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A scanning tunneling microscope that operates at high pressures and high temperatures (430 K) and during catalytic reactions

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We describe the construction and operation of a scanning tunneling microscope (STM) designed in our laboratory that is contained in a reaction cell and allows operation throughout a wide range of pressures (ultra-high vacuum–atmospheric) and temperatures (300–425 K). This thermally compensated, double piezo tube design is entirely mechanically clamped. Samples are inertially translated and can be easily transferred in and out of the STM. With this microscope, we have investigated the stability of Pt(110) as a function of oxygen and hydrogen pressure and temperature.

Keywords: Scanning tunneling microscopy; STM; in situ; platinum

1. Introduction

One of the dreams of surface and catalyst scientists is to monitor the structure of surfaces and adsorbates on the molecular level during surface reactions, in situ, under conditions of high reaction temperatures and pressures. We have moved closer to these conditions by the design of a scanning tunneling microscope (STM) that operates at high temperatures and pressures. In this letter we describe this apparatus and show how we could monitor the structure of a platinum single crystal surface when heated in atmospheric pressures of hydrogen and subsequently in oxygen. We found that the surface structure of the metal changes dramatically when heated under reducing or oxidizing conditions. STM promises to be an excellent technique to monitor the catalyst structure as well as the structure of adsorbate molecules under catalytic reaction conditions of atmospheric pressures and temperatures < 450 K.

2. Experimental

2.1. STM DESIGN

In order to operate an STM in variable pressure (ultra-high vacuum (UHV)–atmospheric) and variable temperature (300–425 K) conditions, several critical design parameters must be considered, including: thermal drift for variable temperature operation, material compatibility, sample transfer in and out of STM, sample preparation, vibrational isolation, and variable pressure control and monitoring. In overcoming these design criteria, an STM head similar, in principle, to one used previously [1] has been employed. This thermally compensated, double piezo tube design is entirely mechanically clamped (see fig. 1). This eliminates the need for adhesives, or mechanical components such as stepper motors, gears or levers which are known to reduce vibrational and thermal stabilities. Samples are inertially translated and can be easily transferred in and out of the STM. The head is enclosed (except for the jerk tube opening) in an alumina heating shroud. For in situ temperature dependent studies, under pressures of gases, the entire head is heated to a uniform temperature, after which the sample is imaged. This method eliminates the problem of uncompensated thermal expansions due to temperature gradients.

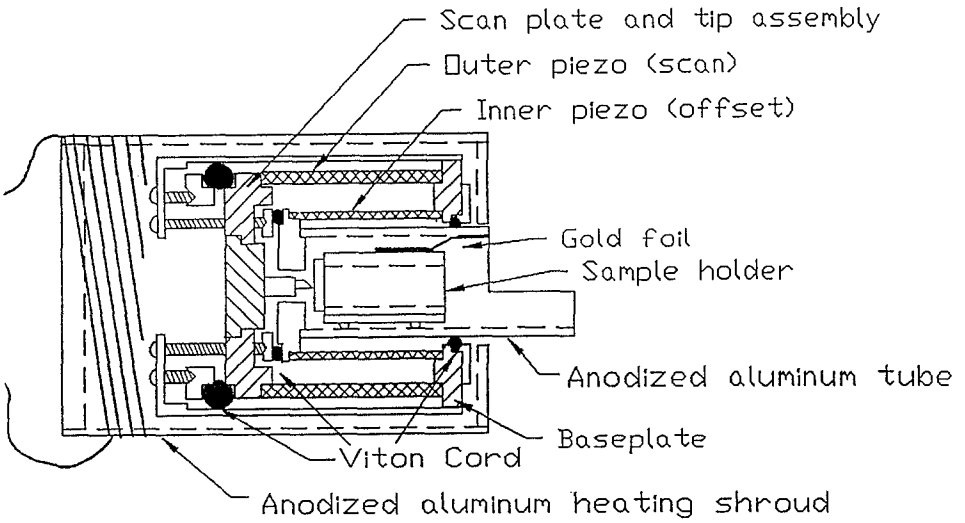


Fig. 1. Schematic of high pressure STM head (side view). This head is entirely mechanically clamped. Machine screws from the back of the STM compress viton or silicone cord against the piezos, making a very stable head assembly. The piezos can exert enormous forces and are able to expand and contract against the compressed elastic material. The sample car rests on sapphire balls inside an anodized aluminum tube and is provided bias voltage by contact with a hanging gold strip. The external anodized aluminum cylinder (heating shroud) is grooved and wound with copper wire for heating.

