of temperatures.

Scientific Achievement

Researchers identified the dominant chemical state of active sites in a cobalt-based catalyst using resonant photoemission spectroscopy under realistic conditions at the Advanced Light Source (ALS).

Significance and Impact

The work will help scientists develop more-efficient catalysts for removing noxious carbon monoxide gas from exhaust streams generated by the burning of fossil fuels.

Quest for maximum efficiency

Catalytic converters have been successfully used for decades to remove noxious gases from exhaust streams produced by fossil-fuel combustion. The central chemical reaction, the conversion of carbon monoxide (CO) to carbon dioxide (CO_2), requires a catalyst that provides special sites where the reactants and products can bind, react, and detach without requiring much energy. In particular, noble metals such as gold or platinum, when combined with "reducible" oxides (i.e., oxygen-containing materials that can exchange electrons with the metal), have been found to exhibit superior catalytic activity. However, to maximize efficiency, scientists need a clearer understanding of the origins of this increased activity.

To this end, researchers used resonant photoemission spectroscopy (ResPES) at the ALS to study thin films of cobalt oxide (CoO_x) on a gold substrate. The findings provide new insight into the enhanced catalytic reactivity of CoO_x catalysts, highlighting both their chemical and topographical evolution in response to varied ambient-pressure environments.

Topographic and chemical restructuring

In previous work done at the ALS, the researchers revealed that many catalysts (platinum, copper, and gold/silver alloys) rearrange their surfaces in response to ambient conditions. More recently, the group explored gains in efficiency when pairing noble metals with transition-metal oxides, particularly CoO_x. When gold and CoO_x come into contact with one another,

they exchange electrons, which means that the Co can have several oxidation states (e.g., Co^0, Co^{2+}, and Co^{3+}). How does this "chemical restructuring" affect catalytic efficiency and under what conditions (temperatures, gas composition) is efficiency maximized?

Answering these questions requires information about Co oxidation states. However, while ambient-pressure x-ray photoelectron spectroscopy (APXPS) can directly probe chemical-state changes of CoO_x under reaction conditions, the Co^{2+} and Co^{3+} spectroscopic peaks are extremely close together and difficult to distinguish. Therefore, the researchers turned to another ambient-pressure technique, ResPES, which uses resonant photoelectron emission to enhance spectroscopic signals. The ResPES

experiments were conducted at ALS Beamline 9.3.2. APXPS studies were also performed at the ALS, NSLS-II, and SSRL. Density functional theory calculations provided deeper insights into reaction pathways and free-energy barriers for the reactions.

Trivalent cobalt dominates

The results revealed that three reaction regimes exist in response to chemical and topographic restructuring of the CoO_x: partially oxidized CoO_x (x<1), fully oxidized CoO, and nonstoichiometric CoO_x (x>1). Under oxygen-lean conditions and moderate temperatures (≤150 °C), the partially oxidized films were found to be efficient catalysts. Fully oxidized CoO films (containing only Co^{2+}) form carbonates in the presence of CO that poison the reaction below 300 °C. Under oxygen-rich conditions, a more oxidized, nonstoichiometric CoO_x phase (x>1) containing both Co^{2+} and Co^{3+} appears. For this case, the ResPES data demonstrated
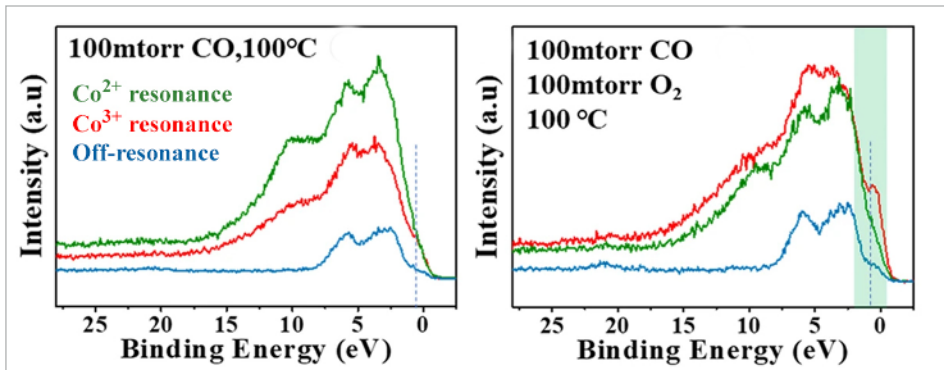
Resonant valence-band photoelectron spectra of CoO_x film on a substrate of Au(111) under CO exposure (left) and under CO oxidation conditions (right). Green and red spectra correspond to Co^{2+} and Co^{3+} resonant excitation energies, while the blue spectrum is measured off-resonance. With resonant enhancement, it can be clearly distinguished that the Co^{3+} sites contribute the most to catalytic activity under CO oxidation conditions.

that Co^{3+} is the most active catalyst site over a wide temperature range.

Identifying the nature of the active site and how to "turn it on" is key to catalyst design, and these findings provide scientists with new avenues for the design of more-efficient catalysts. Future plans include repeating the experiment using a platinum substrate instead of gold and comparing the results. The ultimate goal is to eventually unravel the mystery of what drives the strong interaction between metal and support materials in catalysts.

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U.S. DEPARTMENT OF ENERGY
Office of Science

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