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The Role of Heterogeneous Catalysis in the Gas-Sensing Selectivity of High-Temperature Mixed Potential Sensors

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The sensitivity of a mixed potential electrochemical sensor is determined by the concentration of the analyte gas at the gas/electrode/electrolyte interface. These concentrations, along with the kinetic properties of the three-phase interface and oxygen partial pressure, establish the mixed potential generated by the device. [1] The selectivity of mixed potential sensors is therefore strongly influenced by the heterogeneous catalytic properties of the surfaces that closely surround the sensor including: the metal oxide electrode, solid electrolyte, other components of the sensor body, and the sensor enclosure. Analysis of the change in CO, C₃H₆, and C₃H₈ concentration using gas chromatography shows that the observed preferential sensitivity of a LaCrO₃//YSZ//Pt bulk mixed potential sensor towards C₃H₈ is largely due to heterogeneous catalysis of the C₃H₆ on the sensor body, which in this work, is YSZ. By blocking YSZ heterogeneous catalysis by using a coating of thick Au, the sensor exhibits nearly identical sensitivity to both C₃H₆ and C₃H₈. Although a similar amount of heterogeneous catalytic oxidation of CO takes place, the LaCrO₃//YSZ//Pt sensor exhibits only a small response to CO and this therefore may be associated with the electrode kinetics and electrocatalytic properties of the sensor interface towards the electro-oxidation of the CO. Data for HC and CO selectivity will be presented at 1% O₂ / 12% CO₂ / N₂ and at temperatures between 550 and 600°C.

Introduction

Concerns about air quality and pollution mitigation have generated need for accurate, low cost sensors to measure concentrations of hydrocarbon, carbon monoxide, and oxides of nitrogen in the air. Sources of these pollutant gases include mobile sources from automobiles, light trucks, and diesel truck emissions and stationary sources such as power plants, gas turbines, and industrial/chemical processes. Ideally, the most desired property for sensor applications is that the device be low-cost. It must also be reliable, have a long lifetime with minimal drift and aging, and a simple voltage output that simplifies transduction. With the exception of the automotive lambda oxygen sensor, for most gas sensing needs, sensors with the aforementioned characteristics do not exist.

Mixed potential sensors are a class of electrochemical sensors that rely on high temperature oxygen-ion conducting solid electrolytes. These devices were first reported over twenty years ago. [2] When an oxygen-ion conducting electrolyte is exposed to CO

or unsaturated hydrocarbons at temperatures less than 800°C, a non-Nernstian potential develops at the electrode. [2-5] This non-equilibrium potential arises by the establishment of competing reactions of oxygen reduction (oxidation) and CO or hydrocarbon oxidation (reduction). Under oxygen rich conditions, the potential established by these competing reactions is more negative than that predicted by the Nernst equation and is known as the mixed potential. [3,4] The magnitude of this mixed potential, being dependent on kinetic factors, is a strong function the concentration of reducing gases present, the electrode material and the morphology. [6-10]

A significant amount of research into the development of mixed potential sensors has focused on devices that utilize yttria stabilized-zirconia (YSZ) solid electrolyte and Au and Pt electrodes. Devices of this configuration are simple and inexpensive to make, detect a wide range of gases, and develop a large voltage response even for low concentrations in the presence of oxygen. Although mixed potential devices have been known for some time, and while many prototype devices have been fabricated and reported in the literature, no mixed-potential-based device has been successfully commercialized to date. The principal reason for this has been due to sensor aging problems and a great difficulty in fabricating sensors with reproducible response characteristics between devices. Recently, our group has explored these issues and has published the results of work that shows that both issues from the use of a Au sensing electrode and the subsequent morphological instability of the Au film when the sensor is operated at temperatures above 400°C. [11,12] The changing morphology of the Au leads to a reduction in the gas/electrode/solid electrolyte triple phase boundary which results in an increase in over-potential for oxygen reduction [12]. The oxygen over-potential in part, determines the magnitude of the mixed potential [1]. The difficulty in producing devices with similar voltages – much less identical response characteristics – is due to the random nature of the formation of the triple phase boundary. The same problems occur for Pt electrodes although the mobility of Pt atoms below 800°C is low enough that stable electrodes can be produced.

