

PROJECT FACTS

UNIVERSITY OF KENTUCKY CENTER FOR APPLIED ENERGY RESEARCH

PARTICIPANTS

University of Kentucky
Center for Applied Energy
Research
2540 Research Park Dr.
Lexington, KY 40511

CONTACT

Burtron H. Davis
Gary Jacobs
UK CAER
2540 Research Park Dr
Lexington, KY 40511
Tel: 859-257-0276
Fax: 859-257-0220
burtron.davis@uky.edu
gary.jacobs@uky.edu
www.caer.uky.edu



CLEAN FUELS & CHEMICALS

Low Temperature Water-Gas Shift Catalysts for Producing CO-free H₂ for Fuel Cell Applications

Fuel cells are receiving widespread attention as an alternate source for clean energy, and one of the most important developments are proton-exchange membrane fuel cells (PEMFC) which operate using hydrogen at low temperatures. In the U.S., there is a considerable effort underway to develop H₂ as the preferred fuel due to the potential for decreasing our dependence on imported oil, and the environmental benefits. Due to the difficulties associated with hydrogen storage, it will likely be generated in the near term on an as needed basis by reforming fuels like natural gas, methanol, gasoline, and LPG. Reforming hydrocarbon fuels will still produce CO₂, but it is perceived that levels will be reduced due to the improved efficiency of the PEM fuel cell over the internal combustion engine. In the future, when carbon capture/ sequestration technology, as well as H₂ delivery infrastructure, are in place, H₂ may be generated not only from conventional fossil fuels, but also from biomass, coal gasification, and other sources (e.g., wind, solar, and nuclear).

Hydrogen production requires a number of fuel processing catalysts. In the front-end of a typical reformer, steam reforming, partial oxidation, or a combination of the two (autothermal reforming or ATR) will be conducted at high temperatures using catalysts to convert the hydrocarbon source to hydrogen, with CO as a byproduct. One setback hindering PEMFC implementation is the problem of CO. Platinum catalysts found in the PEMFC are intolerant to CO, and therefore, the CO must be limited to levels on the order of parts per million in the hydrogen feed. Therefore, the reformer product stream must be purified. Catalysts are also employed for CO removal in reactor stages. First, high temperature water-gas shift (HTS) is carried out to convert 7-12% CO to about 3-5%. This is run at close to equilibrium. Since the water-gas shift reaction is equilibrium limited at high temperatures, high conversions can only be achieved at lower temperatures. However, since the reaction is controlled by kinetics at low temperatures, highly active and stable water gas shift catalysts are needed. Low temperature water gas shift (LTS) reduces CO levels to < 1%. Finally, preferential oxidation (PROX) is conducted in a cleanup system to convert the remaining CO, also employing catalysts, to parts per million levels.

At the CAER, we are working to understand the mechanism(s) operating on low temperature water gas shift (LTS) catalysts. One catalyst under study is ceria promoted with noble metals. There are two competing theories as to how the reaction mechanism proceeds. The most well-received is a redox process, where metal-adsorbed CO reacts with ceria to generate CO₂ and a vacancy. Water then reacts with the vacancy to produce hydrogen. Results of our recent research, however, support an earlier claim. That is, partial reduction of ceria is facilitated by the presence of the noble metal, and geminal OH groups are formed on the ceria surface. CO reacts with the geminal OH groups to produce formate intermediates, which are decomposed to H₂ and CO₂ in the presence of water. Our isotopic studies support the view that formate C-H bond breaking is likely the rate limiting step of the reaction. Our work highlights the use of in-situ spectroscopic techniques such as DRIFTS, used to monitor the dynamics of adsorbed surface species, and XANES, a synchrotron method used to explore the redox properties of ceria. Most recently, CAER assisted Honda Research USA, Inc. to characterize alkali-doped Pt/ZrO₂ catalysts. Results suggest that the presence of alkali weakens the formate C-H bond, facilitating its scission, during the catalytic cycle.