Unraveling the Complexity of Industrial Catalysts using in situ X-ray Absorption Spectroscopy

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Introduction

X-ray absorption fine structure (XAFS) spectroscopy has been a stalwart in catalyst characterization for over thirty years [1]. Thousands of manuscripts have been published in the field of catalysis by groups worldwide where XAFS has been used as a primary characterization technique. In the past 10 years, more than 10% of all publications in the field of XAFS are catalysis based, and for the past 2 years the number of citations of catalysis publications using XAFS has grown dramatically to nearly 10,000 per year. Today all synchrotron radiation sources have at least one beamline dedicated to XAFS and several have, or are considering, a dedicated beamline for catalyst-specific XAFS research.

The reason for the widespread use of the technique is a result of several factors. It is known that the reaction environment can change the structure of the catalyst [3]. Hence the power of XAFS is its ability to probe specific elements within a catalyst under relevant reaction conditions, e.g. elevated temperature and pressure (in situ characterization of the catalyst) [1,2]. The element-specific information provided by XAFS includes local atomic structure (bond lengths, number and type of nearest atomic neighbor, degree of disorder), and chemical structure (electronic state, valence, oxidation state); these properties often cannot be obtained by any other method. This information is then coupled with the catalytic activity of the catalyst and used to develop structure-activity relationships.

This presentation will focus on a few key highlights using different experimental methodologies and approaches. Examples will be provided from both UOP and from other groups. Key strengths and weaknesses of the technique will be discussed. Emphasis will be made on the differences between XAFS and other common characterization methods such as XRD and TEM. The focus will be in the application of XAFS to the understanding of industrial catalysts, and their inherent complexity.

Materials and Methods

The authors XAFS data were collected at the NSLS at Brookhaven National Laboratory, or the APS at Argonne National Laboratory. The catalysts were placed into custom-designed reactors, and the sample environment and temperature controlled via a microprocessor-controlled manifold [4-6]. EXAFS data reduction and analysis were performed using Athena [7], which is an interface to IFEFFIT [8] and FEFFIT [9].

Results and Discussion

Experimental methodology. The reaction cell used to collect the XAFS data is a critical and integral component of the experiment. Examples will be provided of different methodologies that have been used.

Catalyst systems. The heart of the talk focuses on the use of XAFS in combination with other techniques to understanding complex industrial catalysts. Examples include Ni-W hydrocracking catalysts [10], Sn-beta zeolite [11], Re/γ-Al_2O_3, and the effect of chemisorbed hydrogen on Pt clusters [12]. These examples will each highlight a different aspect of XAFS in the quest to understand catalyst structure and activity. Other examples from the literature will also be discussed.

The future. What will the future hold for XAFS? Advances are being made in decreasing spatial resolution, increasing energy resolution, and decreasing time resolution. These are then coupled with advanced detectors, and advanced theory. Some examples will be given of experiments that have been conducted using such methodology.

Significance

XAFS continues to provide a unique insight into the working state of catalysts. The future holds significant promise as new beamlines and methodologies, coupled with advanced theoretical and computational support, provide an even deeper understanding of working catalysts.

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