Selective Oxidation of Propylamine to Propionitrile and Propionaldehyde on Oxygen Covered Gold

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Experimental

The experiments reported in this paper were performed in a supersonic molecular beam surface scattering apparatus in which the ultrahigh vacuum scattering/analysis chamber has a base pressure of ~ 1 x 10^{-10} Torr. The supersonic molecular beam source is quadruply-differentially-pumped in order to reduce the non-supersonic component of the beam that effuses into the scattering chamber. The scattering chamber is equipped with a reverse-view low energy electron diffractometer (LEED), an Auger electron spectrometer (AES), a quadrupole mass spectrometer (QMS), and an ion gun. A customized six-way cross attached to the upper portion of the scattering chamber is individually pumped by a turbo pump and can be isolated from the scattering chamber by a gate valve. This portion consists of a home-built gold evaporator, a quartz crystal microbalance (QCM), and a commercial nanocluster deposition system (Mantis, Nanogen 50) placed in line with a quadrupole mass filter (Mantis, MesoQ) for sample preparation as well as serving as the in situ high pressure cell (HPC).

The sample consists of a Au(111) single crystal (11 mm in diameter, 1.5 mm thick) mounted to a tantalum plate that can be resistively heated and is in thermal contact with a liquid nitrogen bath. The temperature of the surface is monitored by a chromel/alumel thermocouple (type K) spot-welded to the top edge of the tantalum plate. Temperature can be accurately controlled by using a PID controller, which is connected to a programmable power supply, allowing for heating of the sample from 77 to 1200 K. The absolute temperature of the sample is calibrated with either the known multilayer desorption temperature for water and/or recombinative desorption temperature of atomic oxygen. Temperature-programmed desorption experiments are conducted in an angle-integrated fashion.

The crystal sample was cleaned by repeated Ar⁺-ion sputtering (1000 eV, ~ 6 μA) for 30 min at room temperature, followed by annealing at 850 K for 10 min. This procedure was repeated until the carbon coverage reached a small, constant value as determined by AES. This final small amount of carbon was removed by exposing the sample to an atomic oxygen beam and then flashing to 700 K for 10 sec. This technique removed all remaining carbon.

Molecular beams were expanded from a 200 μm alumina nozzle resulting in a beam spot of ~ 3 mm in diameter that was much smaller than the sample size to minimize effects from impinging gas interacting with other surfaces in the chamber. Oxygen atoms were deposited on the surface using a radio frequency (RF) generated plasma source that produced a supersonic beam of oxygen atoms from an 8% (vol.) O₂ in Ar gas mixture with ~40% dissociation fraction as determined via time-of-flight (TOF) measurements. Ionic species are deflected out of the beam line using a charged plate biased at 3 kV. The same apertures and nozzle were used for beams of propylamine and the O-plasma (~ 0.04 ML/s) to ensure that the dosed areas on the gold sample were coincident (the ethanol was dosed with the RF power off). Note that, upon heating the Au(111) sample,

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propylamine molecules desorb/scatter from the surface and bounce against walls of the chamber before reaching the QMS zone. Although propylamine has a relatively high vapor pressure (308 Torr @ 25 °C), most of the propylamine molecules stick on the walls and only a small fraction scatter from the wall and are detected by the QMS. This limits the intensity the reflected signal (by QMS) of the propylamine molecules and therefore a precise determination of coverage of the propylamine is not possible. Specifically, we note that a measureable TPD spectrum of propylamine can be only obtained upon dosing propylamine for 30 seconds or longer with a nozzle pressure of 7.0 Torr. By comparing with other similar molecules (i.e., ethanol, propanol) at similar operational conditions, we estimate that 30 seconds dosing (with a nozzle pressure of 7.0 Torr) of propylamine gives a coverage greater than 1 ML.

CH₃CH₂CH₂NH₂ (Acros Organics, 99+%), ¹⁶O₂ (Matheson Trigas, 99.99%), ¹⁸O₂ (Isotec 99.7%), and Ar (Praxair, 99.9%) were used without further purification and their purities were confirmed by mass spectrometry.
Figure S1. TPD spectra of propylamine with varying coverages on clean Au(111) (heating rate $\beta = 1$ K/s). Propylamine was dosed with a nozzle pressure of 7.0 Torr. On the clean Au(111) surface, propylamine weakly adsorsbs and desorbs molecularly. Repeated TPD experiments of propylamine (without cleaning in between) are highly reproducible, and Auger electron spectra confirm that no dissociation products (such as residual carbon, and/or surface bound oxygen/nitrogen) remain on the Au(111) surface following TPD.