An inexpensive plug flow reactor for X-ray absorption spectroscopy at catalytically relevant reaction conditions

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Introduction

X-ray absorption spectroscopy (XAS) is a powerful technique to determine the structure of the metallic phase of catalysts under reaction conditions. Coordination numbers, interatomic distances and oxidation states can be measured by extended x-ray adsorption fine structure (EXAFS) or x-ray absorption near edge spectroscopy (XANES). In addition, it is highly desirable to measure reaction kinetics at the same time the XAS data is collected (*operando*) to assure a proper structure-property relationship, as opposed to an *in situ* cell in which only X-ray absorbance is observed and kinetic data is not measured. Clausen and Topsøe [1] utilized a capillary tube as an *operando* XAS reactor to study high pressure and high temperature Cu-based catalysts. Recently, Bare *et al.* [2] have demonstrated an *operando* Be plug flow reactor (PFR). However, the high cost of Be and handling hazards make this choice non-ideal.

We describe here a novel system that functions as an *operando* XAS reactor at catalytically relevant temperatures up to 550 °C and pressures up to 20 bars. We used a readily available borosilicate glass tube reactor loaded with a 2% Pd, 13.7% Zn on Al_2O_3 catalyst to probe the water-gas shift (WGS) reaction and validate the *operando* plug flow reactor.

Materials and Methods

X-ray absorption measurements were made on the insertion device (ID) beamline, 10-ID-B, of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source (APS), Argonne National Laboratory. The basis for the design of the *operando* XAS cell is a PFR. A borosilicate glass tube reactor (OD: 0.25", ID: 0.152", 10 cm long) was housed in a temperature controlled Al heating block in which X-rays pass through the catalyst by way of a 0.25" through hole. The 2.0% Pd, 13.7% Zn on γ-alumina catalyst was prepared by a standard technique described elsewhere [3]. The reactant gas flow rate was a standard WGS gas composition of 21.4% H_2, 6.4% CO, 11% H_2O, and balance Ar, the latter used as an internal standard. The rate of CO consumption was used to calculate WGS rate and the effluent gas was analyzed with a gas chromatograph. To determine the apparent activation energy the temperature was varied over a 100 °C range under the standard WGS gas composition. A 1.5% Pt on SiO_2 catalyst was used [4] to determine the operability at a lower photon energy.

Results and Discussion

To validate the borosilicate glass tube reactor as a true PFR, it was loaded with a 2.0% Pd, 13.7% Zn on γ-alumina catalyst and tested under WGS before the XAS measurements. The apparent activation energy E_a within the temperature range of 200-300 °C was 65.4 ± 1.7 kJ/mol, in agreement with 69 ± 3 kJ/mol found by Bollmann *et al.* [3], and the rate at 250 °C was $1.2x10^{-6} \pm 0.1x10^{6}$ mol s^{-1} g-cat^{-1}. The rate reported from Bollmann *et al.* adjusted to our conditions is $1.4x10^{-6}$ mol s^{-1} g-cat^{-1}, a difference of 15%. The cell was then placed in the beam path and the WGS rate measured. Figure 1 shows the rate measured away from the beam (labeled 'No beam' in Figure 1a) and in the beam while XAS was being performed (labeled 'Beam' in Figure 1a). At 250 °C, the difference between the measured rates outside the beam path and in the beam path was 18%. Figure 1(b) is a demonstration of the *operando* cell's ability to perform X-ray absorption measurements while simultaneously operating as a PFR. One can see a clear Pd-Pd peak at 2.74 Å, Pd-Zn at 2.52 Å and Pd-O at 2.00 Å.

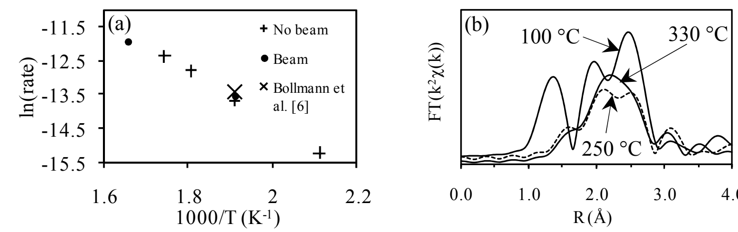

Figure 1: Arrhenius plot of 2.0% Pd, 13.7% Zn on γ-alumina (a). 'No beam' rates were measured outside of the beamline while 'Beam' rates were measured during XAS. The EXAFS data (b) is shown for the corresponding, simultaneous 'Beam' rates.

Figure 1(b) shows that a Pd-Zn alloy is formed at higher temperatures under WGS flow conditions, shown to increase the WGS rate [3]. Additionally, Figure 1 demonstrates the capability of using inexpensive borosilicate glass tubes as *operando* XAS cells at the Pd K edge (24.350 keV). Additionally, at lower energies, e.g. the Pt L_3 (11.564 keV) edge, could still be collected. Different reactor sizes or materials (quartz) can be used if different pressure and temperature requirements are needed.

Significance

The design and test of an *operando* XAS cell design is presented. It is inexpensive to construct and operate and will help answer structural-property relationships in catalysts. In addition to the WGS reaction, this *operando* XAS cell can be used for liquids at temperature up to 550 °C or pressures up to 20 bars. These experiments are possible today thanks to the high flux 3rd generation insertion device beamlines.

References

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