

***In situ* characterization of an inverse CeO₂/CuO powder catalyst for the WGS reaction**

Laura Barrio^{1*}, Michael Estrella¹, Wen Wen², Jonathan Hanson¹, Jose A. Rodríguez¹, Aitor Hornés³, Arturo Martínez-Arias³, Marcos Fernández-García³

¹Chemistry Department, Brookhaven National Laboratory, Bldg 555, Upton, NY 11973, USA

²Current address: Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academy of Sciences

³Instituto de Catalisis y Petroleoquímica, Marie Curie 2, 28049, Madrid, Spain

*lbarrio@bnl.gov

Introduction

The water gas shift reaction (WGS) is a critical process for procuring clean hydrogen from the reforming of hydrocarbons¹. The design and optimization of novel catalysts for the WGS reaction is hindered by the complex reaction mechanism and the difficulty of identifying active species. The mechanism for Cu based catalysts has been a question of study for many years. It has been generally accepted that the active phase are the reduced Cu metal sites supported on metal oxides^{2,3}. Nevertheless, the metal oxide support has been also reported to play an active role in the reaction mechanism³.

In the present work we propose the use of an inverse powder catalyst of cerium oxide nanoparticles dispersed over a CuO/Cu support. The catalytic performance of the inverse system would outline the importance of CeO₂ in the reaction mechanism and its study will help to clarify the roles played by cerium oxide and copper sites in the WGS reaction.

In situ synchrotron characterization techniques are employed to relate the catalyst's structure with its activity. We have performed Time Resolved experiments of X-ray diffraction (TR-XRD), X-ray absorption fine structure (XAFS) and pair distribution function (PDF) analysis.

Materials and Methods

The inverse CeO₂/CuO catalyst was prepared by a microemulsion method². Briefly, the cerium hydroxide precursor was added to the corresponding copper hydroxide precursor at ca. 70 °C. Following separation of the resulting solid, final calcination under air at 500 °C was applied to yield a catalyst with $S_{\text{BET}} \approx 67 \text{ m}^2\text{g}^{-1}$ and Cu/Ce at. ratio of ca. 2.6.

In situ time-resolved X-ray diffraction (TR-XRD) experiments were carried out on beam line X7B of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The sample (5 mg) was loaded into a glass cell of 1 mm diameter, which was attached to a flow system. Two dimensional powder patterns were collected with a Mar345 image plate detector and the powder diffraction rings were integrated using the FIT2D code. Sagittally-focusing double-Crystal Laue monochromator was used to tune the wavelength to 0.3184 Å. Diffraction patterns were collected over the catalysts during the WGS reaction. The WGS reaction was carried out with a stepped temperature program from RT to 500°C,

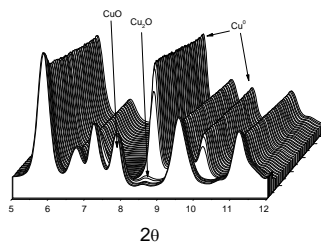


Figure 1: *In situ* XRD patterns during the WGS reaction.

with 3 hour soaks at every 100°C beyond 200°C amid a 1% CO and 99% He gas mixture flow rate of 10 mL/min. This gas mixture passed through a water bubbler before entering the reactor.

Cu K-edge and Ce L_{III}-edge XANES spectra were collected *in situ* under operation conditions similar to those for the TR-XRD experiments, at beamline X19A of the NSLS. The X-ray absorption spectra were taken continuously in the “fluorescence-yield mode” using a PIPS detector cooled with circulating water.

The products of the catalytic reactions were measured with a 0–100 amu quadrupole mass spectrometer (QMS, Stanford Research Systems).

Results and Discussion

Figure 1 shows the time resolved X-ray diffraction patterns for the CeO₂/CuO inverse catalysts during the water gas shift reaction at different temperatures. The starting material was composed of CuO and CeO₂ phases. As the reaction progressed, the CuO was first reduced to the Cu₂O intermediate and finally to pure metallic copper at 200°C.

The activity data obtained by mass-spectrometry reveals that hydrogen production starts once the copper has been fully reduced. The activity profile neither shows deactivation of the catalyst during the long reaction time nor deactivation at reaction temperatures of up to 500°C.

The catalyst was also characterized by XAFS under *in situ* conditions. The Cu K-edge XANES spectra collected confirms the reduction of copper under WGS reaction conditions. The Ce L_{III}-edge was also examined by XANES and the results are displayed in Figure 2. The changes in the spectral features show that CeO₂ was partially reduced under WGS reaction conditions. The amount of oxygen vacancies and Ce⁺³ cations increased continuously with increasing temperature.

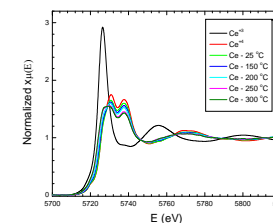


Figure 2: Ce L_{III} edge XANES spectra during the WGS reaction

Significance

An inverse system of CeO₂ nanoparticles supported over CuO/Cu has been analyzed as a catalyst for the WGS reaction. The catalytic performance and stability test show promising results. The formation of CeO_{2-x} and Cu species revealed by TR-XRD and *in situ* XANES accounts for the strong interaction between metal and metal-oxide. Cu favors the reduction of ceria, which helps in the dissociation of water.

References

1. Spivey, J. J., *Catalysis Today* **2005**, 100, (1-2), 171-180.
2. Wang, X. Q.; Rodriguez, J. A.; Hanson, J. C.; Gamarra, D.; Martinez-Arias, A.; Fernandez-Garcia, M. *J. Phys. Chem.B* **2005**, 109, (42), 19595
3. Wang, X. Q.; Rodriguez, J. A.; Hanson, J. C.; Gamarra, D.; Martinez-Arias, A.; Fernandez-Garcia, M., *Topics in Catalysis* **2008**, 49, 7
4. Rodriguez, J. A.; Ma, S.; Liu, P.; Hrbek, J.; Evans, J.; Perez, M. *Science* **2007**, 318, 1757-1760