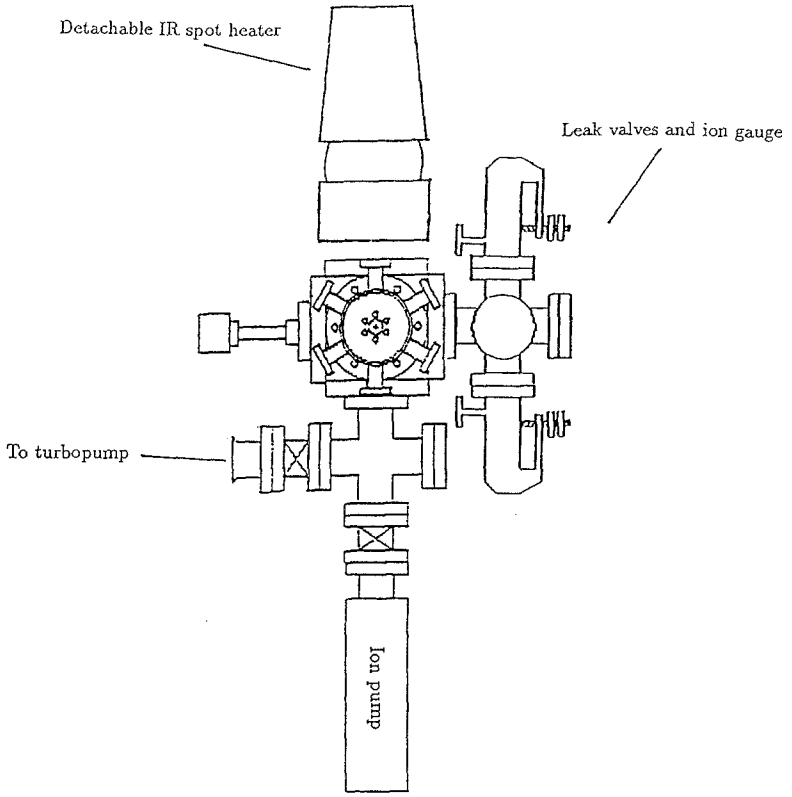


Fig. 2. Schematic of reaction cell. The STM housing is facing out of the page. To the left of the STM housing is the transfer rod/electron beam heater. The transfer chamber and mass spectrometer are not pictured.

With this STM head, atomic resolution on highly oriented pyrolytic graphite (HOPG) has been obtained at temperatures ranging from 300 to 425 K, as limited by the Curie temperature of the piezoelectric transducers, in 1 atm of nitrogen.

The STM head is housed in a small vacuum chamber (approximately 2 L) containing an ion pump and a detachable turbopump station (see fig. 2). Thus the chamber may be pumped down to ultra-high vacuum. The reaction cell has an infrared spot heater which allows samples to be heated up to 1400 K in atmospheric pressures. The chamber is fitted with variable leak valves, ion and convectron tube gauges for gas introduction and control, as well as an electron bombardment heater. This system is also equipped with a quadrupole mass spectrometer which can be differentially pumped for gas analysis while the chamber is pressurized. Finally, the chamber has a turbopumped airlock for in vacuo sample transfer to and from a separate ultra-high vacuum chamber [2] containing various surface analysis instruments including Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and STM.

