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MORPHOLOGICAL ASPECTS OF SURFACE REACTIONS

Progress Report

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Report narrative

Over the past year, our group has completed a number of experimental studies, including the first detailed STM study of thermal faceting of $\text{TiO}_2(001)$, the production of surface vinyl groups in spectroscopically characterizable concentrations, and the photon-driven chemistry of adsorbed SO_2 . Building on this strong base, we plan to examine the structure of Rh on faceted and unfaceted TiO_2 using, among other surface science tools, our custom UHV STM. We also plan to investigate nonthermal methods for activation of adsorbates, e.g., via electrons and photons, with one specific goal being the clean production of catalytically interesting intermediates, e.g., CH_2Cl , CH_2 , i-propyl, hexyl, and phenyl.

The thermal faceting of $\text{TiO}_2(001)$ rutile was studied in ultrahigh vacuum using scanning tunneling microscopy (STM), Auger electron spectroscopy (AES), and low energy electron diffraction (LEED). The predominant facet planes observed with STM after annealing to 510°C were (011) and stepped (011), in agreement with the LEED work of Firment. The step structure on (011) planes is indicative of facet growth by surface migration. A smaller number of (114) and (111) planes were observed, in agreement with work reported in the literature. Facet structures, resembling those based on electron stimulated desorption ion angular distribution (ESDIAD) results, were observed for the (011) planes.

The chemistry, induced by 50 eV electrons, of ethylene (C_2H_4) on clean, Cl-covered and D-covered Ag(111) has been studied. C_2H_4 adsorbs weakly on Ag(111) via its π -electrons, desorbs below 140 K, and lowers the work function by 0.38 eV. Preadsorbed Cl stabilizes C_2H_4 , which desorbs at ~185 K. Preadsorbed D atoms have no effect on adsorption and desorption of C_2H_4 . For C_2H_4 on clean Ag(111), exposure to electrons results in decomposition interpreted in terms of H, vinyl (C_2H_3), acetylene (C_2H_2), and di- σ bonded C_2H_4 . The relative concentrations of these species depend on the electron exposure. The reactions among them during temperature programmed desorption (TPD) produce H_2 , C_2H_2 , C_2H_4 , C_2H_6 , C_4H_6 (butadiene), and C_4H_8 (butene). On Cl-covered Ag(111), the amount of C_4H_6 produced in TPD is much larger than on a Cl-free surface. On D-covered Ag(111), the production of C_4H_6 and C_4H_8 is completely suppressed and the dominant products are isotopically labeled dihydrogen and partially deuterated ethylene and ethane. We have demonstrated that vinyl fragments can be produced by controlled electron-induced decomposition of C_2H_4 on Ag(111).

Regardless of exposure, only submonolayer amounts of vinyl iodide (CH_2CHI) decompose, either during adsorption on Pt(111) at 100 K or during subsequent heating to 165 K. The remainder desorbs molecularly. The dissociation products are vinyl (CH_2CH-) fragments, an important C_2 intermediate in hydrocarbon catalysis, and atomic iodine. Using the tools of surface science we have explored the formation and subsequent reactions of vinyl species, in the presence of unavoidably coadsorbed atomic iodine. While some vinyl exists up to 450 K, there are two important and competitive lower temperature reaction channels, and they lead to ethynyl (CCH_3) and ethylene (CH_2CH_2). From our results, we

conclude that the rate of ethylidyne formation from adsorbed ethylene is controlled by the rate at which the first C-H bond in ethylene breaks and, in agreement with the literature, we find that vinyl is a facile intermediate in the process.

