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**Kinetics and Dynamics of Oxidation Reactions Involving
Adsorbed CO Species on Bulk Supported Pt and Copper Oxides**

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Overview of the Project

This research was an integrated experimental and modeling study of oxidation reactions involving CO as a key player - be it a reactant, adsorbed intermediate, and/or partial oxidation product - in the catalytic sequence and chemistry. The reaction systems of interest in the project include CO, formaldehyde, and methanol oxidation by O₂, and CO oxidation by NO, on both Pt and copper oxide catalysts. These reactions are of importance in automobile exhaust catalysis. There is a paucity of rate data in the literature for these important environmental control reactions. A complicating factor is the propensity of these reactions to exhibit complex steady state and dynamic behavior, including multiple rate controlling steps, steady state multiplicity, and oscillatory phenomena. Such phenomena are rooted in some of the central issues of catalysis, including adsorbate interactions, and catalyst structural instabilities, such as surface reconstruction and surface chemical changes by oxidation-reduction.

The goal of this research is to better understand the catalytic chemistry and kinetics of oxidations reactions involving CO as an adsorbed intermediate. Successfully meeting this goal requires an integration of basic kinetic measurements, *in situ* catalyst surface monitoring, kinetic modeling, and nonlinear mathematical tools. While the kinetics experiments have standard microreactor design, the potential for multiple and periodic rate states demands detailed procedures to pinpoint the bifurcation (ignition, extinction, Hopf) points. Kinetic models are constructed from rational mechanistic sequences and sound surface chemistry. These models should predict the correct experimentally measured features, including the basic kinetic trends (apparent reaction orders and activation energy), the location and shape of the operating

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condition region for which the rate is multivalued or periodic, and the trends in the adsorbed state composition. The development of Fourier transform infrared emission spectroscopy (FTIRES) is an essential aspect of the project. FTIRES provides a means of simultaneously monitoring the surface temperature and vibrational spectra corresponding to the adsorbed species and the substrate during a catalytic reactions. FTIRES is used in this research to link such crucial surface information with the overall kinetics.

Two systems were studied as part of this research:

CO oxidation over noble metal catalysts

Oxidation and selective catalytic reduction, SCR, over Oxides

Our results in each of these areas are described below.

CO oxidation over noble metal catalysts

Summary

In the first stage of this research we have studied CO oxidation by oxygen on noble metals (primarily Pt) since parts of the mechanistic sequence occur in more complex reactions which are our primary interest (e.g., formaldehyde and methanol oxidation). Our main thrust has involved the development of a kinetic modeling methodology for reactions such as CO oxidation which exhibit multiple rate phenomena. Several models were developed which were able to predict the basic kinetic trends and multiplicity features observed by experimentalists at total pressures spanning UHV to atmospheric. These accomplishments are contained in Journal of Catalysis papers listed below. The same models are being used to better understand the kinetics of CO oxidation on Pt, Pd, and Rh. This was a collaborative effort with Prof. Gary Haller's group at Yale.

Results

Given that CO oxidation and related reactions are highly exothermic, we have devoted some effort in understanding the impact of the kinetics and thermal effects in experiments which involve ohmic temperature control of unsupported catalysts (e.g., wires, ribbons, foils). We developed a hot wire model comprised of detailed, isothermal Pt-catalyzed CO oxidation kinetics and the pertinent transport processes. Model simulations were carried out to explain the kinetics data we obtained with our electrically heated Pt wire experiment. We observed rate multiplicity over

a wide range of average wire temperatures ($\hat{T}_w = 100 - 350^\circ\text{C}$), feed compositions ($\text{CO}/\text{O}_2 = 0.01 - 1$), and total pressures ($5 - 760$ torr). Several of the observed multiplicity features are atypical of conventional isothermal CO oxidation behavior, such as a $(\hat{T}_w, \text{CO}/\text{O}_2)$ multiplicity region (bifurcation map) with a local maximum in the extinction branch, which is indicative of a pitchfork singularity. For example, at sufficiently low $\hat{T}_w$ and high CO/O_2 an unexpected high rate state was sustained in addition to the expected CO-inhibited, low rate state. Visual inspection of the wire while in the high rate state revealed a glowing hot spot near the center of the wire. We determined that the apparent kinetic anomalies are a manifestation of temperature nonuniformities along a wire of uniform activity and thermal conductivity. The generality of the observed multiplicity features, the observation of hot spots, and the rational model construct suggests that a more complicated kinetic mechanism is not necessary to explain the data. Close similarities between the CO oxidation data, the simulations, and previously reported data for other Pt-catalyzed oxidations (of propylene and ammonia) suggests that the thermokinetically-induced nonuniformities are a general phenomenon. The results underscore the danger of using ohmic temperature control to study the isothermal kinetics of a metal catalyzed reaction. Model simulations were also carried out to identify conditions for which the impact of nonuniformities can be minimized.

In situ studies of V_2O_5 catalysis:

oxidation and SCR.

