

## Development of Combined X-ray Absorption and Diffuse Reflectance UV-Vis In-Situ Spectroscopy

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The combination of X-ray absorption spectroscopy (XAS) and other techniques such as UV-Vis spectroscopy or XRD adds complimentary information that can aid in our understanding of complex materials. Particularly for in-situ measurements where the gas phase composition and temperature are controlled, and time resolved spectra (diffractograms) are measured, the correlation of data becomes much more effective when a combined technique experiment is used.

Alone, XAS is well suited for in-situ characterization of materials because the compromises to the XAS measurement required for a defined atmosphere and temperature are minimal. XAS provides information on local structure and electronic states of a specific element. UV-Vis spectroscopy can provide information on electronic transitions between atomic or molecular orbitals, and can indicate valence and coordination. The UV-Vis spectra compliment the element specific X-ray spectra by measuring a broader system, e.g. a catalyst – adsorbate – support system. A main obstacle in measuring UV-Vis spectra under in situ conditions is transmission of the light to and from the sample without heating the spectrometer.[1] The combination of these two techniques to characterize a sample simultaneously reduces questions of correlatability and allows for the unambiguous interpretation of time resolved data. This combination of techniques may also assist in the interpretation of the XANES and may lead to a fuller understanding of the near edge fine structure. Here we report on the development of an in-situ cell which allows for the simultaneous measurement of time resolved X-ray and UV-Vis spectra.

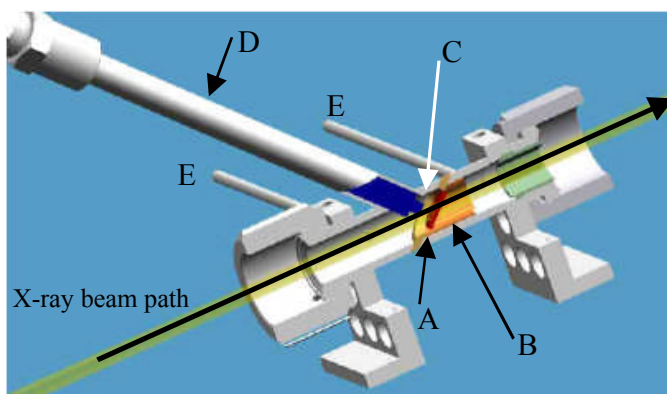


Figure 1: Schematic of UV-Vis XAS cell: A, sample pellet; B, pellet holder; C, tip of optic fiber; D, optic fiber holder; E, gas inlet and outlet.

The newly developed cell is shown in Figures 1 and 2. The requirements for our experiments are temperature control up to 600 °C, a small gas volume for quick gas phase response, and windows to contain the gas phase. The new cell is based on the design of an in-situ XAS cell for time resolved

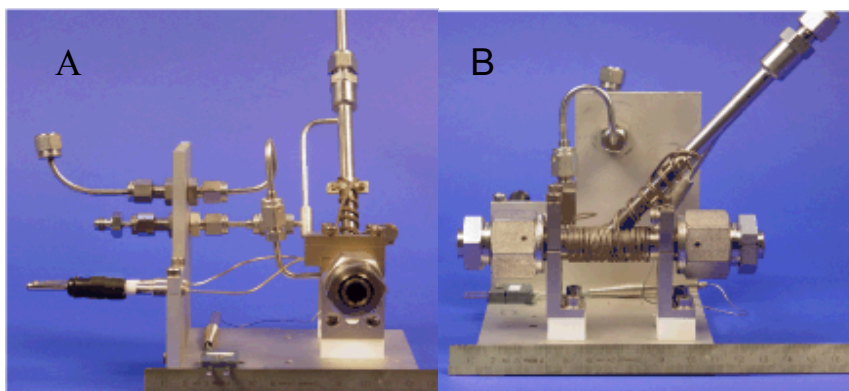


Figure 2: Combined in-situ XAS and UV-Vis spectroscopy cell

measurements.[2] The X-ray spectrum is measured in transmission mode through a 10 mm sample pellet which is held in a sample holder at 45° to the X-ray beam path. The UV-Vis spectrum is measured in diffuse reflectance mode with the light conducted through an Avantis high temperature optical fiber bundle from a Ocean Optics DH2000 combination deuterium and halogen lamp to shine onto the sample pellet at 90°. The reflected light returns through the fiber bundle to an Ocean Optics HR2000 CG-UV-NIR spectrometer. The cell is wrapped with a coaxial heating wire that uniformly heats the cell wall but retains low thermal inertia to allow quick heating and cooling. The cell temperature is measured in the cell wall and controlled by a Eurotherm PID controller. Gas flow is controlled using Brooker HI-TEC mass flow controllers and gas composition is measured with a Pfeiffer Omnistar quadruple mass spectrometer.

