High Pressure In Situ XAS Reactor for Catalysis

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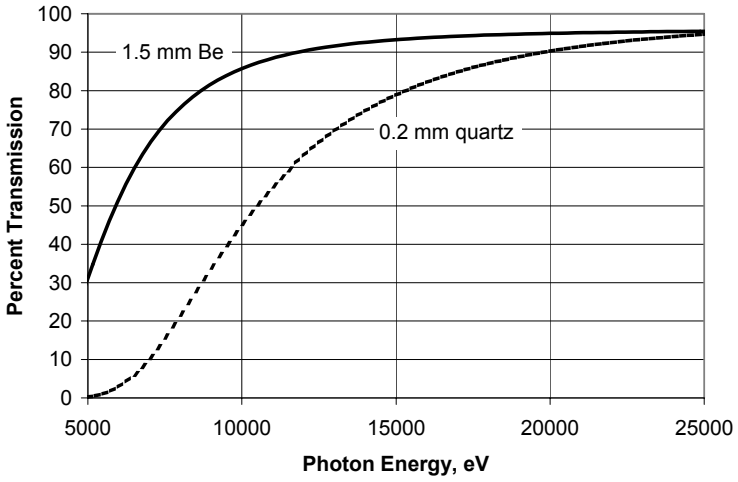
Introduction

It has been a long-standing goal in virtually all catalyst characterization techniques to study the catalyst under working conditions. While it is often easy to study catalysts at elevated temperatures, examining working catalysts at elevated pressures in the presence of reaction mixtures can be quite difficult, and compromises are often made. Simultaneous measurement of catalyst performance under realistic conditions can be even more difficult. A new reactor fabricated from beryllium has been developed that enables the measurement of X-ray absorption spectra of a catalyst in operation at elevated temperatures and pressures and in virtually any reaction mixture. The plug-flow design also allows simultaneous measurement of catalyst performance.

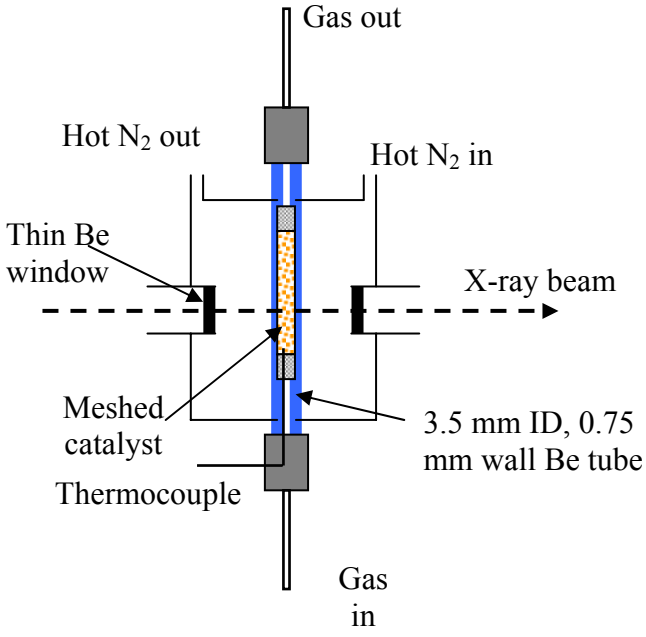
Results and Discussion

The most common in situ XAS cell design uses catalyst pressed into a wafer and held in an atmosphere believed to approximate that encountered by real catalysts. This pressed-wafer design, however, leads to significant mass transfer limitations, making it difficult to ensure that the catalyst is performing correctly, and making it virtually impossible to correlate the observed catalyst characteristics with activity and selectivity. In addition, the large void volume limits the extent of conversion attainable and lengthens the time required to reach steady state after a change in process conditions. A true plug-flow in situ cell was proposed by Clausen, et al[1], in which the catalyst was packed into a 0.4 mm OD quartz tube and heated by hot air. A similar design was reported by Barton, et al[2] with a somewhat larger diameter quartz tube (1.0 mm OD). While both of these designs represent a significant improvement over the pressed-wafer reactor, both suffer from high X-ray absorbence by the quartz tube at energies below 20 keV. Moreover, the small diameter of these reactors constrains the X-ray path length, limiting their usefulness for dilute samples.

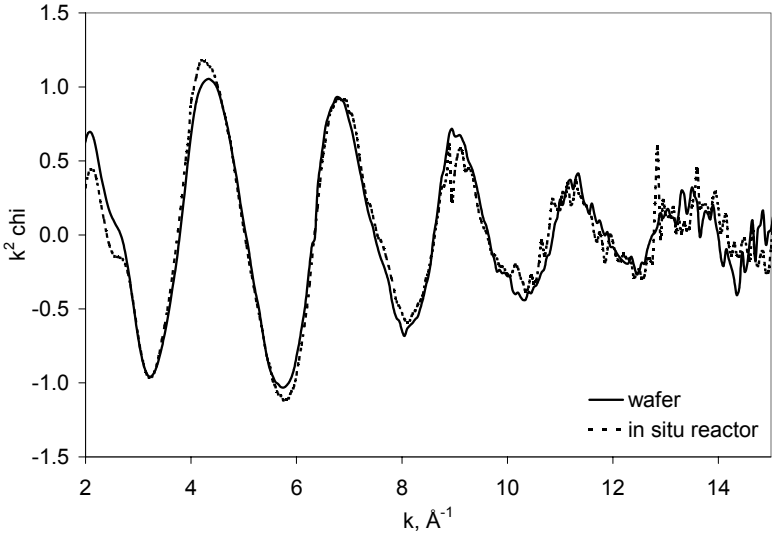
Our design uses a plug-flow reactor made entirely from beryllium. The tube is 100 mm in length, 5 mm OD, 3.5 mm ID, and is heated by hot gas (air or nitrogen), supplied by a serpentine heater. As can be seen in the graph, the 1.5 mm



beryllium walls transmit more than 85% of the X-ray intensity at 10 keV. Furthermore, beryllium is extremely strong, and the reactor is rated at 600°C and 1000 psig, making it possible to do true in situ experiments on a wide variety of working catalysts. The reactor is connected to the gas and feed handling system by compression fittings and graphite ferrules at either end. A custom-designed oven with two thin Be windows fits around the reactor.



The spectroscopic performance of the beryllium tube reactor is demonstrated by the figure at right, which shows two spectra of the same catalyst (0.7 wt% Re supported on γ-alumina). One spectrum was taken on a pressed wafer, while the other was taken with the catalyst packed into the beryllium tube reactor. While the signal-to-noise is degraded somewhat by the reactor walls, the quality is more than adequate for EXAFS characterization.



References

1. B.S. Clausen, G. Steffensen, B. Fabius, J. Villadsen, R. Feidenhans'l, H. Topsoe, *J. Catal*. 132 (1991) 524
2. D.G. Barton, S.L. Soled, G.D. Meitzner, G.A. Fuentes, E. Iglesia. *J. Catal*. 181 (1999) 57.