Monday Morning, October 2, 2000

Surface Science Room 208 - Session SS1-MoM

Atomic-Scale Studies of Model Catalysts

Moderator: S.H. Overbury, Oak Ridge National Laboratory

8:20am SS1-MoM1 STM Study of H - Al (111): From Alane-Formation Reactions to Absorption-Induced Roughening, *M. Noh, J.E. Reutt-Robey,* University of Maryland

We investigated the reaction of atomic hydrogen with Al (111) with STM under UHV conditions. We show that hydrogen reacts strongly with the substrate to form aluminum hydride oligomers (alanes) which are stable up to ~350K. At lower reaction temperatures (T< ~230K), the distribution of surface alanes is highly nonuniform, with one dimensional strings of alanes extending for thousands of Å. These strings act as mass barriers that direct the distribution of later-form alanes. The alane strings run roughly parallel to crystallographic steps and exhibit a terrace-width-dependent nucleation. We discuss the physical origin of these intriguing reaction patterns. These surface reactions are accompanied by hydrogen absorption. Subsurface hydrogen is sensed indirectly by regions of increased surface roughness that can eventually leads to delamination. * Supported under NSF contract DMR-9632521 and CHE-9800470.

8:40am SS1-MoM2 Dynamic Imaging and Chemical Probing on the Atomic Scale: NO/H@sub 2@ and NO@sub 2@/H@sub 2@ on Pt, *T. Visart de Bocarm@aa e@, T. Baer, C. Voss, N. Kruse,* Universit@aa e@ Libre de Bruxelles, Belgium

The reaction of NO and NO@sub 2@ with hydrogen has been studied on a Pt single crystal using field ion microscopy (FIM) and atom-probe field ion mass spectrometry (APFIMS) under conditions of applied temperatures (395-530 K), pressures (10@super -4@ - 10@super -2@ Pa) and field strength (8.7 V/nm). The 3D-Pt sample ("field emitter tip") has been found to undergo a transformation from a nearly hemispherical shape into a topand edge-truncated pyramid. Kinetic instabilities, including rapid ignition and oscillations, were found for both reactions on this reshaped crystal. Video-FIM (time resolution: 20ms) revealed the rough areas lying between the (001) top plane and the (111) slopes of the pyramid to be catalytically most active. Catalytic ignition to water production was seen to occur in (012) areas with subsequent wave propagation either predominantly along the (for NO/H@sub 2@) or along the zone lines (for NO@sub 2@/H@sub 2@). Thus in either case a strongly anisotropic reaction behavior was observed. Under oscillatory conditions the catalytic cycles lasted for several 100ms only. The local chemical analysis of (012) and (133) planes (comprising several ten Pt atoms) demonstrated the formation of water product (desorption as H@sub 2@O@super +@ and H@sub 3@O@super +@) during the catalytic cycles. Major amounts of NO@sub x@@super +@ were registered due to surface diffusion of either NO or NO@sub 2@ into sites emptied by either reaction. Moreover, the mass spectrometric results strongly suggest NO@sub x@@super +@ to be the imaging species at otherwise rather low field strengths.

9:00am SS1-MoM3 STM Studies on Model Systems Relevant for Catalysis, F. Besenbacher, University of Aarhus, Denmark INVITED

Scanning tunneling microscopy (STM) has proven to be a fascinating and powerful technique in the field of surface science. The fact that sets STM apart from most other surface sensitive techniques is its ability to resolve single atoms and molecules on surfaces and furthermore to reveal the dynamics of surface processes by recording many sequential STM images with a fast-scanning, variable-temperature STM.@footnote1@ In this talk I will show how STM can be used in the design of new catalysts. More specifically, I will show how STM studies have lead to the design of new alloy catalysts for the steam reforming reaction,@footnote 2@ to atomicscale information on the sintering of Pt nanoclusters promoted by hydrogen,@footnote 3@ and to a new insight into the morphology and edge structures of MoS@sub 2@ nanoclusters, which are of interest as model systems for hydrodesulfurization catalysts.@footnote 4@ @FootnoteText@ @footnote 1@ F. Besenbacher, Scanning Tunneling Microscopy studies of metal surfaces, Reports on Progress in Physics 59 (1996)1737 @footnote 2@ F. Besenbacher, I. Chorkendorff, B.S. Clausen, B. Hammer, A. Molenbroek, J.K. Norskov and I. Stensgaard, Design of a surface alloy catalyst for steam reforming, Science 279 (1998) 1913 @footnote 3@ S. Horch, H.T. Lorensen, S. Helveg, E. Lagsgaard, I. Stensgaard, K.W. Jacobsen, J.K. Norskov and F. Besenbacher, Enhancement of surface self-diffusion of platinum atoms by adsorbed hydrogen, Nature

(1999) 134 @footnote 4@ S. Helveg J.V. Lauritsen, E. Lagsgaard, I Stensgaard, J.K. Norskov, B.S. Clausen, H. Topsoe and F. Besenbacher, The atomic-scale structure of single-layer MoS@sub 2@ nanoclusters, Phys.Rev. Lett. 84 (2000) 95.

