

XANES for Investigating Catalyst Chemical States

By Dr. Srivatsan Seshadri, Dr. Ruimin Qiao, Sylvia Lewis | Sigray, Inc

ABSTRACT | Determining the chemical state, particularly the oxidation state, of catalysts is critical to their performance. XANES is commonly employed to determine chemical states, but typically requires access to a synchrotron. Sigray's QuantumLeap™ is the first laboratory system that provides synchrotron-like XANES capabilities. Fe-based and V-based catalysts were analyzed with the QuantumLeap™ to identify their chemical state at ~0.2 eV resolution and compared to references collected both on the QuantumLeap™ and at the synchrotron.

INTRODUCTION

An estimated 90% of all commercially produced chemical products involve catalysts [1], ranging from the manufacturing of plastics, carbon nanotubes, and biofuels to the production of foods such as margarine. The chemical state of catalytic materials (active element, carrier, promoter, inhibitor, etc.) can significantly impact the activity (e.g. rate) and selectivity of the chemical reactions [2]. As a consequence, determining the influence of different preparations, activation treatments, and environmental conditions such as temperature on the chemical state of catalysts is critical to optimizing the final end product.

X-ray absorption near edge spectroscopy (XANES) is a powerful technique used frequently for chemical state analysis. XANES measures the slight changes in the absorption characteristics of elements based on its chemical state. Typically, XANES requires the use of synchrotron facilities, which are large centers in which electrons are accelerated to produce intense x-ray beams.

A NEW LABORATORY APPROACH

The Sigray QuantumLeap™ x-ray absorption spectroscopy system is the first laboratory instrument with synchrotron-like XANES capabilities. The system provides a wide range of x-ray energies, ranging from 2.1-12 keV, for both modes of x-ray absorption spectroscopy: XANES and EXAFS. For XANES analysis, the system provides high energy resolutions of <0.5 eV and spatial resolutions of 100 μm for investigating heterogeneous samples.

In this study, we used the QuantumLeap™ on several iron (Fe) and vanadium (V) based catalysts to demonstrate its chemical state identification capabilities. For these studies, Sigray's multi-target

microstructured source was employed using a W target. The system was operated in an off-Rowland geometry for simultaneous acquisition of XANES data, which were then normalized relative to each other.

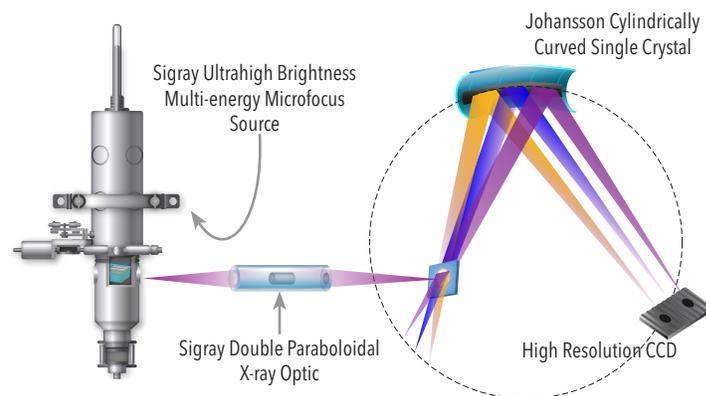


Figure 1: QuantumLeap's XANES off-Rowland geometry: Sample is placed within the Rowland circle to enable simultaneous detection of multiple wavelengths (vs. conventional energy scanning approach, which is lower throughput). High energy resolution of <0.5 eV is achieved by using Johanson crystals coupled with a high resolution CCD.

EXPERIMENT AND RESULTS

Iron-based Catalysts

Iron is one of the most commonly used catalyst materials and can present up to 16 oxidation states [3]; we analyzed hematite (Fe₂O₃) nanopowder, magnetite (Fe₃O₄) nanopowder, and a 5%Pt/FeMgAl catalyst and compared the results to a reference Fe foil of 7.5 μm thickness. The powders were placed on an adhesive tape and layered to a few microns thickness. A Ge (440) Johansson crystal was used to acquire the spectra around the K-α absorption edge of Fe (7.11 keV).

The XANES data was collected at 0.2 eV resolution for hematite, magnetite, and 5%Pt/FeMgAl, and the Fe foil reference collected at 0.8 eV resolution. The data (Figure 2) shows clear absorption signature

differences, with peak shifts and pre-edge features clearly visible due to the high energy resolution. Moreover, the Fe foil data for the QuantumLeap and synchrotron were consistent, with similar resolution.