Figure 3 shows the near edge region of spectra taken during the reduction of  $V_2O_5$  using the new combined technique cell (10 wt% in BN, heating to 500°C at 6 K/min in 2%  $H_2$ ). Each spectrum required 9 minutes to measure. Factor analysis of the data in Figure 3 indicate that three spectra components are significant for the changes in the near edge spectrum. Additionally, from the factor analysis, the abstract concentrations are obtained. The abstract concentrations are the amount of each spectra component that is required to simulate the measured spectrum. Because the spectral components can correspond to material components in the sample, the abstract concentrations are indicative of the changes to the material components in the sample. In Figure 4, abstract concentrations are presented after normalization, and for the concentration of components 1 and 2, inversion.

Figure 5 show UV-Vis spectra measured using the new cell.  $V_2O_5$  is reduced by heating to 500°C in 2%  $H_2$ . The  $V_2O_5$  shows two distinct adsorption bands at about 330 and 490 nm. These bands decrease during reduction of the  $V_2O_5$ . While mixtures of BN and powdered samples to form pellets works well for XAS, it is often preferable to have a

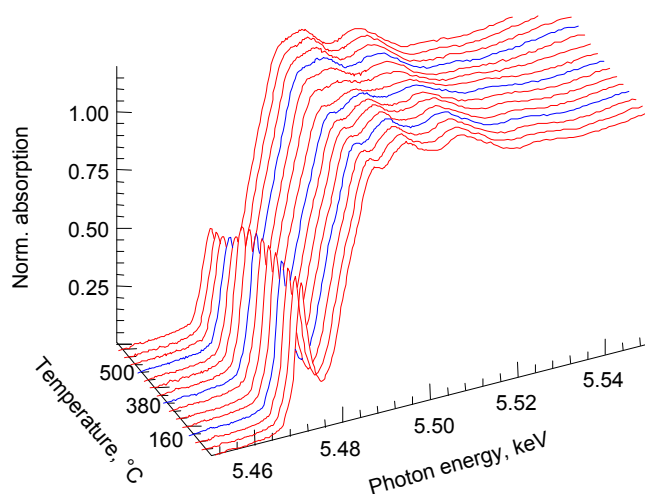


Figure 3: X-ray spectra taken of  $V_2O_5$  during heating to 500 °C in 2%  $H_2$

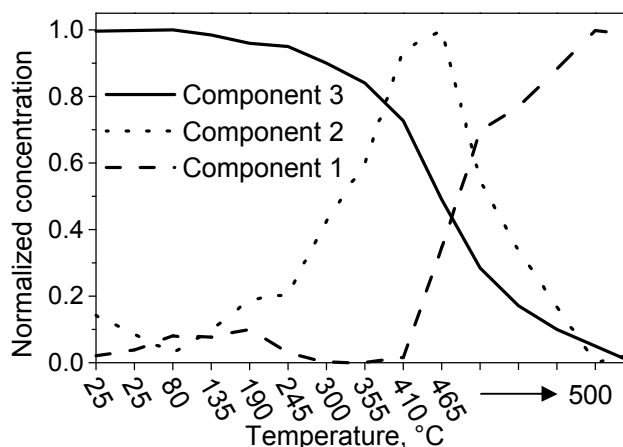


Figure 4: Normalized abstract concentrations from principle component analysis of data in Figure 3.

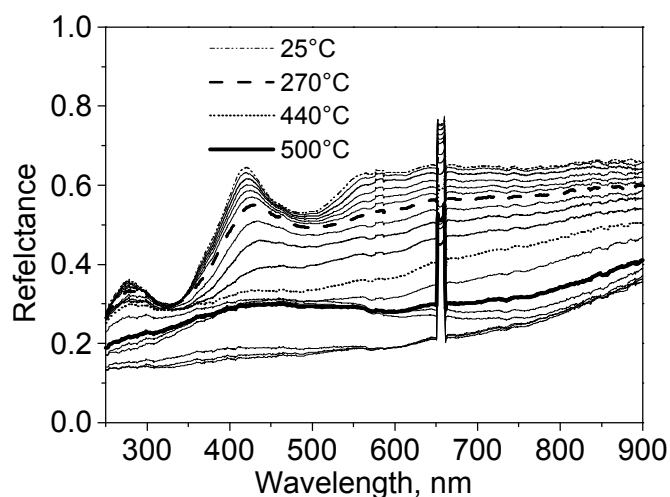


Figure 5: UV-Vis data measured during heating of  $V_2O_5$  to 500°C in 2%  $H_2$



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pure sample for the UV-Vis measurements. This has been accomplished through the formation of layered pellets using a BN layer to support a thin layer of sample.

We have shown here that our combined in-situ XAS and UV-Vis cell is able to produce high quality data for both energy ranges. In combination with gas phase analysis this cell can be used for the investigation of solid catalysts under reaction conditions.

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## References

- [1] J. Melsheimer M. Thiede, R. Ahmed, G. Tzolova-Müller, and F.C. Jentoft, *Phys.Chem.Chem Phys.* 5 (20), 4366 (2003)
- [2] The design of this original XAS cell for time resolved measurement was by Michael Hagelstein and Thomas Neisius in a cooperation between ID24 at ESRF and the Fritz-Haber-Institute.