Design and Operation of an In Situ High Pressure Reaction Cell for X-Ray Absorption Spectroscopy

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Abstract. The design and initial operation of an in situ catalysis reaction cell for x-ray absorption spectroscopy measurements at high pressure is described. The design is based on an x-ray transparent tube fabricated from beryllium. This forms a true plug flow reactor for catalysis studies. The reactor is coupled to a portable microprocessor-controlled versatile feed system, and incorporates on-line analysis of reaction products. XAFS data recorded during the reduction of a NiRe/carbon catalyst at 4 bar are used to illustrate the performance of the reactor.

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INTRODUCTION

The use of in situ X-ray absorption spectroscopy has proven to be a critical characterization technique for the understanding of the local atomic and geometric structure of catalysts. However, in order for XAFS data to be collected an appropriate in situ reaction cell must be designed and constructed. This process has led to many different designs being published in the literature [1-4, and references therein]. Each new design that is published has its own set of advantages and disadvantages, and there is usually a compromise made between the quality of the XAFS data that is needed and the physical characteristics of the reaction cell. In this paper we briefly describe the design and initial operation of a reaction cell that is a true plug flow reactor and is designed to operate at pressures up to several hundred psig. Specific design and operational parameters and additional examples are provided elsewhere [5].

EXPERIMENTAL

XAFS Measurements and Sample Preparation

Data reduction and analysis were performed using Athena and Artemis [6] which are an interface to IFEFFIT [7]. The data were modeled in R-space with theoretical models constructed from FEFF [8]. The EXAFS data were collected at beamline 33-BM-B at the Advanced Photon Source, Argonne National Laboratory. The APS was operated at 7 GeV with a constant ring current of 105 mA.

The Ni/Re on activated carbon was prepared using standard impregnation procedures using nitrate salts. Details of the beamline and sample preparation are given elsewhere [5].

XAFS Catalytic Reactor Cell Design

The heart of the design uses a tube fabricated from PF-60 grade beryllium [9] as the X-ray transparent reactor. This tube contains the meshed catalyst. In many respects beryllium is the ideal material for the fabrication of a catalytic reactor. It is relatively inert, strong, and for the purposes of x-ray spectroscopy, has a low absorption cross-section. This latter property means that reactors of significantly thicker walls can be used than, for example, those made from quartz. For example, 1.5 mm of Be has the same x-ray transparency at 0.04 mm of quartz.

Figure 1 shows a picture of the Be tube reactor housed in the oven. The seal to the Be tube is made using graphite ferrules in bulkhead compression fittings. One of the compression fittings is a “tee.” The straight through part of the “tee” holds the thermocouple in place. The thermocouple extends by 1-2 mm into the catalyst bed, ensuring that the actual catalyst bed temperature is measured. Heating is via hot nitrogen, heated using a serpentine heater, that is

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connected to an oven that fits around the Be tube reactor. The cylindrical oven has two standard pipe thread fittings arranged perpendicular to the Be tube. At the end of these fittings a thin Be foil has been brazed to act as an x-ray transparent window through

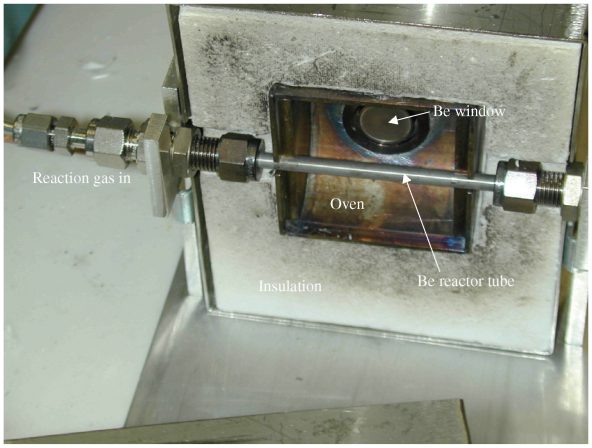

FIGURE 1. Photograph of the tube and oven with one-half of the oven removed to allow visualization of the placement of the Be tube.

the oven walls. The extra 0.5 mm thickness of the Be windows has minimal impact of the x-ray transparency at >10 keV. The oven is surrounded by ceramic insulation as shown in Figure 1. The catalyst temperature is controlled using a Eurotherm controller, and the axial temperature is uniform within two degrees along the length of the catalyst bed. The Be tubes are pressure rated to 350 bar, and could be used for in situ reactions up to this pressure. In the current configuration the pressure is limited to 8 bar due to the choice of solenoid valves in the gas/liquid feed system.

Gas/Liquid Feed System and Product Analysis

The gas/liquid feed system to the reactor is modular allowing easy movement and assembly at the beamline. There are six mass flow controllers for gas feeds. Two of the mass flow controllers supply helium (low and high flow), one for hydrogen, one for 20% oxygen in helium, and two reserved for hydrocarbon or other gases. A three-legged saturator is used for saturated vapor delivery. An Isco syringe pump is used to deliver liquids. The liquid feed is vaporized using a temperature-regulated vortex mixer. The total pressure in the reactor is established using a back pressure controller. Pressure transducers are used to monitor the pressure of the feed, and the reactor pressure. The whole system is micro-processor controlled using LabView-based automation software and FieldPoint distributed I/O hardware. This allows full control of the gas atmosphere and pressure inside the reactor from outside the hutch. The reaction products are analyzed using either a micro-GC or a mass spectrometer with appropriate gas sampling manifolds.