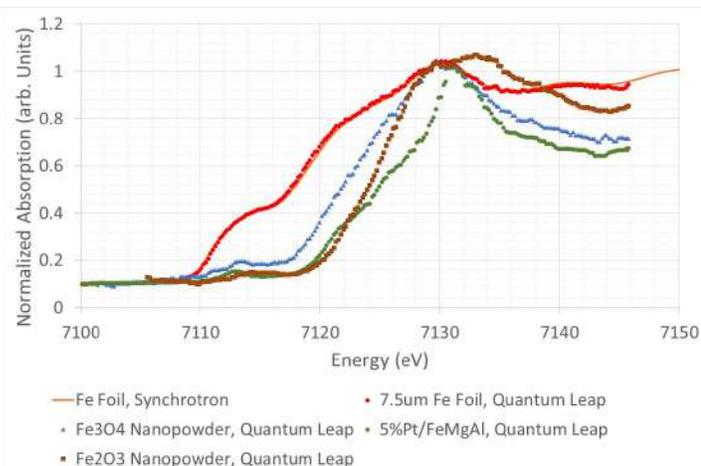


Figure 2: Fe catalyst XANES spectra. Data for Fe foil (orange line: synchrotron, red dots: QuantumLeap) are consistent. QuantumLeap-210 scaled acquisition times and energy resolution for the samples are as follows: (1) Fe foil: 20 min @0.8 eV, (2) Fe₃O₄: 49 min @0.2 eV, (3) Fe₂O₃: 3 hr* @0.2 eV, (4) 5%Pt/FeMgAl: 1.3 hr @0.2 eV

* Fe₂O₃ acquisition time longer due to the thinness of sample

Vanadium Catalyst (Ammonium Vanadate)

Ammonium metavanadate (NH₄VO₃) is being explored as a cost-effective catalyst to synthesize alpha-hydroxyphosphonate and benzimidazole derivatives, which are used for medicinal applications [4-5]. The ammonium metavanadate was compared to a reference V foil using a Ge (400) Johansson crystal around the K- α absorption edge of V (5.465 keV) shown in Figure 3.

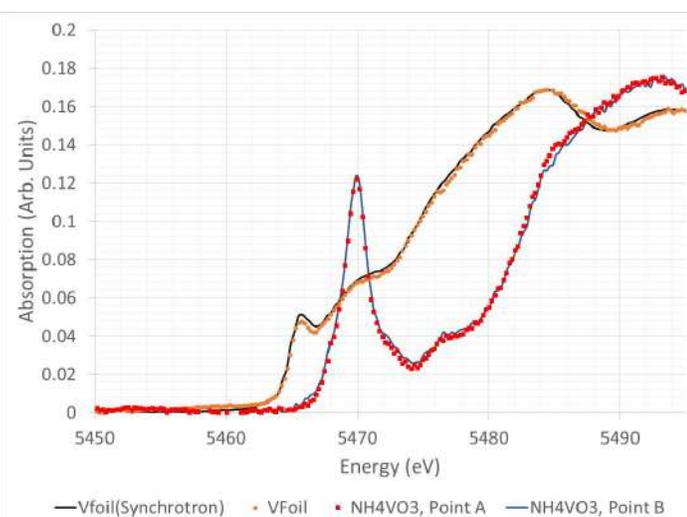


Figure 3: NH₄VO₃ and V foil XANES spectra, showing agreement between synchrotron (black) and QuantumLeap (orange) for V foil and between different points on the NH₄VO₃ sample. QuantumLeap-210 scaled acquisition times and energy resolution for the samples are as follows: (1) V Foil: 22.5 min @0.22 eV, (2) NH₄VO₃ Point A: 45 min @0.22 eV, (3) NH₄VO₃ Point B: 19.5 min @0.22eV

The absorption peak shift is clear with the excellent 0.22 eV resolution. In addition, reference V foil showed good agreement with synchrotron results. To verify the repeatability of the ammonium metavanadate sample, a second point (point B) was taken 3 mm away from the first one (point A) and in less than half the acquisition time of the first. The two datasets demonstrate the reliability of the results.

SUMMARY

QuantumLeap™ has demonstrated synchrotron-like capabilities for analyzing chemical states of catalysts, with high throughput and energy resolution of down to 0.2 eV for XANES.

References

1. American Chemical Society report: "Technology Vision 2020: The US Chemical Industry" 2013.
2. M Fernandez-Garcia. "XANES analysis of catalytic systems under reaction conditions." *Catalysis Reviews* Vol. 57 (2015): 59-121.
3. E Teblum, et al. "Role of catalyst oxidation state in the growth of vertically aligned carbon nanotubes." *J Phys Chem C* (2012)
4. SS Sonar, et al. "Ammonium metavanadate: an effective catalyst for synthesis of α -hydroxyphosphonates." *ARKIVOC* 2009: 138-148.
5. GR Jadhav, et al. "Ammonium metavanadate: a novel catalyst for synthesis of 2-substituted benzimidazole derivatives." *Chinese Chemical Letters* Vol. 20, Issue 3 (2009): 292-295.

SIGRAY

5750 Imhoff Drive, Suite I,
Concord, CA 94520 USA
P: +1-925-446-4183

sigray.com
info@sigray.com