The replacement of Au electrode has been the focus of recent work for several research groups in the past few years. The avenues of investigation range from substitution of Au with simple binary and ternary oxides [8,9,13-15] and thick coatings of perovskite materials [9,16], to completely dense thin films of perovskites [10,17-19]. As we have shown in previous work, simple substitution of oxide materials for the Au electrode has proven insufficient to resolve the aforementioned problems inherent to mixed potential sensors. [10,18,19] Intelligent design and engineering of the entire electrode are very important. [20,21]

A mixed potential sensor with a stable response has been demonstrated. [21] And, multiple devices have been made with nearly identical voltage response levels. [20,21] Figure 1 is an illustration of a LANL “bulk” mixed potential sensor. The electrodes consist of a fully sintered $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ cube embedded into YSZ electrolyte via co-sintering at high temperature in such a way that the interface between the electrode and the solid electrolyte -the triple phase boundary – does not change over time. Moreover, ratio of electrode surface area to perimeter can easily be controlled and reproduced. A Pt

wire embedded into the solid electrolyte serves as a counter electrode. The interface between the Pt wire and the YSZ is equally reproducible. Figure 2 is the response of this configuration of mixed potential sensor to C_3H_8 at $550^\circ C$ in a background of 1% O_2/N_2 balance. The data in figure 2 shows many desirable response characteristics.

Substantial effort has been invested into studying the properties that affect the sensitivity and selectivity that a mixed potential device exhibits. A significant problem exhibited by mixed potential sensors that use Au electrodes is that they are non-selective and respond to many HC gases along with CO , H_2 , NO_x and SO_x . [7,22-24] In this work we investigate the role that heterogeneous catalysis plays in influencing the response characteristics in this type of mixed potential sensor. Specifically, we will investigate the rate of heterogeneous catalysis on and around the sensor environment for C_3H_6 , C_3H_8 , and CO and its influence on determining sensor response.

Experimental

The specific devices that were tested in this work had the following configuration: “ $La_{0.8}Sr_{0.2}CrO_3 // YSZ // Pt$ ”. The $La_{0.8}Sr_{0.2}CrO_3$ powder was obtained from Praixair[®] and was pressed into a pellet and sintered at $1550-1650^\circ C$ for 10 hours in order to form a dense ($\approx >60$ of theoretical density) ceramic. The ceramic pellet was cut into smaller pellets with dimensions of approximately $0.2 \times 0.3 \times 0.2$ cm. The pellet was buried in YSZ powder and pressed uni-axially at 1500lbs in either a 1/2” diameter or 3/4” diameter die for 5 min. The excess YSZ was removed from the surface of the chromate pellet using a razor blade. Once a clear electrode/electrolyte interface was exposed, the pellet was sintered at $1100-1200^\circ C$ for 10-12 hours. The resulting YSZ pellet (the sensor body) had sintered to $> 60\%$ of theoretical density. A 0.004” Pt wire was buried onto the surface of the chromate electrode and co-sintered. The other electrode was a Pt (0.01”) wire buried into the YSZ electrolyte. A schematic illustration of the sensor is shown in figure 1. A more detailed explanation of sensor preparation can be found elsewhere [21] The sensor was attached to Pt (0.01”) leads and placed onto a platform made from machinable ceramic (MACOR). The sample platform/sample was held in the center of a quartz tube, which was heated to $400-600^\circ C$ in various gas atmospheres in order to test the sensor response.

A Hewlett Packard 5890 Series II gas chromatograph was used to measure CO and HC inlet and exhaust concentrations. The GC was set up in a dual column configuration: the gas to be analyzed was flowed through a VALCO sampling valve ($250 \mu l$ sampling loop) and was subsequently split into two equal volumes. One half of the gas sample was sent through a Molseive 5A capillary column and onto a thermal conductivity detector (TCD). This column/detector combination was used to measure permanent gases such as N_2 , O_2 , H_2 , etc. The other half of the gas sample was sent through a PoraPlot Q capillary column. The Poraplot Q column effectively separated the HC 's, CO , and CO_2 . In order to accurately measure these latter gas species, the gas sample was passed over a Ni catalyst in the presence of H_2 , which converted the CO and CO_2 into CH_4 . The gas sample then flowed to a flame ionization detector (FID) and measured the concentration of the analyte

gas. Prior to measuring inlet and exhaust gas concentrations, a Scott's Specialty calibration gas mix was used to simultaneously calibrate both the TCD and FID responses to known concentrations.

