

Simultaneous *in situ* X-ray Absorption Spectroscopic Analysis of Multiple Catalytic Samples

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Introduction

X-ray absorption spectroscopy (XAS) analysis is a powerful tool for heterogeneous catalysis, as it allows for the analysis of the atomic state and environment of the metal species under realistic operating conditions. Commonly, XAS spectra can be collected continuously during a temperature-programmed reaction, allowing for correlation between reactivity of the catalyst and the changes the catalyst undergoes during the reaction.

However, it is often desired to examine the nature of many different catalysts that incorporate the same metal but at a different loading or by a different means of preparation, in order to determine the role synthesis or composition has on the catalytic activity. While it is possible to run a series of XAS-assisted temperature-programmed reactions on a set of similar samples, slight differences in reactor preparation, thermocouple placement, and beam quality can hinder the direct comparison of the resulting XAS spectra. Additionally, scarce beamline time can be lost between runs while waiting for equipment to cool down and to switch reactor units.

Thus, a special sample cell was developed in order to examine by XAS up to four different samples under equivalent operating conditions simultaneously during a temperature-programmed reaction. The design and operation of this cell are discussed further, along with two examples showing the effectiveness of using this multicell sample holder.

Methods and Materials

The *in situ* reactor vessel consisted of a quartz tube, capped at both ends with stainless-steel flanges. The flanges were modified to include gas and thermocouple ports, and cutouts for x-ray windows covered with Kapton. For prior work, samples would be pressed into a self-supporting wafer inside a 2-cm-long, 1-cm-ID stainless-steel cell, which was then placed inside the quartz reactor. Based on this design, a stainless-steel multi-cell holder was manufactured (see Fig. 1) to hold up to four different samples in 30-mm-ID channels. Smaller holes were added to allow for determining the orientation of the sample cell holder via x-ray detection. Samples were loaded into each cell as self-supported wafers. The entire assembly was then loaded inside a clamshell furnace mounted on an x-y table in the path of the beamline and connected to a gas delivery system.

Experiments were performed on the 10-ID beamline of the Materials Research Collaborative Access Team

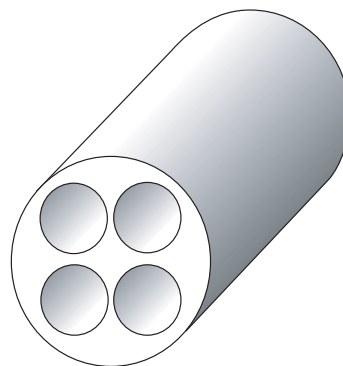


FIG. 1. Multicell sample holder.

(MR-CAT) at the Advanced Photon Source (APS). Prior to the experiment, the beam was raster-scanned over the sample cell holder via the x-y table in order to determine the holder's orientation and the optimal absorption point for each sample. Once the sample alignment was fine-tuned, the reactant gas flow was begun, and a controlled temperature ramp was initiated for the furnace. The XAS scans, comprising data for both x-ray absorption near-edge structure (XANES) and extended x-ray absorption fine structure (EXAFS), were collected repeatedly for each sample, using the x-y table to bring each sample into the beam path in sequence. Scan times were typically of the order of 1 to 3 minutes per sample, allowing 50 to 60 scans for each sample to be collected over the typical 3-to-4 hour run.

Data were analyzed using various tools, including WinXAS, the UWXAFS toolset, and FEFFIT. All spectra for a single sample, and for the sample set when possible, were handled in a batch manner for rapid processing. Most importantly, a rigorous calibration of the spectra over an extended energy range around the absorption edge (as opposed to a single point) using a reference foil scan was performed in order to use batch analysis methods such as factor/principle component analysis.

Results

Two example data sets are presented below. The first set is a series of palladium samples supported on various materials, observed during the process of hydrogen reduction. In general, palladium can reduce fully to Pd metal at very low temperatures, so the reduction program was started at subambient temperatures and slowly raised to 100°C. For three of

