

# Structural and spectroscopic study of the WGS activity for the CuFe<sub>2</sub>O<sub>4</sub> catalyst

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## Introduction

The water gas shift reaction (WGS) represents a very important step in the industrial production of hydrogen from the reforming of hydrocarbons. In addition, the employment of hydrogen for mobile fuel cell applications requires the development of new and efficient systems<sup>1</sup>. Along this work we propose the use of copper spinel as a catalytic system for the WGS reaction. Copper-iron oxides are employed as WGS catalysts in industrial processes but their performance needs to be improved<sup>2,3</sup>.

The CuFe<sub>2</sub>O<sub>4</sub> lattice is an inverse spinel structure in which the copper ions occupy the octahedral sites and the iron ions occupy both the tetrahedral and octahedral sites<sup>4</sup>.

Here, we will present an *in situ* study of the structural and chemical changes of the CuFe<sub>2</sub>O<sub>4</sub> in order to be able to relate WGS activity with the catalyst's structure. We have performed *in situ* X-ray diffraction (XRD) experiments to follow the changes of crystallographic phases as well as X-ray absorption near-edge spectroscopy (XANES). The *in situ* XANES of the Cu-K edge and Fe-K edge have revealed information on

the oxidation state and coordination chemistry during the WGS reaction. The obtained results will shed light on the interesting structural features of the copper spinel system.

## Materials and Methods

*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 was loaded into a glass cell of 1 mm diameter, which was attached to a flow system. A small resistance heater was wrapped around the capillary, and the temperature was monitored with a 0.1 mm chromel–alumel thermocouple that was placed in the capillary near the sample. Two dimensional powder patterns were collected with a Mar345 image plate detector and the powder diffraction rings were integrated using the FIT2D code. 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, with 3 hour soaks at every 100°C beyond 200°C amid a 1% CO and 99% He gas mixture with a flow rate of 10 mL/min (space velocity: 3·10<sup>4</sup> h<sup>-1</sup>). This gas mixture passed through a water bubbler before entering the reactor. The relative ratio of water vapor pressure to CO in the gas mixture was 0.6.

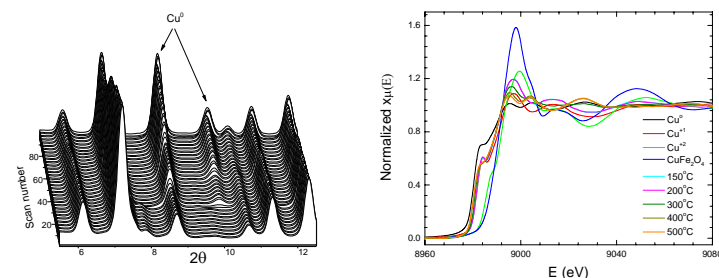
Cu K-edge and Fe K-edge XAFS spectra were collected *in situ* under operational conditions similar to those for the TR-XRD experiments, at beamline X19A of the NSLS. The same cell was used for the XANES experiments as that for *in situ* XRD, except that the sample

was loaded into a kapton capillary and heated with a hot air blower. The X-ray absorption spectra were taken repeatedly in the “fluorescence-yield mode” using a PIPS detector cooled with circulating water. XANES data was analyzed using the Athena IFEFFIT code.

The products from both TR-XRD and TR-XANES experiments were measured with a 0–50 amu quadrupole mass spectrometer (QMS, Stanford Research Systems). A portion of the exit gas flow passed through a leak valve and into the QMS vacuum chamber. This allowed us to measure reactivity by tracking the H<sub>2</sub> and CO<sub>2</sub> signals.

## Results and Discussion

The XRD signal from the sample shows the presence of a single phase in the starting material that corresponds to the copper spinel structure. *In situ* measurements taken during the WGS reaction are displayed in Figure 2a. The diffractograms show the appearance of a metallic copper phase as the reaction takes place. Despite the presence of this new Cu<sup>0</sup> phase, the Fe spinel structure is stable under reaction conditions and no significant change in the peaks of the iron spinel can be observed. The relative partial pressure of the products, as measured by mass-spectrometry, shows production of H<sub>2</sub> at 400°C. At this temperature all the copper species have been fully reduced to their metallic state.



**Figure 2:** *In situ* a) XRD diffractograms and b) XANES spectra during the WGS reaction

Further analysis of the electronic characteristics of the CuFe<sub>2</sub>O<sub>4</sub> sample was performed by X-Ray absorption spectroscopy. The *in situ* XANES spectra of the Cu K-edge confirm the reduction of Cu during the WGS reaction. The analysis of the Fe K-edge XANES spectra shows that the predominant oxidation state of the iron in the spinel structure is Fe<sup>+3</sup>, as indicated by an intense pre-edge peak. This characteristic pre-edge peak remains constant during the reaction, indicating no change in the oxidation state of iron during the WGS process.

## Significance

Thus, from our experiments we have been able to characterize the inverse spinel system and establish that metallic copper is the active phase for the WGS reaction in this system. In addition, this work demonstrates the advantage of time resolved *in situ* studies for heterogeneous catalytic reactions.

## References

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