



Atomic force phase imaging for dynamic detection of adsorbed hydrogen on a catalytic palladium surface under liquid



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ABSTRACT

Dynamic observation of hydrogen on catalytic metal surfaces is a challenging aspect of studying liquid-phase heterogeneous catalysis. Current methods suffer from one or more of the following limitations: the requirement to observe the surface in high vacuum, the inability to provide nanometer-level spatial resolution, the inability to deal with opaque catalysts and/or liquid immersion phase, the lack of real-time scanning of the surface area, and the inability to assess pronounced topographies or mixed materials. Atomic force microscopy (AFM) phase-shift imaging remedies these issues and provides an opportunity for dynamic direct observation of catalyst surfaces at or near actual reaction conditions immersed in liquid.

Hydrogen was delivered to a palladium surface immersed in water by diffusion through a support film of dense polycarbonate. The palladium surface was continuously probed by tapping-mode AFM. The theoretically predicted time-dependent appearance of hydrogen on the water-covered palladium surface matched the experimental observation reasonably well. The technique demonstrated here is unique in that the appearance of hydrogen is dynamically detected in real time on a catalyst surface immersed in water with nanometer-scale spatial resolution. The results presented here supply a new level of information for heterogeneous catalysis that is not available with existing techniques. This work opens new avenues in the study of heterogeneous catalysis, a field with tremendous practical importance and serious analytical challenges.

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1. Introduction

More than 80% of all synthetic chemicals are produced using catalysis. Interactions of hydrogen with catalytic metal surfaces during heterogeneous catalysis are of great interest for a number of important processes including petrochemical processing, soybean oil hydrogenation, [1] pharmaceutical production, [2] fine chemical production, [2] and conversion of biomass to fuels and chemicals [3]. Adsorption of hydrogen on solid (metal) surfaces is the necessary first step for heterogeneous hydrogenation catalysis [4–6]. Of particular interest is therefore the availability of hydrogen on catalytic surfaces because it impacts productivity and selectivity [1].

The efficiency of heterogeneous catalysis is often constrained by mass-transfer limitations based on the low solubility of gases like hydrogen in liquids. This leads to low conversion rates, undesirable product distribution, or even highly detrimental byproducts

like coke [7,8]. Catalytic membrane reactors have been shown to improve reactor performance by allowing delivery of a gaseous reactant directly to the catalyst surface, avoiding hydrogen starvation of the catalyst surface [1,9]. Studies of catalytic membrane reactors have been conducted based on overall analysis of products and reactants, but the in-situ study of the catalytic surface at nanometer scale resolution as hydrogen is dynamically added and/or depleted was up to now not possible due to the difficulty of probing liquid/solid interfaces [10,11].

Despite being so commonly used in large-scale chemical processes and so thoroughly studied, the primary method of studying heterogeneous catalytic systems is mostly phenomenological [12]. This is due to the limitations of analytical technology to study liquid/solid interfaces at conditions near those often used for chemical reactions including temperatures above 100 °C and pressures of multiple atmospheres. Interest in in-situ and in-operando approaches to studying heterogeneous catalysis has increased with the sophistication of microscopy and spectroscopy techniques. Atomic force microscopy (AFM) allows for the study of surfaces at non-ideal conditions and under liquid without the

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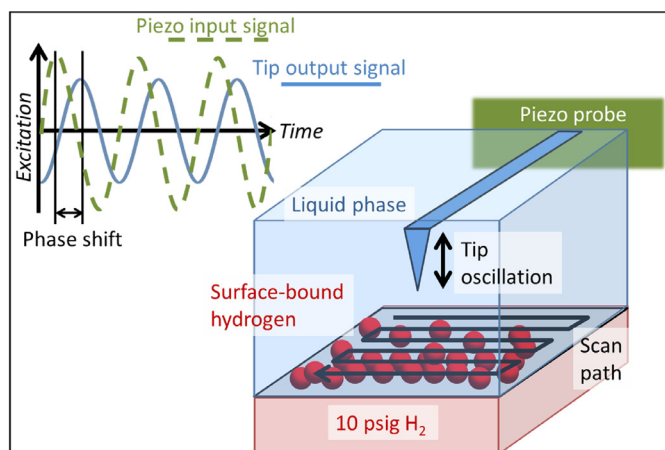


Fig. 1. Phase-shift AFM for detection of adsorbed hydrogen on a surface immersed in liquid. Hydrogen is supplied to the underside of a flat palladium (Pd) layer deposited onto a polymer support. Dissociate hydrogen diffuses through the Pd and appears at the liquid-Pd interface. The process is reversed by replacing hydrogen with nitrogen under the Pd.

need for extreme sample preparation procedures. Furthermore, it has been demonstrated that AFM can be used to study surfaces of heterogeneous composition and differentiate between materials using the phase shift of the cantilever probe [13–25]. In the work presented here, the interpretation of AFM phase-shift imaging is investigated as a way to study the dynamics of adsorbed hydrogen on a Pd surface. It is demonstrated here that AFM phase-shift data can be used to observe the dynamics of the adsorption of hydrogen on a Pd surface at room temperature, atmospheric pressure, and immersed in water (Fig. 1). The magnitude of the phase shift between the piezo input and the tip oscillation changed when hydrogen appeared on the surface. The technique demonstrated here may enable further insights into real-time mass transfer, kinetics, surface-bound chemical reactions, and the appearance and disappearance of materials during heterogeneous catalyzed reactions.