Gas mixing and flow control to the sensor was carried out using an automated test stand. MKS™ digital flow controllers were used. A base gas of 1%O₂/12%CO₂/N₂ balance was flowed through the quartz tube and over the sample at 200 sccm. A second mass flow controller flowed a test gas that contained 2500 ppm of an analyte test gas along with 1% O₂ and 12 % CO₂ so as not to change PO₂ during mixing. Either the input gas stream from the mixing mass flow controllers or the exiting gas stream from the tube furnace could be directed to the GC sampling valve. A Keithley 2400 source-meter was used to measure open-circuit potentials of the sensor during testing.

Results and Discussion

Figure 1 shows an illustration of the device studied in this work. The dimensions of the device were a diameter of 0.49 in and a height of 0.30 in. The sensor was mounted at the end of a MACOR platform, which was affixed to the end of a 0.125" dia. two-bore alumina rod. The sensor was situated in a quartz tube of a high-temperature tube furnace. Figure 2 is a plot of sensor response versus time for propane at 0, 250, 500, 750, 1000, and 1250 ppm concentrations at 550°C. Total gas flow was 200 sccm of a base gas consisting of 1% O₂/12%CO₂ with a balance of N₂. The CO₂ was included to represent the concentration of CO₂ in a lean burn automobile exhaust gas (and applies more directly to another research project and can be ignored for this study). As can be seen in figure 2, the response shows good sensitivity, excellent voltage level reproducibility and stability during exposure to each level of propane.

The response of this sensor to CO and propylene exhibits similar behavior although different voltage levels are produced for these gases. Figure 3 shows the sensor's response to CO, C₃H₆, and C₃H₈ at 600°C. The temperature of the experiment was raised to 600°C to augment heterogeneous catalysis because it was felt that higher temperature would simplify analysis. The order of sensitivity to the two hydrocarbons and to CO is C₃H₈> C₃H₆>>CO. There is very little voltage generated by the presence of CO. This order of sensitivity is quite different from previous thin film mixed potential sensors studied by our group. [1,10,12] E.g. mixed potential sensors that utilize Au/LaMnO₃ and Au/Tb-doped YSZ electrodes typically are more sensitive to CO and C₃H₆ and much less sensitive to C₃H₈. [10,18] However, thin film-based devices with La-Sr-Cr-O/YSZ interfaces controlled through thin film-PVD patterning exhibit very similar gas sensitivity behavior. [19] The fact that devices of this configuration are preferentially sensitive to HCs and not to CO is quite valuable for many applications. One valuable application of particular importance is On-Board Diagnostics (OBD) of an automobile's catalytic converter. In order to provide some insight as to why the sensor shown in figure 2 exhibits this particular response characteristic, we studied the composition of the test gas after being exposed to the sensor.

The gas compositions at the furnace inlet and outlet were analyzed using a GC. Figure 4 is a plot of the outlet gas concentration versus the inlet concentration for CO, C₃H₆, and C₃H₈. Figure 4 shows that while most of the C₃H₈ exits the furnace tube unoxidized, a significant amount of CO and C₃H₆ was heterogeneously oxidized. Analysis of the change in HC and CO gas concentration due to homogeneous catalysis and heterogeneous catalysis on the quartz furnace tube walls, i.e. the amount of oxidation due to the quartz tube at 600°C, was studied up to 800°C at 200 sccm and the percentage of CO and C₃H₆ oxidized in the apparatus at 600°C was less than 2% and 5% respectively. Therefore the principal cause for the amount of oxidation measured in the experiment must be attributed to the presence of the sensor.

Figure 5 shows the response of the sensor re-plotted versus the actual CO and HC concentration as measured by the GC. The slope of both the C₃H₆ and C₃H₈ is very similar: approximately 0.024 mV/ppm of HC. The slope of the CO curve remains small: 0.002 mV/ppm CO.