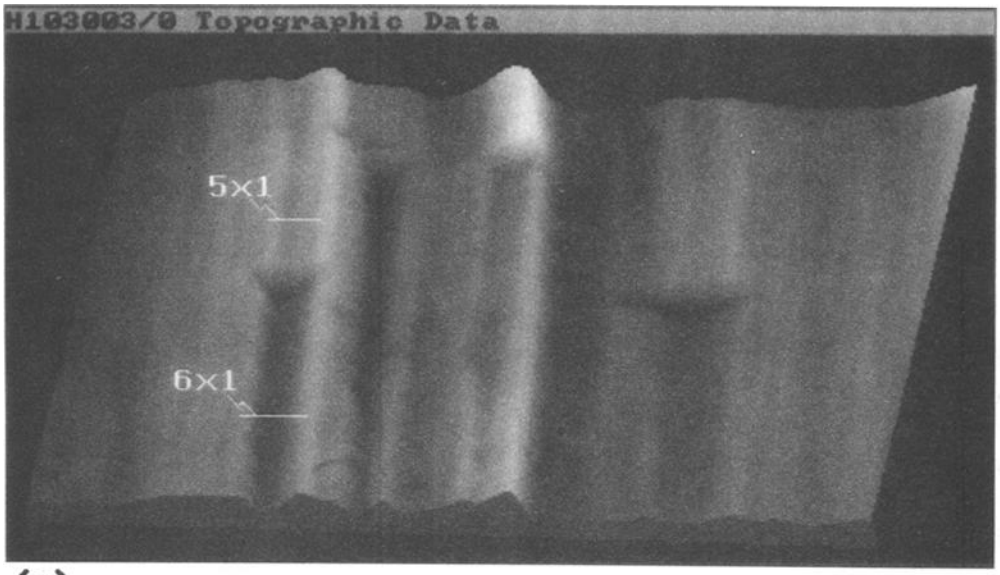
2.2. EXPERIMENTAL PROCEDURE

A Pt(110) surface was cleaned and annealed in a separate UHV chamber as described earlier, and transferred in vacuum (10^{-5} Torr) to the reaction chamber. Transferring back into the UHV chamber and analyzing by AES we found that carbon is present on the surface, due to contamination in the limited vacuum of the transfer chamber. Heating to 800 K in 5×10^{-6} Torr of oxygen, however, removed the carbon in all cases. Thus, it was assumed that by heating under the same conditions in the reaction cell (where the base pressure was in the 10^{-9} Torr range), as was done in the UHV chamber, the sample would be free of contamination, excepting oxygen. After removing the surface contamination by heating in oxygen, the surface was introduced to atmospheric pressures by opening the leak valve to the gas desired and closing off the ion pump. It was found by analysis with the mass spectrometer that the most efficient method of switching from one gas to another is to pump the chamber with the turbopump to 1×10^{-6} Torr and then introduce the new gas. Since impurity levels in the compressed gas cylinders were not better than 1 ppm, it was not necessary to bake out the reaction cell before changing gases.

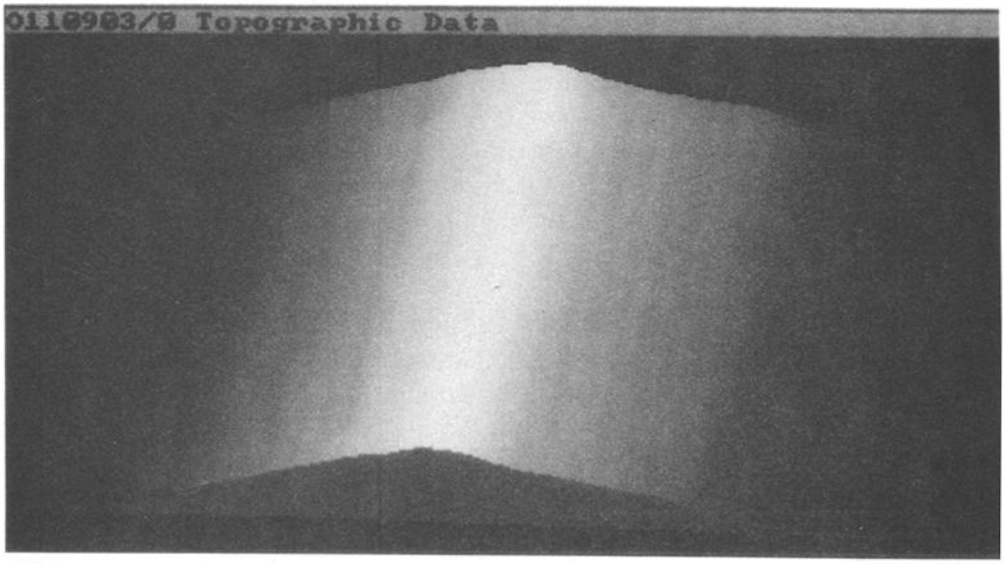
3. Results

After cleaning the platinum sample, the reaction cell was brought up to 1 atm of oxygen. The surface was imaged by STM. Evacuating the chamber with the turbopump, hydrogen was introduced and the surface was imaged again. The STM and sample were heated to 425 K for 5 h. The sample was imaged during and after this heating treatment. Afterwards, the hydrogen was replaced with oxygen and the sample was imaged. After imaging, the STM and sample were heated to 425 K for several hours and the sample was imaged both during and after heating.

Fig. 3 shows the surface after heating in hydrogen and oxygen. The surface in hydrogen shows missing row reconstructions of various sizes. We have obtained a large number of images in different areas of the surface, all of which exhibit missing row structures. The images often show the surface as having nested reconstructions or areas with small domains of (2×1) or (3×1) reconstructions separated by larger reconstructions of various sizes ($(n \times 1)$ for $n = 4, 5, 6, 7$) and of no apparent order. Defects within the $(n \times 1)$ domains are also observed (some defects and nested structure are shown in fig. 3a). In these cases, a reconstructed row will disappear or a missing row will appear suddenly where, up to that point, a larger reconstruction existed. These reconstructions were also stable in vacuum following the hydrogen experiments and preceding the second oxygen exposure. Overall, the surface corrugation was approximately 1.5 nm as in fig. 3a.