2. Experimental

2.1. Materials and instrument specifications

The atomic force microscope was an Asylum Research (Asylum Research, Santa Barbara, CA 93117) MFP-3D instrument operated in AC mode using WaveMetrics Igor Pro 5.0.5.7 software (WaveMetrics, Inc., Portland, OR 97223). Olympus (Olympus Corporation, Center Valley, PA 18034) BL-AC40TS nitride cantilever probes with silicon tips (rectangular tip geometry with a radius $\sim 9 \pm 2$ nm and a spring constant of 0.09 N/m) were used throughout. The cantilevers exhibited free amplitude voltages in liquid between 250.00 mV and 400.00 mV. The set-point amplitude voltages used during scanning ranged between 116.24 and 152.10 mV. The cantilevers' drive frequencies ranged between 67.877 and 68.584 kHz in HPLC-grade water. Quality factors for the cantilevers ranged between 25.4 and 30.1. Scanning was performed with the cantilevers operating in the repulsive mode. Ethanol (Sigma-Aldrich, ACS reagent, ≥ 99.5 wt%), toluene, and chloroform (both Fisher Scientific, Certified ACS, 99.9 wt% assay) were used for cleaning the probes. HPLC-grade water (Fisher Scientific, Submicron Filtered) was used as the samples' immersion medium. Static charge on samples and probes was removed by exposure to a 500 μ Ci polonium-210 source (NRD LLC, Model 3C500) for about 10 s immediately prior to installation [26]. Samples were attached to the aluminum sample holder using Loctite Quick Set epoxy (Henkel Corp., Rocky Hill, CT 06067). Polycarbonate (PC) support films were

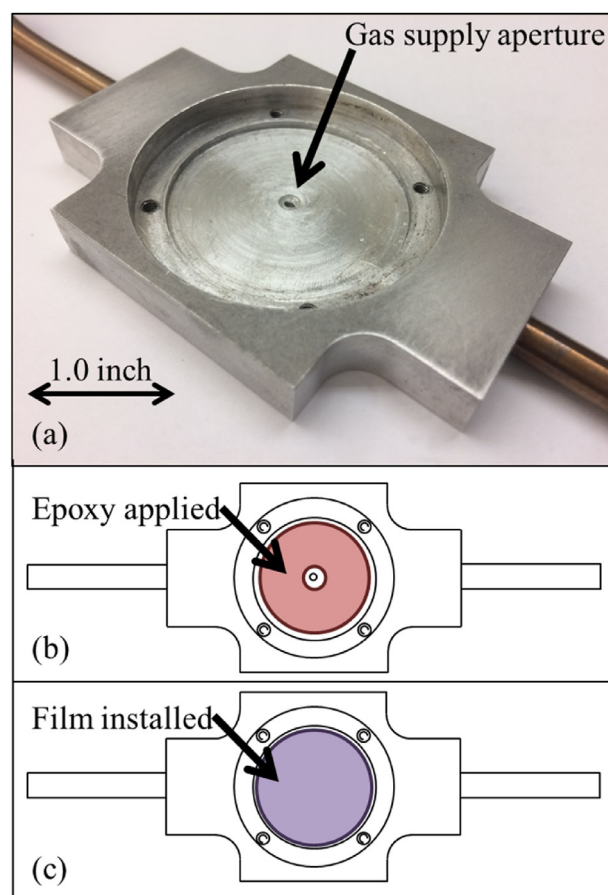


Fig. 2. The custom sample holder shown with (a) the gas supply aperture, (b) epoxy adhesive applied, and (c) a film sample installed. Note that gas was supplied only to the area of the aperture where scanning took place.

cut from sheets of Lexan PC film with a nominal thickness of 254 μ m (ePlastics, San Diego, CA) and a measured thickness of 260 ± 3.3 μ m (standard deviation of 20 measurements made using a micrometer screw). Some of these samples were sputtered using a 99.95 wt% Pd sputter target (Ted Pella, Redding, CA) using a DESK II magnetron sputter coater (Denton Vacuum, Moorestown, NJ) for three 15 s intervals with a 45 mA current in 100 mTorr of ambient air. The surfaces of the polymer film and sputtered films are flat with root-mean-square (RMS) roughnesses of 3.205 nm and 3.265 nm, respectively. Hydrogen and nitrogen (99.999 vol% purity) were supplied by Matheson Tri-Gas, Manhattan, KS. 316 stainless steel valves and tubing were used (Swagelok, Kansas City, KS).

A custom machined aluminum sample holder (Fig. 2) allowed for gas to be supplied beneath the film sample via the gas supply aperture (Fig. 2(a)). AFM scanning took place on the top surface of the film, which was covered with water.

Measuring the effect of hydrogen concentration on the sample surface using phase shift required that the AFM probe scan over the aperture. Aiming the AFM probe at an area above the open gas supply was not trivial since no system to monitor the relative position of the probe and sample was available. The probe was visually aligned with the aperture although the AFM head obscures the sample surface.

A 2-mL reusable glass syringe with metal Luer lock nozzle with an attached 10-cm long stainless steel tip was used to transfer degassed HPLC water to the gap between the sample and AFM probe holder, filling the gap.

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