RESULTS AND DISCUSSION

XAFS data recorded during the reduction of a NiRe/carbon catalyst at 4 bar are used to illustrate the performance of the reactor. Seventy five mg of 100/120 mesh particles of the 5 wt% Ni/ 1wt% Re on activated carbon were loaded into the Be tube. After collecting Re L_3-edge EXAFS data on the as-received catalyst, the catalyst was reduced in a flow of 5% H_2/95% He at a flow rate of 100 cm^3/min and a total pressure of 4 bar. The temperature was ramped at 3 deg/min to 320°C, and held at 320°C for one hr.

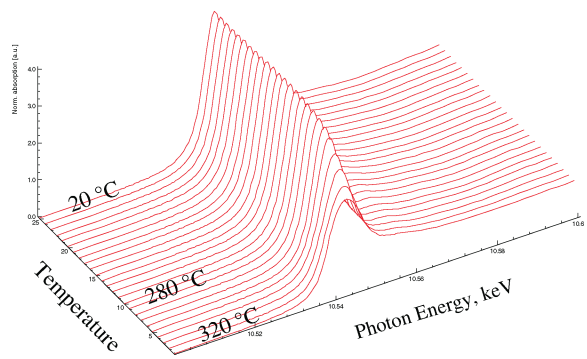

FIGURE 2. In situ Re L_3-edge XANES of the NiRe/carbon catalyst recorded in a flow of 100% hydrogen at 4 bar while the temperature was ramped at 3 deg/min to 320°C.

Figure 2 shows the Re L_3-edge XANES recorded in situ as the catalyst undergoes reduction. The intensity of the white line at the Re L_3-edge diminishes and moves to lower energy as the reduction progresses. Clearly the quality of these XANES data is such that they could be used to extract both the kinetics of reduction and the temperature where the metals reduce. The Re L_3-edge $k^2.\chi(k)$ EXAFS data recorded at 320°C in 4 bar of hydrogen after the ramp and hold in hydrogen are shown in Figure 3A, and the magnitude of the Fourier transform (FT) shown in Figure 3B. The data quality is excellent, with good signal/noise out to >12 $Å^{-1}$. A 5-shell fit to the data has been performed, and the fit is plotted together with the data in Figure 3. The details of the fit are shown in Table 1.

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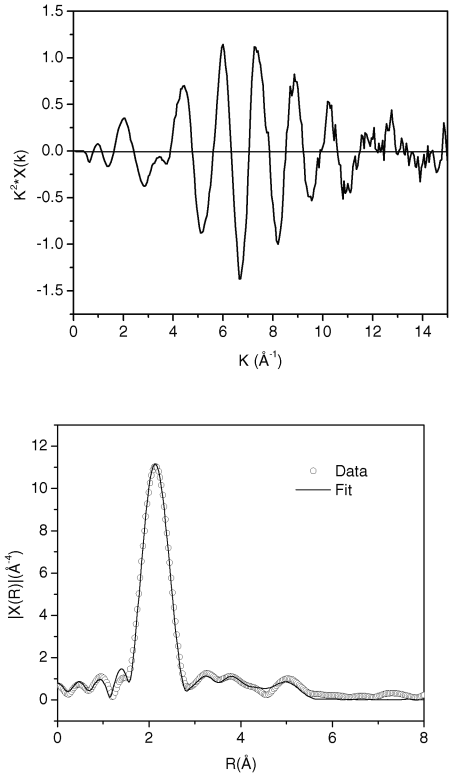

FIGURE 3. Re L_3-edge EXAFS data of the reduced NiRe/carbon catalyst recorded at 320°C in 4 bar hydrogen. (top) $k^2 \cdot \chi(k)$ plot of the EXAFS data. (bottom) The magnitude of the FT of the EXAFS data (symbols) and best fit (line). The FT range is from 3.0 to 10.6 Å $^{-1}$. The fit range is from 1.0 to 5.6 Å.

The fit to the data was performed in the range Δk = 3.0 – 10.6 Å and ΔR = 1.0 – 5.6 Å, and with k-weights of 1, 2, and 3. The EXAFS data show that the rhenium is reduced to metallic rhenium, that it forms bimetallic clusters with the Ni, and that the clusters have the fcc structure. A good quality fit is obtained by using only Ni neighbors. Significantly worse fits are obtained if Re neighbors are added in any of the shells. On average the Re atoms only have Ni neighbors due to the high Ni/Re ratio in this particular catalyst. The Re-Ni bond length that is obtained in the fit (2.50±0.02 Å) is consistent with this model as this is a slight expansion of the Ni-Ni bond length (2.49 Å) due to substitution of the larger Re atom in the Ni lattice. The distances for the first five Ni shells for Ni metal are all consistent with the Re EXAFS results. The CNs are lower for the NiRe catalyst than bulk Ni metal due to the small average particle size of the Re-Ni particles.

Thus the Re forms a homogeneous alloy with the Ni, and there is no indication of a separate Re phase or segregation of the Re from the Ni in the bimetallic clusters. This is to be expected since Ni and Re form a solid solution throughout the whole phase diagram [10].

TABLE 1. EXAFS Modeling Results for Re L_3-edge.

Shell	Ni-Metal CN@R(Å)	CN	R (Å)	σ^2 ($\cdot 10^{-3}$ Å^2)
Re-Ni1	12 @ 2.49	10.0(6)	2.50(2)	9(1)
Re-Ni2	6 @ 3.52	1.3(7)	3.54(2)	11(1)
Re-Ni3	24 @ 4.32	5.8(16)	4.33(3)	12(1)
Re-Ni4	12 @ 4.98	3.0(11)	5.01(3)	12(1)
Re-Ni5	24 @ 5.57	4.0(31)	5.59(3)	12(1)

SUMMARY

The design and initial operation of a versatile capillary-type transmission XAFS reactor has been demonstrated. The overall experimental arrangement of the Be tube cell, gas feed system, and on-line analysis is able to provide high quality XAFS data. The reactor can be used over a wide range of x-ray energies.

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