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Vehicle Exhaust Gas Chemical Sensors Using Acoustic Wave Resonators

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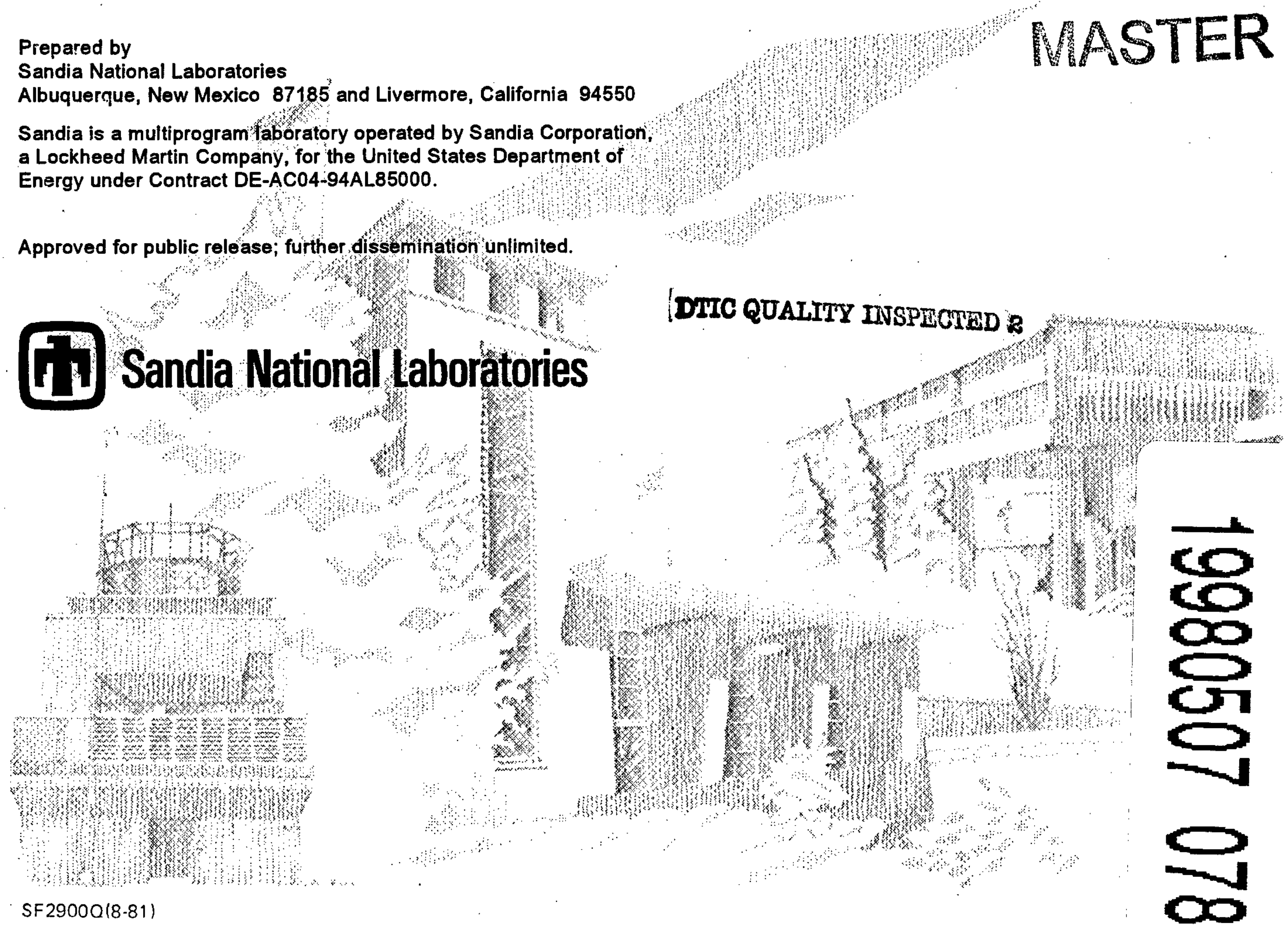

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Abstract

Under Sandia's Laboratory Directed Research and Development (LDRD) program, novel acoustic wave-based sensors were explored for detecting gaseous chemical species in vehicle exhaust streams. The need exists for on-line, real-time monitors to continuously analyze the toxic exhaust gases - nitrogen oxides (No_x), carbon monoxide (CO), and hydrocarbons (HC) - for determining catalytic converter efficiency, documenting compliance to emission regulations, and optimizing engine performance through feedback control. In this project, we adapted existing acoustic wave chemical sensor technology to the high-temperature environment and investigated new robust sensor materials for improving gas detection sensitivity and selectivity.

This report describes one new sensor that has potential use as an exhaust stream residual hydrocarbon monitor. The sensor consists of a thickness shear mode (TSM) quartz resonator coated with a thin mesoporous silica layer ion-exchanged with palladium ions. When operated at temperatures above 300 °C, the high surface area film catalyzes the combustion of the hydrocarbon vapors in the presence of oxygen. The sensor acts as a calorimeter as the exothermic reaction slightly increases the temperature, stressing the sensor surface, and producing a measurable deviation in the resonator frequency. Sensitivities as high as 0.44 (ppm-Δf)/(ppm-gas) have been measured for propylene gas, with minimum detectable signals of <50 ppm of propylene at 500°C.

