

Water gas shift reaction for CeO₂-supported Pt catalyst occurs at Pt perimeter

The uses of hydrogen gas and carbon dioxide (CO₂) as precursors to reactions are as varied as they are abundant, ranging from applications in gas sensing to synthesis and optimization. The water gas shift (WGS) reaction [$\text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2$] has hydrogen and carbon dioxide gas as products. However, understanding where this reaction takes place when in the presence of a CeO₂-Pt catalyst can reveal the mechanisms that govern it and help develop catalysts with high efficiency.

Now, a research group has studied ceria (CeO₂) supported platinum (Pt) nanoclusters (1.7 nm ± 0.3 nm) in the presence of CO and H₂O by performing in situ multimodal studies. Environmental transmission electron

microscopy, x-ray absorption spectroscopy, ambient pressure x-ray photoelectron spectroscopy, and diffuse reflectance infrared Fourier-transform spectroscopy revealed the heterogeneous changes that occur in the structure of the Pt nanoclusters, and showed that the reaction took place at the perimeter Pt⁰–O vacancy–Ce³⁺ sites.

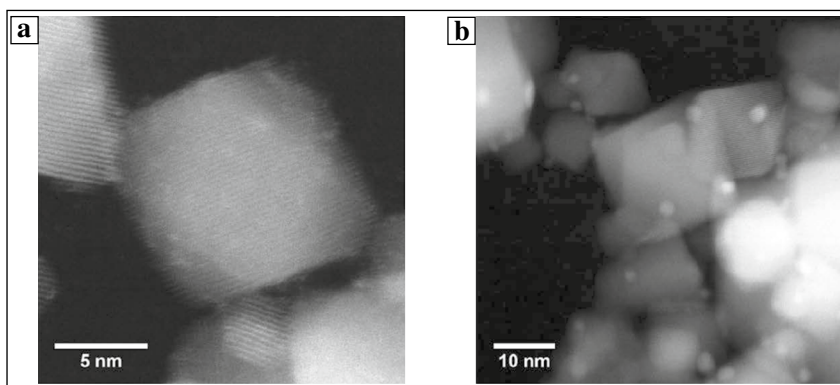
This multimodal approach, reported in a recent issue of *Nature Communications* (<https://doi.org/10.1038/s41467-021-21132-4>), allowed the researchers to gather data about the distinct properties and changes in their system and provided new understanding of the reaction mechanism. Ralph G. Nuzzo of the University of Illinois, Urbana and KTH Royal Institute of Technology says, “The part that blows me away is how sophisticated that level of characterization is.” Anatoly Frenkel of Stony Brook University and Brookhaven National Laboratory adds that, since a multimodal study gains knowledge by

analyzing the sample by different techniques, it tends to get that much more intricate. The way the data are managed and connected is the key to a successful multimodal study, he says.

The research team noted that the atoms at different sites within the nanocluster dynamically and heterogeneously change under in situ and working conditions. The dynamicity of the catalyst could be required for the proceeding of the reaction. The researchers propose that the reaction more likely follows the regenerative redox mechanism at the active site. It begins with the association of CO molecules with Pt and the dissociation of water into hydroxyl (OH) and atomic hydrogen on the surface of ceria supports. At the vicinity of active Pt sites, the hydroxyl groups donate atomic oxygen to the reduced support, which is subsequently reduced by donating the atomic oxygen to CO. The oxidation of ceria at the perimeter of the nanocluster would cause the corresponding oxidation of the perimeter Pt atoms and strong bonding between the perimeter Pt atoms and the support. Furthermore, the mechanism requiring oxidation state changes are dynamically reversible (reversible change of Pt⁰ to Pt²⁺ and Ce³⁺ to Ce⁴⁺). These changes in the valence state of the active species cause the dynamic structural changes responsible for facilitating the transport of CO to the external Pt.

For future work, lead author Yuanyuan Li of Stony Brook University hopes “to modify the catalyst in a way that allows their functionality at lower temperatures, using less platinum and achieving a higher efficiency.”

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(a) Scanning transmission electron microscope (STEM) annular dark field (ADF) image of the as-prepared Pt/ceria catalysts; (b) STEM-ADF image of the reacted Pt/ceria catalyst. Credit: *Nature Communications*.