To test the hypothesis that it is the sensor itself that is responsible for the observed sensitivity trends observed in figure 3, we used a second sensor - identically-prepared except for the size of the sensor body (3/4" die was used instead of a 1/2" die) - that was already in use and being tested at 550°C. We coated the sensor body of this second sensor with a thick film of Au ink (ElectroSciences Laboratories Ink # 8880-H) and fired it at 800°C for 10 min. The thickness of the ink was approximately 30 μm which was measured using a profilometer. The purpose of the Au ink was to prevent the test gas from coming into contact with the surface of the YSZ. The Au ink was applied such that only a small area of YSZ electrolyte, immediately adjacent to the Pt and La-Sr-Cr-O electrodes, were exposed to the test gas. The Au-coated sensor was returned to the MACOR platform and the sample and holder were placed back into the tube furnace. This second sensor was tested in the same manner as the first. Figure 6 shows the extent of C₃H₆ conversion and the sensor response before and after the application of the Au ink. There is more than a factor of three increase in the concentration of C₃H₆ leaving the tube furnace at 500 ppm inlet concentration after coating the YSZ surface of the sensor. This shows that the porous YSZ that makes up the sensor body plays a significant role in the heterogeneous catalysis of the HCs and is presumably responsible for the CO oxidation as well. Figure 6 also shows a commensurate increase in the sensor voltage response to C₃H₆ after coating the sensor body with Au. At 500 ppm inlet C₃H₆ concentration, the sensor voltage more than triples after the application of the Au. Although we did not measure the heterogeneous catalytic activity of the alumina rod, the MACOR platform, or the exposed segment of the Pt wire leads, this hardware was present in both experiments before and after the application of the Au ink. Therefore, the changes in exhaust gas composition and in the sensor response must be attributed to removing the YSZ surface from participating in heterogeneous catalysis.

Figure 7 shows the response of the second sensor operated at 550°C for C₃H₆ and C₃H₈ prior to sequestering the YSZ surface and the C₃H₆ response after the Au film was applied to the sensor. The sensor response is plotted versus the outlet C₃H₆ and C₃H₈ gas concentration. All three curves exhibit similar slopes: approximately .045 mV/ppm of

HC. For each curve, the maximum inlet [HC] injected was 500 ppm. From figure 7, it is apparent that the percentage of oxidation due to heterogeneous catalysis was 81% and 35% for the uncoated sensor for C₃H₈ and C₃H₆ respectively and 49% conversion for C₃H₆ after the sensor was coated with an Au film.

The reason for the low sensitivity towards CO can probably be attributed to the particular CO electro-oxidation kinetics exhibited by the La_{0.8}Sr_{0.2}CrO₃/YSZ interface and not – as shown in this work – attributable solely to heterogeneous catalysis on the YSZ sensor body. Unfortunately, the direct measurement of CO electro-oxidation is difficult [11, 12] and cannot be done under sensor operating conditions. Further experimental work will be pursued to measure the selectivity of other suitable working electrode candidates to various gas species taking into account the role of heterogeneous catalysis.

Conclusions

The heterogeneous catalysis, which takes place at elevated temperature in presence of excess O₂, can have a large effect on the observed response of a mixed potential sensor. The approximately 60% dense sintered YSZ sensor body of the sensors tested in this work played a significant role in changing the concentration of CO and C₃H₆ in the vicinity of the device. Effectively, the rough YSZ surface greatly reduces the amount of C₃H₆ and CO available for electrochemical oxidation at the electrode/YSZ interface. Through the use of inert coatings, the amount of unwanted heterogeneous catalysis can be reduced so that subsequent studies can now focus on the selectivity properties of other potential electrode candidates. As shown in this work, a La_{0.8}Sr_{0.2}CrO₃ working electrode shows a large preferential selectivity to HCs over CO and therefore may enable mixed potential sensors of this type, or thin film variations, to be useful for important applications such as monitoring state-of-health of automobile catalytic converters.

