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MORPHOLOGICAL ASPECTS OF SURFACE REACTIONS

PROGRESS REPORT

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TECHNICAL PROGRESS REPORT

Overview

This work focuses on substrate morphology and on fragments synthesized by thermal, electron, and photon activation. The following work is complete: (1) Low energy electron diffraction, Auger electron spectroscopy and scanning tunneling microscopy were used to determine the local morphology of rhodium films on titania. (2) A new tool was developed for diagnosing surface reactions that involve C-H bond cleavage -- predosed oxygen TPD (POTPD), a technique based on scavenging surface H(a) by small amounts of preadsorbed O(a) to form water. (4) For π -bonded benzene on Ag(111), exposure to low energy electrons results in *selective* decomposition of C₆D₆(a) to surface D atoms and phenyl fragments, which recombine and desorb as biphenyl between 275-390 K. Similarly, vinyl fragments have been prepared from ethylene. These fragments open the way for kinetic and spectroscopic characterization of interesting hydrocarbon reactions on transition metals. (5) Using Fourier transform infra-red spectroscopy, we have studied how coadsorbates, particularly carbon monoxide, inhibit the decomposition of ethylidyne. The experiments were done in an ambient pressure of CO in order to maintain a sizable coverage into the temperature regime where ethylidyne normally decomposes.

One aspect of our present work involves morphological studies of Rh on planar TiO₂ surfaces using scanning tunneling microscopy and scanning electron microscopy. The objective is to measure, in some cases in real-time, how the surface morphology changes as oxidation and reduction processes are carried out. In another interesting project, we are preparing spectroscopically significant and reasonably pure concentrations of methyl groups on Pt(111) by exposing physisorbed methane to controlled doses of low energy electrons.

Predosed oxygen temperature programmed desorption.

Based on the propensity of surface atomic oxygen, O(a), to react fiercely with H(a) on Pt(111) to form water that desorbs at low temperature, we have developed a thermal reaction and desorption technique -- predosed oxygen temperature programmed desorption (POTPD) -- which is useful for probing the kinetics of dehydrogenation on Pt(111). The method relies on very low

coverages of O(a) which react with available adsorbed atomic H to form water, which desorbs promptly. Thus, the H₂O TPD reflects the dehydrogenation process. We have successfully utilized POTPD to determine the dehydrogenation temperatures of methylene (CD₂), methyl (CD₃), vinyl (CHCH₂), ethylene (C₂D₄), ethyl (C₂D₅), thioethoxy (SC₂H₅) and diethyl sulfide (S(C₂H₅)₂) on Pt(111). From the data, a mechanism and kinetic parameters for vinyl to ethynyl conversion are presented.

Synthesis of surface vinyl and phenyl fragments by low energy electron activation.

Low energy electron activation of monolayer ethylene and benzene, adsorbed on Ag(111) at 100 K, leads selectively to vinyl and phenyl fragments. An electron impact ionization model, followed by rapid reneutralization and C-H bond cleavage, is proposed. Upon heating, neither fragment undergoes further C-H or C-C bond cleavage; rather, both undergo carbon-carbon coupling to form 1,3-butadiene and biphenyl. When coadsorbed with methyl or ethyl fragments, temperature programmed desorption yields propene or 1-butene for vinyl, whereas it yields toluene or ethyl benzene for phenyl. Kinetic parameters describing the electron-stimulated fragment synthesis and their subsequent thermal reactions were determined in the presence and absence of atomic iodine.

Scanning tunneling microscopy study of rhodium films on titania.

Rhodium films were vapor deposited on TiO₂(001) rutile and examined *in-situ* at various coverages and following various annealing procedures using scanning tunneling microscopy (STM) and Auger electron spectroscopy (AES). Rh deposition at ambient temperature leads to STM images which indicate nucleation and growth of 3-dimensional particles. The particles have a narrow size distribution centered around 30 Å with an aspect ratio of 0.3 and are not arranged with long-range order. AES results corroborate the film thickness measured by STM. Annealing in vacuum decreases both the Rh/Ti Auger intensity ratio and the number density of particles indicating particle coalescence at the onset of surface diffusion. Simultaneously, the apparent included volume of the particle film increases, an effect which is consistent with Rh particle encapsulation but may also be due to tip convolution. The utility of STM in morphologic

characterization of oxide-supported metal particles, such as those found in catalysts and gas sensors, is demonstrated.