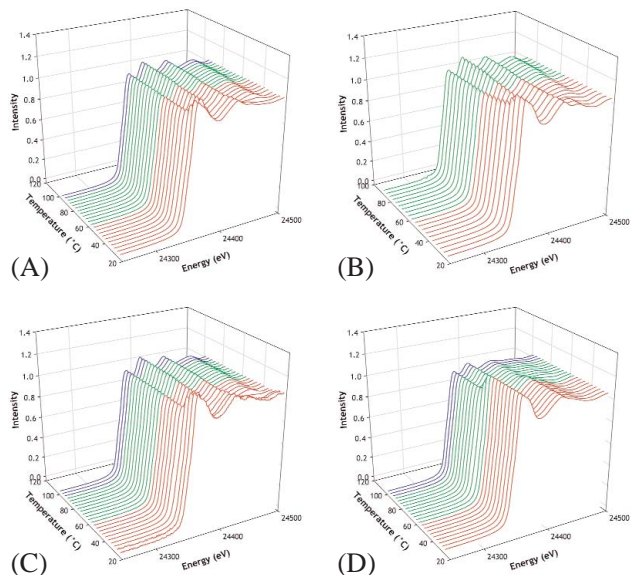


FIG. 2. XANES spectra at the Pd K edge collected during temperature-programmed reduction in H_2 . A) Pd/C, B) Pd/SiO₂, C) Pd/ZnO₂ (aqueous prep.), D) Pd/ZnO₂ (organic prep.).

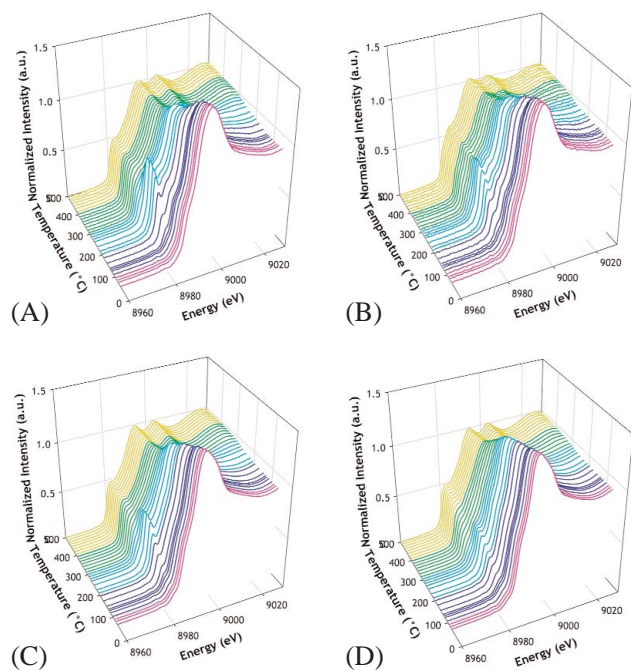


FIG. 3. XANES spectra at the Cu K edge collected during temperature-programmed analysis of modified Cu-ZSM-5 samples. Samples A through D have increasing levels of the modifier.

the samples (Pd/C, Pd/SiO₂, and Pd/ZnO₂ prepared by aqueous addition), the reduction of small PdO clusters is very apparent near 30°C, and the samples are completely reduced to the metallic state (Fig. 2).

However, for a Pd/ZnO₂ sample prepared from an organic solution, the reduction did not occur until 50°C and did not completely reduce to the metal state. The confidence in the reliability of such differences is enhanced by the simultaneous treatment and analysis of each sample by XAS. We are able to confirm that the Pd/ZnO₂ (organic preparation) has a different reduction behavior than the other Pd samples.

A second example of analysis performed with the multicell sample holder was the reduction in hydrogen of a series of modified Cu-ZSM-5 samples. The modification was added at various loadings in order to try to alter the redox properties of Cu-ZSM-5 and maintain a large amount of the more active Cu¹⁺ species (indicated by a large pre-edge feature in the Cu XANES spectra) without generating metallic Cu, which is generally detrimental to catalytic activity. During hydrogen reduction, all four samples undergo the transition from Cu²⁺ to Cu¹⁺ to Cu⁰, but there are subtle differences in both the amount of each phase and the temperatures where these transitions occur (Fig. 3). With increasing content of the modifier, metallic copper does not appear until higher temperatures, shifting by nearly 100°C between the extreme samples. However, increasing the amount of modifier also appears to reduce the amount of Cu¹⁺ formed as a transition stage. Thus, there would be some practical limit to the amount of modifier that could be added as to retain a necessary quantity of the Cu¹⁺ phase to higher temperatures. Without simultaneous analysis of the samples, the subtle difference may have been overlooked.

Discussion

The use of the multicell sample holder for XAS analysis during *in situ* catalytic conditions appears to be an excellent method for analyzing multiple samples simultaneously, thus improving experimental observations and beam time efficiency. While up to four samples can be analyzed at once, additional time is still needed for determining the sample cell orientation, optimal positioning on each sample, and programming of the sequential methods for analysis; however, when all time aspects are considered over a typical beamline shift, the use of the multicell holder effectively doubles the rate at which samples can be analyzed. While this cell only works in transmission mode and without plug flow of the gas through the sample, this method allows for a higher throughput of catalytic testing to be performed on the beamline.

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