Application of *operando* XAS and FTIR in gaining fundamental understanding of catalyst kinetics and active sites for NH_3-SCR and WGS

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Introduction and Objectives

The application of *operando* techniques is becoming a more common tool to help unravel catalytic functions. Our group has custom built two *operando* reactors, one for measurements by X-ray absorption spectroscopy (XAS) the other for transmission FTIR. The objective of this presentation is to show the great advantage and sometimes necessity of performing *operando* experiments over conventional *in situ* experiments using the NH_3 selective catalytic reduction (SCR) of NO_x and water-gas shift (WGS) reaction.

Results and Discussion

Operando XAS for Selective Catalytic Reduction

We have constructed a vitreous carbon based, powder bed, down-flow catalyst reactor to study the active site of Cu/zeolite catalysts for SCR (Figure 1 on right) [1]. Under standard SCR conditions of 300 ppm NO, 300 ppm NH_3, 5% O_2, 5% H_2O and 5% CO_2 we found that 15, 45, and 65% of Cu on Cu/SSZ-13, Cu/SAPO-34 and Cu/ZSM-5 was in the reduced Cu(I) state, the remainder maintaining its fully oxidized Cu(II) oxidation state suggesting a redox nature for the SCR reaction. Further evidence of this redox nature comes from unsteady-state experiments where various reactants are systematically cut out of the reaction mixture, thus isolating either the oxidative or reducing portion of the SCR reaction and which leads to the removal or generation of Cu(I). Using a 200 x 200 μm X-ray beam also allowed our group to measure the oxidation state change of Cu over the length of the catalyst bed under non-differential conditions. With a NO_2:NO_x ratio of 1:5, for example, there is a marked increase in Cu(I) as the X-ray beam is moved from the top to the bottom of the catalyst bed (i.e more oxidizing to less oxidizing conditions).

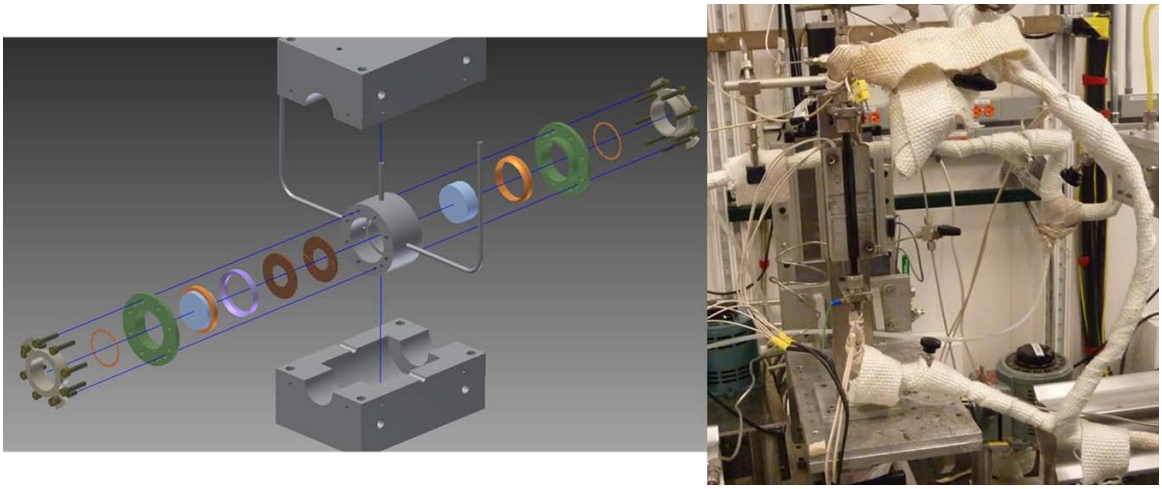

Figure 1. Left: Exploded view of transmission IR cell CAD drawing with heater block. Right: *Operando* XAS cell (with front heater plate removed) and associated gas lines installed at APS Sector 10 MRCAT.

Operando FTIR of Au/TiO_2 for the WGS Reaction

Studying the deactivation of a fresh 2.3 wt.% Au/TiO_2 catalyst at 200 ˚C in our custom built *operando* transmission FTIR cell (Figure 1 on left), we found that the change in rate directly correlated with the amount of CO adsorbed on Au metal sites (2100 cm^{-1}). A surface regeneration step, which removed nearly all carbonate- and formate-like species while leaving the deactivated catalytic rate unchanged, ruled out accumulation of these surface species as a cause for deactivation. Similarly, CO adsorbed on $Au^{\delta-}$ (2040 cm^{-1}), sites did not correlate with the decrease in rates either. These results, together with TEM measurements, indicate that a loss of surface sites (i.e. particle sintering) caused deactivation and showed metal corner atoms to be the active sites for WGS at these temperatures. More specifically, these metals sites are low coordinated corner atoms on cubo-octahedral particles.

Significance

We describe two new cells that allow us to simultaneously collect high quality spectroscopic (FTIR or XAS) and kinetic data. We have successfully applied each cell to answer fundamental questions about the active site and mechanism of the SCR and WGS reactions.

References

[1] V. F. Kispersky, J. A. Kropf, F. H. Ribeiro, J. T. Miller. Phys. Chem. Chem. Phys., 2012, DOI: 10.1039/C1CP22992C