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Wednesday, November 17, 2010
Crowne Plaza Hotel, Somerset, New Jersey

Federico Barrai
Ph.D. Candidate
Columbia University

***“Preferential Oxidation of CO on Pt: Regimes of Operation
and the Impact of Transport on Selectivity”***

Preferential Oxidation (PROX) of CO is a selective catalytic process consisting of competitive oxidation of CO and H₂ with O₂, and the reverse water gas shift reaction (rWGS). This reactor can be employed as a prototype reactor for complex selective processes such as the reforming of fuels via O₂ and H₂O. For this research 5% Pt on - Al₂O₃ was employed as a catalyst. A comparison between PROX and rWGS reactor operation identified two regimes. In the high temperature regime, where CO conversion decreases with increasing temperature, rWGS and PROX results overlap. This suggests that the rWGS reaction is responsible for the CO conversion trend. In the intermediate temperature regime, where CO conversion levels off, experimental data were inconclusive and a microkinetic model was developed to shed light into the reaction mechanism. The model determined that these two regimes are the expression of a switch in rate limiting step of the same reaction network. Heat and mass transfer effects were investigated by testing two different catalyst substrate geometries: the monolith and wire-screens. Results show that wire-screens exhibit a higher conversion and selectivity towards CO oxidation compared to the monolith. An analysis using a kinetic-transport model of the PROX reactor suggests that O₂ and CO concentration gradients between catalyst wall and bulk gas, as well as oxidation reaction orders are affecting the CO oxidation selectivity. This finding enables tuning process selectivity by tailoring heat and mass transfer characteristics by using the appropriate catalyst substrate.

Christopher L. Marshall
Chemical Sciences and Engineering Division
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“In Situ Characterization of Small Metal Particles Using XAS”

Characterization of catalysts under working conditions (sometimes referred to as Operando) has become increasingly important for elucidating structures and reaction pathways. X-ray Absorption Fine Structure Spectroscopy (XAFS) provides valuable information regarding the oxidation state of the metal along with the number and type of coordinating ligands. This talk will highlight two separate systems examined via in situ XAFS.

In the first system, we will elucidate the mechanism of deposition of platinum metal alumina via Atomic Layer Deposition (ALD). X-ray absorption fine structure was utilized to monitor the changes in the Pt species during each step of the synthesis. The temperature, precursor exposure time, treatment gas, and number of ALD cycles were found to affect the Pt particle size and density. Lower-temperature MeCpPtMe₃ adsorption yielded smaller particles due to reduced thermal decomposition. A 300 °C air treatment of the adsorbed MeCpPtMe₃ leads to PtO. In subsequent ALD cycles, the MeCpPtMe₃ reduces the PtO to metallic Pt in the ratio of one precursor molecule per PtO. A 200°C H₂ treatment of the adsorbed MeCpPtMe₃ leads to the formation of 1-2 nm, metallic Pt nanoparticles.

In the second system, we use XAFS to elucidate the mechanism for Pt catalysts for the conversion of paraffins to alcohols. Site isolation of organometallic moieties by interaction with a metal oxide support is a powerful strategy for the formation of solid-state 'molecular' catalysts. However, the connections between the structure/activity relationships seen in solution and those of the supported catalysts are not well understood. In acidic aqueous solution, Shilov demonstrated that PtHCl₄²⁻ selectively oxidizes methane to methanol and methyl chloride at 120°C and ~100 atm. We have supported H₂PtX₆ (X = Cl, Br, I) on gamma-alumina, which yields an adsorbed [PtIVX₆]²⁻ anion. In a gas-phase flow reactor, these solid catalysts selectively oxidize propane to functionalized products (alcohols, alkyl halides, alkenes) at 100 - 200°C and atmospheric pressure. This is a remarkable decrease in pressure and residence time relative to the solution reactions. In-situ EXAFS under reaction conditions show that propane in the absence of O₂ reduces Pt(IV) to Pt(II). Exposure to O₂ then reoxidizes the metal without incorporating oxygen into the coordination sphere. Time-dependent, XANES was also used to determine the rate limiting step. Recent results including trends in selectivity and reactivity will be discussed.

In both cases, XAFS provides unique insights into the changing chemical nature of the supported metals in catalytic systems.

Dinner is a buffet, and includes <u>a choice of beef, chicken or fish</u>		Members	\$37
Social Hour (Cash Bar)	6:00 PM	Non-members	\$45
Dinner	7:00 PM	Students	\$17 (<i>Student Members = \$5</i>)
Presentation	7:45 PM	Retired/Post-Doc/ Unemp.	\$37 (<i>Members = \$27</i>)
		Annual Dues	\$15

Deadline for dinner reservations is 2:00 p.m. Friday, November 12, 2010

Call or email Amanda Josey (973) 245-6173 (amanda.josey@basf.com) for reservations. With the exception of extreme circumstances, anyone not canceling reservations by the above deadline will be billed for dinner regardless of attendance.

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