Effect of Alkanethiol Functionalization on Surface Reactivity in Catalytic Sensors

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Introduction

The interaction of organic adsorbates is known to play a significant role in a large number of chemical reactions[1], yet the catalytic systems that exploit these effects on a fundamental level to improve selectivity are lacking. Alkanethiols represent a possible platform for the modification of catalytic surfaces through their ability to form well ordered monolayers on the surface of metals such as palladium[2]. We have modified the surface of a metal-insulator-semiconductor (MIS) hydrogen sensor with an alkanethiol self-assembled monolayer (SAM) to modify the surface environment to be highly selective toward the hydrogenation of an analyte of interest: acetylene.

MIS sensors consist of a layer of a catalytic gate metal (e.g., Pd) and a semiconductor separated by a dielectric (e.g., SiO_2). Hydrogen can diffuse from the metal surface to the metal-insulator interface and cause a shift in the capacitance-voltage curve which can be measured for many decades of gas phase partial pressure (Fig. 1). Additional analytes can react on the surface of the sensor, altering the hydrogen absorption dynamics and enabling the detection of many compounds other than hydrogen. MIS sensor are highly sensitive to hydrogen, so they are excellent for evaluating the ability of unsaturated hydrocarbons to react on the catalytic metal surface. In this work, we present results of surface functionalization with alkanethiols for the highly selective detection and reaction of acetylene over ethylene.

Materials and Methods

MIS structures were fabricated using facilities at Sandia National Laboratories with commercially supplied n-type Si wafers coated with a thin thermal oxide on one side [3]. Metal films were deposited on the oxide using a dual electron beam evaporator. Sensors were coated with self-assembled monolayers (SAMs) of alkanethiolates using standard techniques described in previous work [2] to modify surface functionality. Once prepared, the capacitance-voltage response of sensors was tested using a flow cell device that enabled the dosing of 100-1000 ppm levels of analyte gases to the sensor surface including acetylene and ethylene.

Results and Discussion

Sensor response has been characterized for a variety of SAMs. Sensors were functionalized with alkanethiol SAMs of 6, 12, and 18 carbon tail lengths as well as H_2S (a "0" tail length system) and a hydrophilic SAM with polyethylene glycol units. The alkanethiol SAMs showed near perfect selectivity for the detection of acetylene over ethylene at 50 and 75°C with negligible variation between tail lengths compared to no response for either acetylene or ethylene on an uncoated surface. Some response was also noted for H_2S, indicating that surface sulfur plays a role in promoting this selectivity.

The mechanisms for this enhanced response are still under investigation, but appear to be related to an improvement in the rate of acetylene hydrogenation relative to the rate of dissociative hydrogen adsorption on the catalytic metal film. In the case of the SAM films, this effect is unexpected; however, the use of SAMs as a coating offers many advantages in determining the mechanism for acetylene response enhancement, since SAM coatings are well-ordered layers, and the head and tail groups of the SAM-forming molecules may be altered to change the chemical environment. We will present our studies of variables such as SAM tail length and functionality, and discuss parallels between sensitivity for unsaturated molecules on MIS devices and hydrogenation activity trends for high-surface area supported metal catalysts.

Significance

Development of highly selective surfaces for reactions of interest represents a major challenge in heterogeneous catalysis. These studies of a parallel system for sensors demonstrate a possible approach for meeting this challenge for the hydrogenation of unsaturated hydrocarbons.
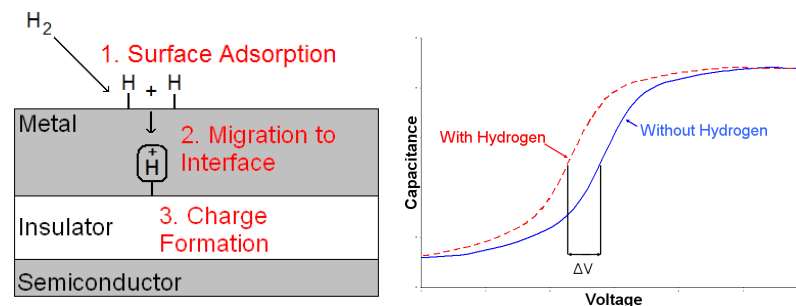

Figure 1. Metal-Insulator-Semiconductor sensing mechanism and resulting Capacitance-Voltage curve shift.

References

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