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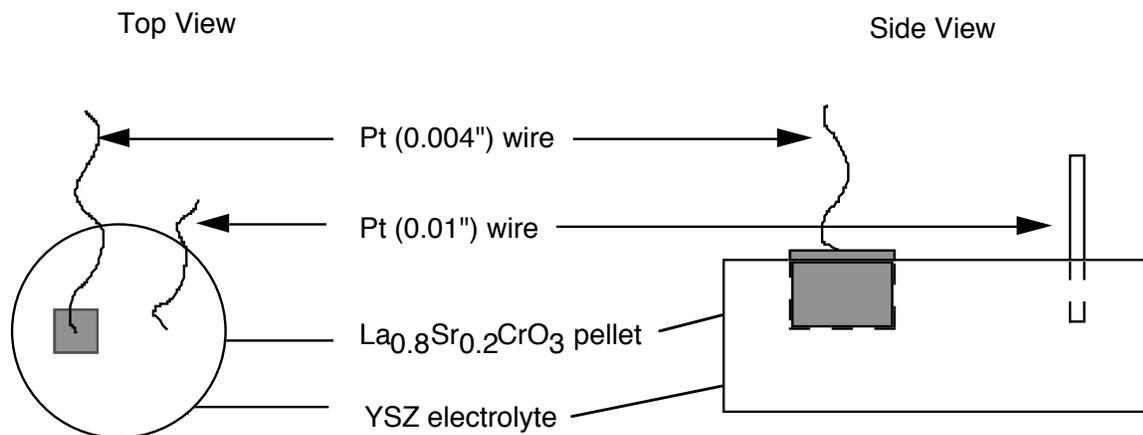


Figure 1. Illustration of LANL ceramic HC mixed potential sensor that utilizes the controlled-interface concept. U.S. patent applied for.

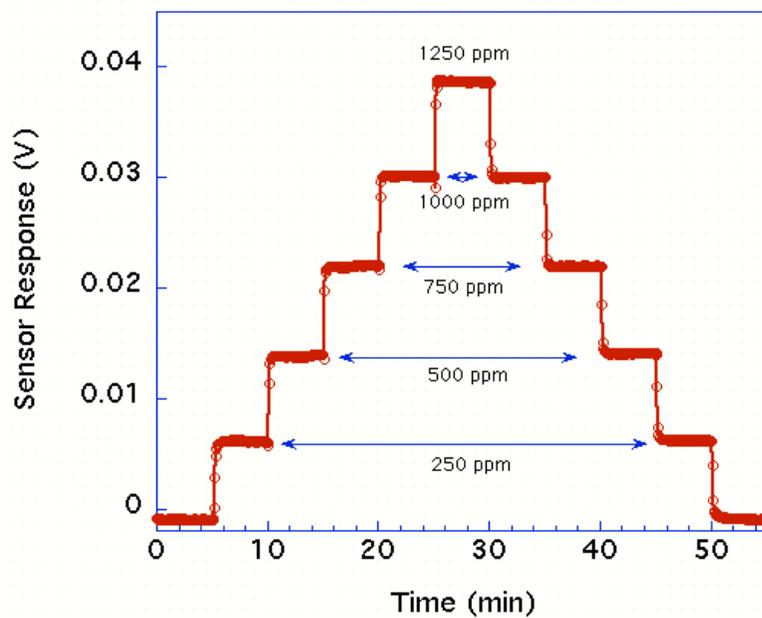


Figure 2. Typical propane response of the mixed potential sensor shown in Figure 1. The test conditions were 550°C and 200 sccm base gas flow consisting of 1%O₂/ 12%CO₂/ balance N₂.