9:40am SS1-MoM5 Reactivity of Carbonate and Chemisorption of Carbon Dioxide on Ag(110):A Combined STM, LEED, and TPRS Study, X.-C. Guo, *R.J. Madix*, Stanford University

Twenty years have passed since we first indentified the surface carbonate species formed by the reaction of carbon dioxide with preadsorbed oxygen on Ag(110) by isotope-labeled TPRS (temperature programmed reaction spectroscopy) studies. In the intervening years the same system has been extensively investigated by many groups with various surface techniques including LEED, HREELS, XPS, UPS, NEXAFS, and STM. The carbonate species was confirmed and a bonding configuration proposed. However the stoichiometry of this basic reaction has recently come into question as a result of STM studies by three independent research groups - each believing to image the carbonate structure on Ag(110). Here we present new results of a combined STM, LEED, and TPRS study in this laboratory. Carbonate is shown to form at modest exposures of preadsorbed oxygen to carbon dioxide, and its structure is readily imaged. However, a high reactivity of the carbonate toward CO is observed, which leads to a stable chemisorbed state of CO2 chemisorption on a Ag(110)-(1x2) reconstructed surface, in dramatic contrast to the weakly adsorbed physisorbed state of CO2 on Ag(110)-(1x1). Thus high exposures of preadsorbed oxygen to carbon dioxide in ultrahigh vacuum are expected to lead to the formation of this species, since one expects there to be a background CO partial pressure accompanying the carbon dioxide dose. Indeed we have duplicated this result with high CO2 exposures. The STM images of the chemisorbed CO2 we obtain agree precisely with those previously attributed to carbonate by other groups, and they are distinctly different from those of carbonate. The carbonate species was correctly imaged with STM and its formation was followed in situ at 300 K. We also report here on the structure and surface mobility of the chemisorbed CO2 species.

10:00am SS1-MoM6 Surface Structure and Chemical Properties of a MnO/Rh(100) Model Catalyst, *J. Nakamura*, *H. Nishimura*, *J. Ogawa*, University of Tsukuba, Japan; *T. Fujitani*, National Institute for Resources and Environment, Japan

The atomic structure of a MnO-deposited Rh(100) surface was studied using STM and LEED. The STM image of MnO/Rh(100) at a Mn coverage of 0.80 showed two hexagonal MnO domains rotated by 90 degree with respect to each other. One of the unit vectors for these hexagonal domains had same direction as the unit vector of the Rh(100) substrate. An averaged spacing of 0.31 nm was obtained by the STM for the nearest neighbor atoms of the hexagonal layer. The LEED pattern showed two hexagonal domains, which were consistent with the atomic structure observed by STM. The structure of hexagonal monolayer was very similar to MnO(111) in terms of lattice constant and symmetry. Adsorption of CO on the MnO/Rh(100) was studied using in-situ IRAS. Linear and bridge CO was observed on the clean Rh(100) and MnO/Rh(100) surfaces. New peaks or peak shifts were not observed on the MnO/Rh(100) in disagreement with the powder catalyst results of a Mn-promoted Rh catalyst. No IRAS peaks of CO were observed on the MnO/Rh(100) above the MnO coverage of unity, indicating that a monolayer MnO species grew on the Rh(100). The ratio of linear and bridged CO species varied with MnO coverage, suggesting that the surface area of bare Rh(100) planes on the MnO/Rh(100) controlled the ratio. The oxygen of MnO/Rh(100) is readily reacted with CO to form CO@sub 2@ at 300-400 K in UHV. The reaction probability at 373 K is close to unity.