The thermal and photon-induced chemistry of SO_2 on Ag(111) has been studied using temperature programmed desorption (TPD), Auger electron spectroscopy (AES) and work function change ($\Delta\Phi$). SO_2 adsorbs reversibly on Ag(111) and desorbs in peaks at 180 and 130 K for monolayer and multilayer, respectively. The work function increases to 0.33 eV upon saturation of the chemisorbed monolayer (ML), but drops to 0.20 eV for a physisorbed multilayer. UV photons (250-542 nm) induce desorption, but not decomposition, of chemisorbed SO_2 . The photodesorption rate is first order in the photon flux, increases linearly with coverage up to 1 ML, but decreases sharply at higher coverages. For coverages up to 1 ML, the photodesorption cross section is $(2.8 \pm 0.2) \times 10^{-20} \text{ cm}^2$ at $(313 \pm 10) \text{ nm}$. The wavelength dependence is consistent with substrate, including bulk plasmon, excitation. Photodesorption mechanisms involving hot electron and hole attachment processes, only in the first monolayer, are discussed.

The reaction products of $\text{C}_2\text{H}_3\text{I}$, $n\text{-C}_3\text{H}_7\text{I}$, $i\text{-C}_3\text{H}_7\text{I}$, ClCH_2I , and $\text{Cl}(\text{CH}_2)_3\text{I}$ adsorbed on Ag(111) at 100 K have been examined using temperature programmed desorption (TPD). All the molecules dissociate thermally on Ag(111), producing surface hydrocarbon fragments and halogen atoms. The hydrocarbon fragments recombine and desorb as higher hydrocarbons below room temperature; they do not hydrogenate. Surface Cl and I desorb as AgCl and I, respectively, above 700 K. The desorbing hydrocarbon products are butadiene for $\text{C}_2\text{H}_3\text{I}$, n-hexane for $n\text{-C}_3\text{H}_7\text{I}$,

2,3-dimethylbutane for $i\text{-C}_3\text{H}_7\text{I}$, ethylene for ClCH_2I , and cyclopropane for $\text{Cl}(\text{CH}_2)_3\text{I}$.

Using TPD, work function measurements, ultraviolet photoelectron spectroscopy, and X-ray photoelectron spectroscopy, we studied the decomposition promoted by potassium of methyl bromide (CH_3Br) on $\text{Ag}(111)$. While adsorption of CH_3Br on K-free $\text{Ag}(111)$ lowers the work function, on $\text{K}/\text{Ag}(111)$ it increases the work function. In contrast to the K-free surface, on which CH_3Br adsorbed and desorbs with no detectable decomposition, it adsorbs both molecularly and dissociatively on both submonolayer and multilayer K-covered $\text{Ag}(111)$ at 100 K. A new adsorption state of CH_3Br on $\text{K}/\text{Ag}(111)$ desorbs at 160--165 K, higher than for desorption of CH_3Br from the K-free surface (142--145 K). Most of the CH_3 radicals desorb upon dissociation. The small fraction retained reacts to form CH_4 and C_2H_4 above 250 K. All Br atoms are retained and react with K to form KBr , which desorbs at 650 K. The dissociation, attributed to electron harpooning from K to CH_3Br to form temporary CH_3Br^- ions, which then dissociate, is not thermally activated. Mechanistic comparison is made with photon-induced dissociation of CH_3Br on K-free $\text{Ag}(111)$.

Listing of publications in the past year

1. X.-L. Zhou, S. R. Coon, and J. M. White, "Potassium-Promoted Decomposition of Methyl Bromide on $\text{Ag}(111)$," *J. Chem. Phys.* 94 (1991) 1613.
2. X.-L. Zhou and J. M. White, "Reactions of $\text{C}_2\text{H}_3\text{I}$, $n\text{-C}_3\text{H}_7\text{I}$, ClCH_2I , and $\text{Cl}(\text{CH}_2)_3\text{I}$ Adsorbed on $\text{Ag}(111)$," *J. Phys. Chem.* 95 (1991) 5575.
3. M. E. Castro and J. M. White, "Photochemistry of SO_2 on $\text{Ag}(111)$," *J. Chem. Phys.* (in press).

Three copies of each of publications 1 and 2 are attached.* Copies of publication 3 will be sent after reprints are received.

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