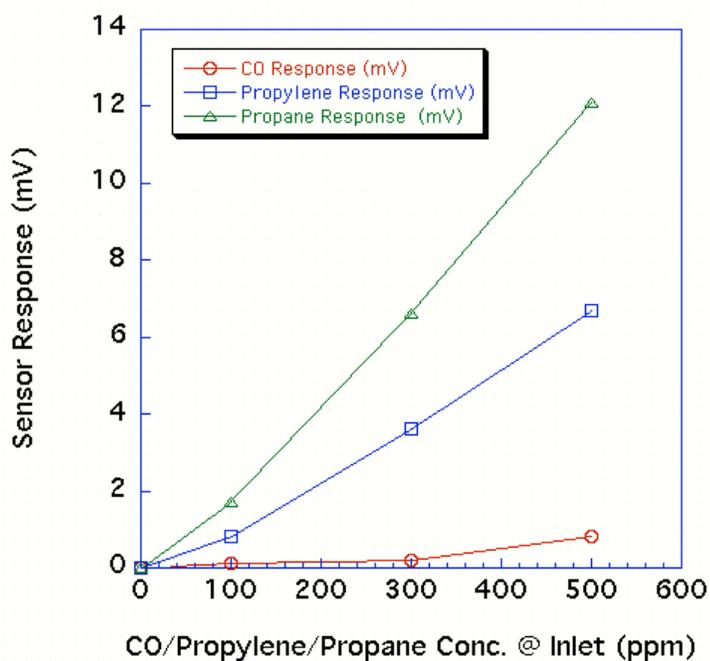


Figure 3. Sensor response to 100, 300, and 500 ppm of CO, C₃H₆, and C₃H₈ in a 200 scfm flow of 1%O₂/12%CO₂/N₂ at 600°C.

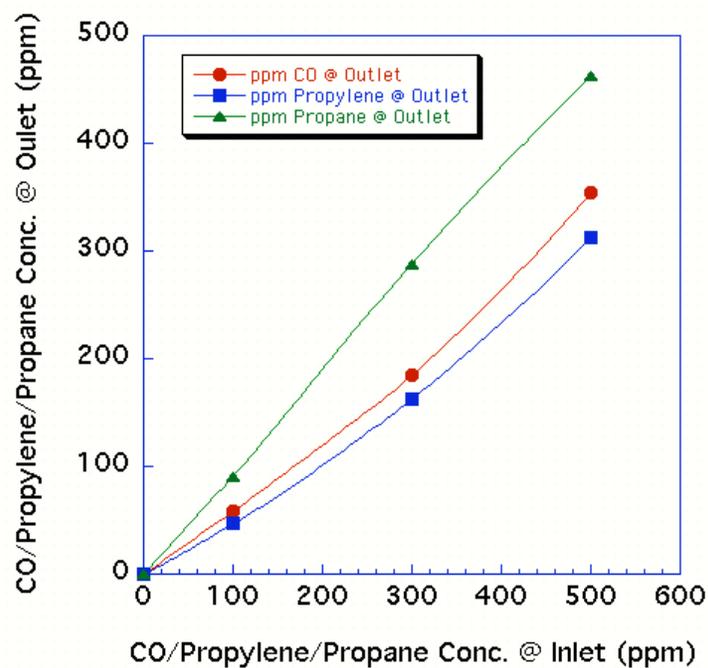


Figure 4. CO, C₃H₆, and C₃H₈ concentration at the furnace tube outlet versus the CO, C₃H₆, and C₃H₈ concentration at the furnace inlet as determined by gas chromatography analysis.