10:20am SS1-MoM7 Adsorption and Reaction on Oxide-supported Pd, Rh and Ir Particles, *M. Baeumer*, *M. Frank*, *S. Shaikhutdinov*, *H.-J. Freund*, Fritz-Haber-Institut, Germany

Supported metal clusters and nanoparticles are of fundamental and technical interest. One important area of application is heterogeneous catalysis, for example. On a microscopic level, however, there is only limited knowledge about the dependence of adsorption behaviour and catalytic activity on particle size and morphology. In order to contribute to an understanding of these relationships, we have studied oxide-supported Pd, Rh and Ir particles and their interaction with adsorbates. As a support, a thin alumina film grown on NiAl(110) was employed so that scanning tunneling microscopy and electron spectroscopies could be applied without charging problems. The STM results show that particle sizes ranging from a few atoms up to several thousand atoms are accessible via growth under vacuum conditions. By changing the temperature during deposition,

Monday Morning, October 2, 2000

disordered as well as crystalline aggregates are obtainable. After having dealt with the structure, we discuss the adsorption and reaction of ethene on these systems. The studies, which have been carried out using infrared and photoelectron spectroscopy, shed light on the formation of differently co-ordinated species and their thermal dehydrogenation. Gradual changes depending on the metal and the particle size are observed. Finally, we turn to the hydrogenation of ethene with hydrogen which has been investigated by thermal desorption spectroscopy.

10:40am SS1-MoM8 Reactive Intermediate Species on WO@sub 3@ Resolved at the Atomic Scale during Alcohol Dehydration, R.E. Tanner, P. Meethunkij, E.I. Altman, Yale University

In order to better relate structure and reactivity on monoclinic @gamma@-WO@sub 3@(001), we have studied reactions on the surface using scanning tunneling microscopy (STM), temperature-programmed desorption (TPD), Auger electron spectroscopy and low-energy electron diffraction. The ordered $c(2 \times 2)$ reconstruction may be reproducibly generated by heating in O@sub 2@. The termination of the bulk structure is seen in LEED and STM to correspond to a WO@sub 2@ plane in which half the W@super 6+@ cations are covered by terminal O. The catalytic activity was probed by exposure of the $c(2 \times 2)$ surface to a series of alcohols. Methanol, 1-propanol, 2-propanol, and 2-methyl-propan-2-ol (tbutanol) all adsorbed on the surface. The sticking coefficient is similar for all alcohols indicating the ease of deprotonation and formation of alkoxide. TPD showed desorption of water and unreacted alcohol at temperatures less than 600 K, independent of the alcohol. The alkoxide all desorbed as alkenes at higher temperatures, so the $c(2 \times 2)$ surface displays only dehydration activity. The peak of the alkene desorption trace decreases from primary to tertiary alcohol (1-propanol --> t-butanol), indicating that desorption is limited by the rate of C-O bond scission of the adsorbed alkoxide, and is independent of the deprotonation rate. STM images revealed terraces covered with adsorbates that have no preference for attachment at steps or other defect sites. Further images are presented where the WO@sub 3@(001)-c(2 x 2) substrate atomic periodicity is seen simultaneously with the alkoxide intermediates. The sites for oxidative dehydration of the alcohol molecules are identified as the exposed five-fold coordinated W@super 6+@ ions on clean terraces, in agreement with the theory of enhanced activity at coordinatively unsaturated sites. The STM tip can be used to remove the alkoxide adsorbates from the surface to reveal the structure of the underlying, reactive adsorption sites.

Author Index

Bold page numbers indicate presenter

-- A --Altman, E.I.: SS1-MoM8, 2 -- B --Baer, T.: SS1-MoM2, 1 Baeumer, M.: SS1-MoM7, 1 Besenbacher, F.: SS1-MoM3, 1 -- F --Frank, M.: SS1-MoM7, 1 Freund, H.-J.: SS1-MoM7, 1 Fujitani, T.: SS1-MoM6, 1 - G -Guo, X.-C.: SS1-MoM5, 1 - K -Kruse, N.: SS1-MoM2, 1 - M -Madix, R.J.: SS1-MoM5, 1 Meethunkij, P.: SS1-MoM8, 2 - N -Nakamura, J.: SS1-MoM6, 1 Nishimura, H.: SS1-MoM6, 1 Noh, M.: SS1-MoM1, 1 - 0 -Ogawa, J.: SS1-MoM6, 1 - R -Reutt-Robey, J.E.: SS1-MoM1, 1 - S -Shaikhutdinov, S.: SS1-MoM7, 1 - T -Tanner, R.E.: SS1-MoM8, 2 - V -Visart de Bocarm@aa e@, T.: SS1-MoM2, 1 Voss, C.: SS1-MoM2, 1