Summary

We have developed a novel in situ technique to monitor changes in the bulk oxidation state of the near-surface region of a metal oxide catalyst using infrared emission spectroscopy. The reduction of bulk crystalline vanadium pentoxide with H_2 , C_2H_4 , and NH_3 , as well as during the $\text{NO}-\text{NH}_3$ reaction (used for NO_x emission control) were studied in the temperature range $250-375^\circ\text{C}$. The reoxidation of ethylene-reduced vanadium oxide by O_2 was also studied. We had to change the focus of these studies from copper oxides to vanadium oxides as the copper oxides proved to have little activity and the far infrared emissivity was not suited

to monitor the oxidation states *in situ*. Development of active vanadia based catalysts led us to continue the research with this system. The reduction and reoxidation of V_2O_5 was shown to be rate-limited in the diffusion of oxygen through the crystal lattice of the vanadium oxide. The apparent activation energy for the reduction and reoxidation was 170–206 kJ/mol. Reduction occurred for all NO-NH₃ mixtures tested up to 10:1. NO to NH₃ ratios as high as 100:1 failed to reoxidize a pre-reduced vanadia sample after 1 hr at 400 °C.

Results

We have successfully demonstrated the use of FTIRES as an *in situ* catalyst surface probe (Sullivan et al., 1992) and we first focused our efforts on near-IR monitoring of V_2O_5 during reaction between ethylene and oxygen (to acetaldehyde and carbon oxides). This reaction was chosen because of the trade-off between selectivity and activity, and the redox chemistry involving the vanadium oxides. Our goal is to correlate changes in the oxide surface composition with activity and selectivity, while spanning a wide range of operating conditions (catalyst temperature, ethylene/oxygen feed ratio). To this end, in the past year a dedicated kinetics/FTIRES experiment has been constructed. Detailed kinetics data were obtained in the isothermal packed bed microreactor. FTIRES Spectra are obtained in the *in situ* cell. Thus, differential rates were obtained with the microreactor setup. The same gas is flowed over the catalyst sample held at the same temperature within the cell for *in situ* emission characterization of the surface.

The effect of oxidation state on the catalytic performance of unsupported vanadia for the NO-NH₃ reaction, in the absence of O₂, was also studied using a transient technique. Nitrous oxide (N₂O) production increased with the degree of reduction of the catalyst. The behavior was explained by a change in the NO-NH₃ mechanism from an Eley-Rideal process between adsorbed NH₃ and gaseous NO on V_2O_5 to one involving both adsorbed species on V_2O_4 or V_2O_3 .

The fully oxidized sample has a sharp peak at 1030 cm⁻¹ and a broader one at 800-850 cm⁻¹ (Fig. 2). These peaks are assigned to terminally-bonded V=O and V-O-V, respectively. In contrast, a severely reduced sample shows no features. A partially reduced sample has an

additional peak at 915 cm^{-1} . These initial results are encouraging since they imply a correlation between the IR features and the degree of surface oxidation.

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A key aspect of this project was to develop Fourier transform infrared emission spectroscopy (FTIRES) as an *in situ* probe of the catalyst surface. The principal motivation was to monitor changes in the composition of a metal oxide during a oxidation, and, if possible, adsorbed species as well. The coupling between oxidation and reduction of a particular metal oxide is a crucial process in determining the activity and selectivity. Moreover, the interaction of the reaction exothermicity and redox chemistry can lead to complex steady state features (e.g., multiplicity) and dynamic behavior (e.g., long transients, oscillations). Thus, knowledge of the catalyst composition under reaction conditions can provide insight into the identification of active sites and their reactivity.

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Publications and Presentations

Journal Articles

Harold, M. P., and M. E. Garske, "*Kinetics and Multiple Rate States for CO Oxidation on Platinum: Model Development and Multiplicity Analysis*," J. Catalysis, **127**, 524-552 (1992).

Harold, M. P., and M. E. Garske, "*Kinetics and Multiple Rate States for CO Oxidation on Platinum: Linking UHV and High Pressure Behavior*," J. Catalysis, **127**, 553-575 (1992).

Garske, M. E. and M. P. Harold, "Observed Kinetics of an Exothermic Reaction on a Temperature-Controlled Catalytic Wire," Chem. Eng. Sci., **47**, no 3, 623-644.(1993)

Sullivan, D. H., W. C. Conner, and M. P. Harold, "Surface Analysis with FT-IR Emission Spectroscopy," J. Appl. Spectroscopy, **46**, no. 5, 811-818. (1992)

Sullivan, D. H., W. C. Conner, and M. P. Harold, "Solid State Transformations over V₂O₅ during Oxidation Reaction" in preparation

Theses Published by the following Graduate Students Participating in this Research

Martha Garske - Martha completed her PhD thesis in February, 1991. Her thesis was entitled "Kinetics and Multiple Rate States of Platinum-Catalyzed CO Oxidation."

David Sullivan - Dave completed his degree in April, 1994. His thesis was entitled "Kinetics and Dynamics of Carbon Monoxide Oxidation by Nitric Oxide on Vanadium Oxide Using IR-Emission Spectroscopy."

Andrew Olivicro - Andrew is completing his PhD degree in 1995 and is studying the influence of CeO₂ on supported Pt.

Presentations: over a dozen presentations were delivered on this research.