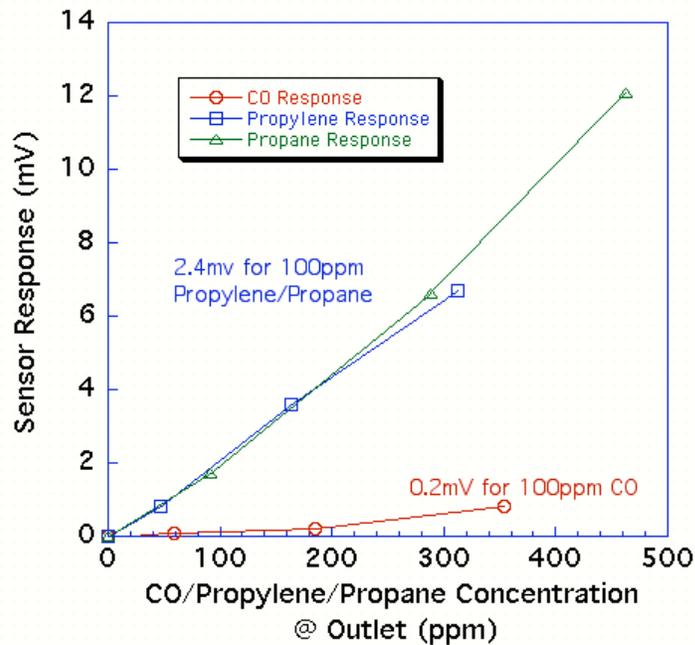


Figure 5. Sensor response to CO, C₃H₆, and C₃H₈ at 600°C and 200 sccm base gas flow plotted versus CO, C₃H₆, and C₃H₈ concentration post heterogeneous catalysis as determined by gas chromatography. The sensitivity to HCs and CO is indicated.

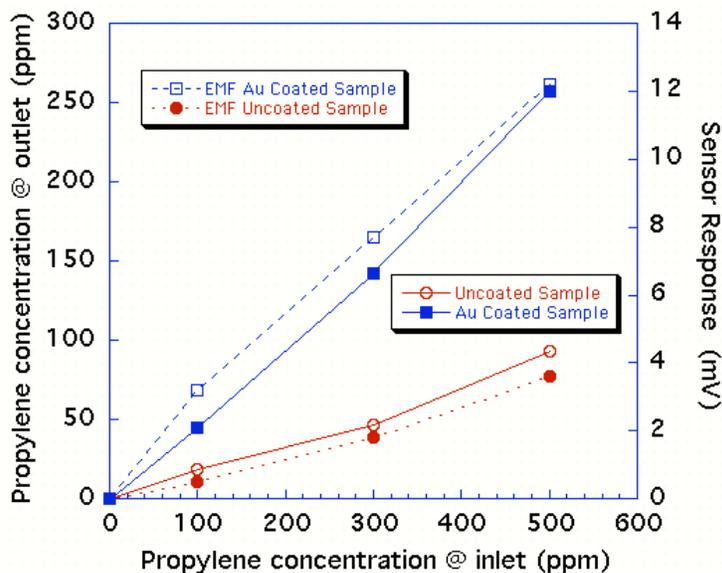


Figure 6. The amount of C₃H₆ heterogeneous catalysis and measured sensor voltage to C₃H₆ at 600°C before and after coating YSZ sensor body of a second sensor with Au ink. The purpose of the Au is to reduce surface area of the electrolyte available to heterogeneously catalyze C₃H₆. The working La-Sr-Cr-O oxide working electrode and Pt wire counter electrode were not disturbed.

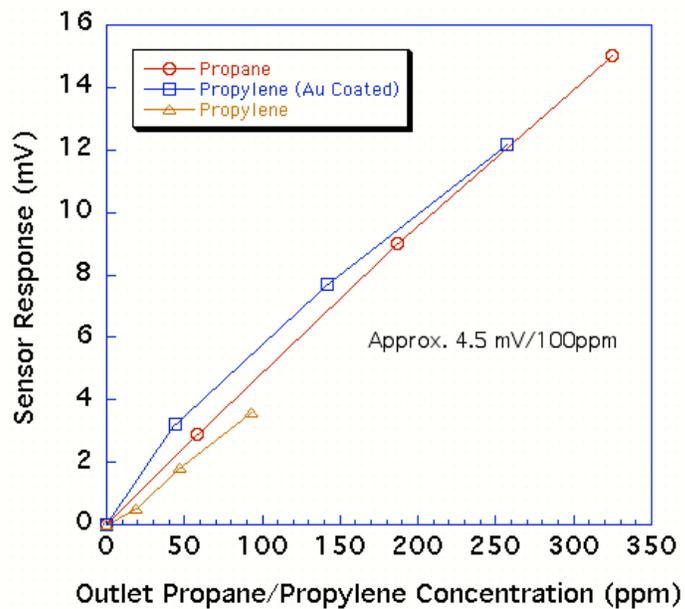


Figure 7. Sensor response of the uncoated second sensor to C_3H_6 , and C_3H_8 at $600^\circ C$ and 200 sccm base gas flow and of the C_3H_6 response after coating the device with Au plotted versus the C_3H_6 and C_3H_8 concentration post heterogeneous catalysis as determined by GC.