Active metals finely dispersed on oxide supports are useful in a broad class of applications. We have used scanning tunneling microscopy (STM) to characterize and to manipulate 30-50 Å rhodium particles grown on TiO₂(001) rutile. Tunneling barrier height values of ≈5 eV (close to the mean tip-sample work function) indicated a good vacuum tunneling gap. The tunneling probe was used to manipulate individual nano-particles via intimate tip-sample point contacts. The results are consistent with cohesive/adhesive tip-particle interactions. This study indicates that supported catalyst and sensor research can be done on a particle-by-particle basis.

How coadsorbates influence the decomposition kinetics of ethylidyne.

Utilizing *in-situ* FT-IRAS we have investigated the decomposition kinetics of ethylidyne in the presence of co-adsorbates on Ru(001). The results demonstrate that the stabilizing effect of co-adsorbed CO and hydrogen is significantly enhanced at elevated pressure, supporting a model wherein an empty neighboring metal site is required before decomposition can proceed. We identify a weakly adsorbed CO species in threefold hollow sites in close proximity to the ethylidyne, whose coverage is controlled by the CO pressure at elevated temperatures. The results demonstrate the importance of weakly adsorbed species at high coverage in controlling surface reactions at elevated pressures and temperatures.

PLANS FOR THE COMING YEAR

Major emphasis will be given to the spectroscopic and kinetic characterization of adsorbed hydrocarbon fragments, e.g., methyl, vinyl, ethyl, and phenyl, synthesized on Pt and Ag surfaces. Non-thermal activation methods will be used to synthesize these fragments and, after structural characterization, their thermal reaction properties will be assessed in transient kinetic experiments. With known initial coverages, the latter will involve both temperature-programmed and isothermal measurements of known coverages of fragment reaction rates, with and without coadsorbates.

Another major effort involves morphological studies using scanning tunneling microscopy and our new environmental scanning electron microscope. Single crystal titania, covered with various amounts of Ag and Rh, will be used in studies of morphological changes of the metal during oxidation and reduction processes. With the ESEM, we plan to investigate these changes in real-time at reaction pressures up to 10 torr.

Throughout our program, we intend to give even-handed attention to both structure (morphology) and kinetics. While these two fit naturally together, the latter is often more time consuming and tedious because many time- and temperature-dependent measurements must be made on a system whose structural parameters are already known. It is our view that understanding the *kinetics* of structurally well-characterized laboratory model systems is crucial to making connections between these models and technical catalysts and that these connections will assist in the design of catalytic systems with potential for future technologies. Morphology is a core issue, particularly in the context of surface reactions. We take a very broad view of this term, i.e., *morphology includes the arrangement of the reacting adsorbates as well as the substrate*. In other words, morphology has time-dependent and time-independent characteristics, and, for completeness, must take into account the whole system -- support, active metal, additives and coadsorbates, and reactants/products. In the midst of this complexity, building models that mimic technical materials is, in our view, important. Thus, this program involves thin metal films and metal particles on planar oxide supports, as well as single crystal metals.

RECENT PUBLICATIONS ARISING FROM THIS PROJECT

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2. X.-L. Zhou, A. L. Schwaner and J. M. White, "Syntheses and Reactions of Vinyl and Phenyl Fragments Ag(111)", JACS, 115 (1993) 4309.
3. G. E. Poirier, B. K. Hance and J. M. White, "Scanning Tunneling Microscopic and Auger Electron Spectroscopic Characterization of a Model Catalyst: Rhodium on TiO₂(001)", J. Phys. Chem. 93 (1993) 5965.
4. G. E. Poirier, B. K. Hance and J. M. White, "Tunneling Probe Manipulation of Individual Rhodium Nano-Particles Supported on TiO₂", J. Phys. Chem. Letts., 27 (1993) 6500.
5. C. A. Mims, M. D. Weisel, F. M. Hoffmann, J. H. Sinfelt and J. M. White, "Site Blocking Effects in Ethylidyne Decomposition Kinetics on Ru(001): In-Situ Study with FT-IRAS at Elevated Pressure", (submitted).

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