(a)



(b)

Fig. 3. (a) STM topographic image of a 47 nm × 67 nm region of Pt(110) in 1.6 atm of hydrogen after heating to 425 K for 5 h, showing ($n \times 1$) reconstructions ($n = 3, 4, 5, 6$) and defects, $dz = 1.5$ nm. (b) Topographic image of a 51 nm × 66 nm region of Pt(110) in 1 atm of oxygen after heating to 425 K for 5 h.

The surface in oxygen does not show this small scale structure, rather, there is some larger (10–30 nm) scale structure present. We believe that the larger hill and valley structure is due to (111) facets. For a model surface made up of (111) facets with periodicities of 10–30 nm, one would expect to see a corrugation greater than 20 nm. The images we have obtained do not show the very sharp peaks and valleys expected but rather the facets appear to be rounded, as a result of the tip shape being convoluted with the surface topography. Within a facet, the surface appears to be smooth to within 0.5 Å. These images are very characteristic of those taken under their respective conditions.

4. Discussion

An important property of the STM is its ability to image ordered and aperiodic surfaces with atomic lateral and vertical resolution in a wide variety of conditions. Heterogeneous catalysis is one field where this type of information may be extremely useful. While our present knowledge of the atomic structure of catalyst surfaces is largely limited to those structures which are stable in ultra-high vacuum before and after reaction, STM may provide an insight into both adsorbate and catalyst surface structure during the reaction.

An important limitation is the reduced temperature range available. With the requirement that both STM and sample be heated to uniform temperatures, one cannot heat above the Curie point of the piezoceramics (temperature at which the piezoceramics become depolarized, usually around 500 K). This is a very different situation than heating in vacuum where one can heat only the sample and shield the microscope. Thermal conduction through the high pressure environment is a big limitation for temperature dependent studies. Using quartz or other piezoelectric materials with high Curie temperatures may be one way around this problem.

However, operating the STM under pressures of gases is not a limiting factor. At 1 atm, for example, the average distance between molecules is about 3 nm, much larger than the tunneling gap (approximately 0.5 nm). Even in dense environments (liquids), only two atomic diameters fit inside the gap, and in these cases there is no strong interference with the tunnel process when the discrete atomic or molecular electronic states are outside the energy range covered by the bias voltage of the tip. Typical piezotransducers are capable of operating at pressures ranging up to 550–700 atmospheres before total degradation occurs. We have not looked at surfaces under pressures greater than two atmospheres in the present setup because of the viewports on the chamber which cannot be subjected to large internal pressure differences. Replacing the ports by solid flanges would allow experiments to be carried out in extremely high pressures.

Comparing the experimental results of Pt(110) to previous ex situ STM studies of Pt(110) treated under high pressure oxidizing and reducing conditions, one finds similar characteristics [3]. Frohn et al. found that heating the Pt(110) crystal in 1 atm flowing oxygen at 1200 K for 2 h produced facet heights of several nanometers. However, after annealing in flowing hydrogen at 1200 K for 2 h, a flatter surface containing some small scale structure is generated.

LEED experiments carried out in UHV on the Pt(110) surface have shown the effects of oxygen or hydrogen adsorption to be much less severe. The clean metal has been shown to be most stable in the (2×1) reconstructed arrangement [4]. A clean unreconstructed (1×1) surface can be formed, but is found to be less stable than the (2×1) surface [5]. Ferrer and Bonzel have also shown that exposing the clean (1×1) and (2×1) surfaces to hydrogen in vacuum does not change their respective morphologies. Adsorbing oxygen on Pt(110) has been shown to generate a wide range of $(n \times 1)$ missing row reconstructions, where $n = 2, 3, 5, 7$ [6,7].

From the images of the Pt(110) surfaces obtained in high pressures, it appears that the presence of oxygen induces larger (111) facets in the surface. The presence of hydrogen tends to reverse this effect, generating smaller scale reconstructions which are more typical of the clean surface.

In conclusion, the utilization of the STM's power of detecting atomic structure could allow surface science to bridge the pressure gap of almost twelve orders of magnitude that separates atomic level studies and the real world of catalysts as they are used in industry.

Acknowledgement

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