Introduction

A new acoustic wave-based sensing device for high-temperature detection of gaseous hydrocarbons has been investigated for potential application as an exhaust monitor for internal-combustion (IC) engine vehicles. Residual hydrocarbons, along with NO_x and CO gases, are present in the vehicle exhaust stream as a result of incomplete fuel combustion. Typical hydrocarbon levels are $< 0.1\%$ by volume, with higher concentrations existing for rich-operating engines. Specifications for on-board hydrocarbon sensors require a measurement range from 25 ppm to 1000 ppm (0.1%) with a detection resolution of 25 ppm. The new acoustic sensor under development shows a capacity to meet these requirements.

The sensor utilizes AT-cut quartz resonators operating in the thickness shear mode (TSM) and coated with a thin layer of surfactant-templated periodic mesoporous silica ion-changed with metals [1,2]. AT-cut resonators are commonly used as mass deposition monitors [3] and usually are operated near room temperature where the resonant frequency deviates little with temperature fluctuations. At much higher temperatures, the frequency response exhibits a nonlinear temperature dependence (see Fig. 1) [4]. Coefficients are > 100 (ppm Δf)/°C above 385 °C and have approximately a quadratic variation with temperature. As seen in Fig. 1, the presence of the thin film has no significant effect on the frequency-temperature curve. The large temperature dependence along with the strain sensitivity of the quartz resonator sensors make them useful for detecting exothermic or endothermic gas reactions as long as the operating temperature is stable and does not exceed the quartz Curie point (α to β phase transition) of 573 °C. At higher temperatures, other piezoelectric materials such as lithium niobate ($LiNbO_3$) or gallium orthophosphate ($GaPO_4$) [5] could be used since they maintain their piezoelectric properties.

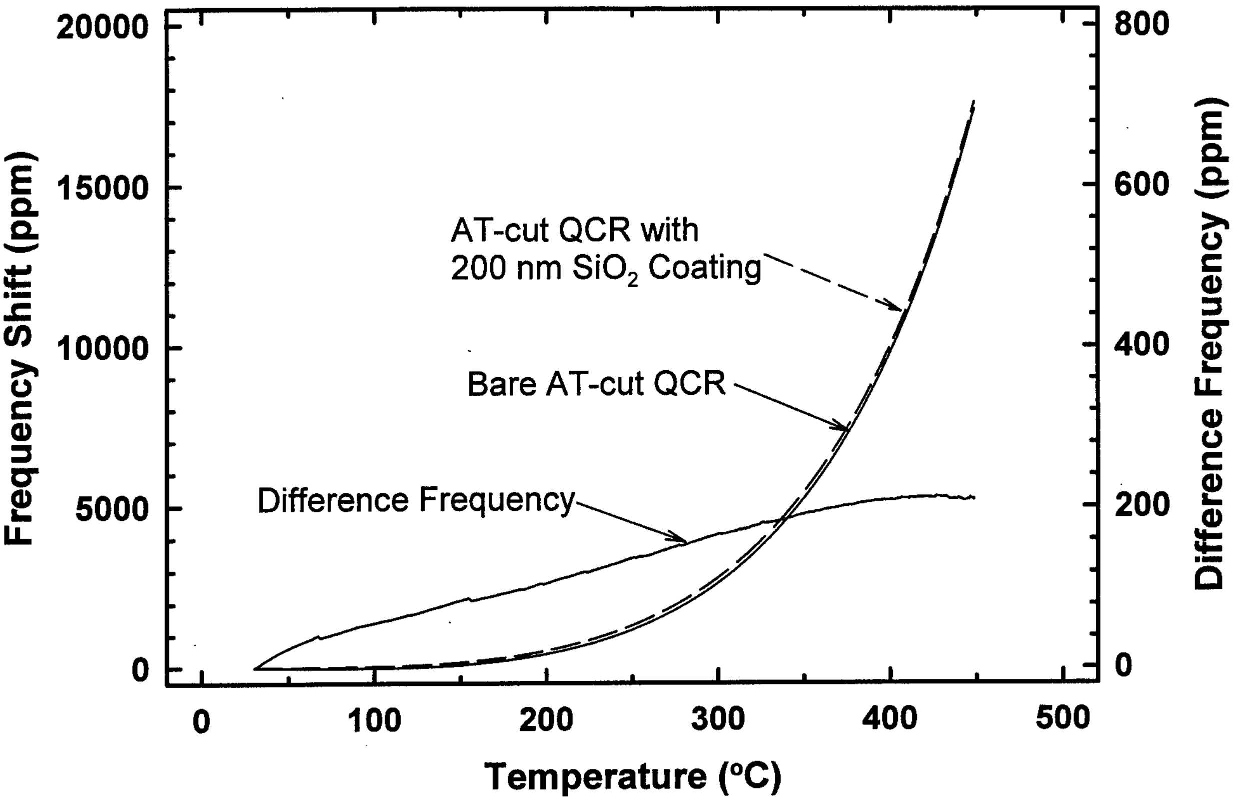

Fig. 1. Measured frequency shift vs. temperature for a bare and an SiO_2-coated TSM resonator. Temperature coefficients exceed 100 ppm/°C above 385 °C, but thermal noise reduction is possible using reference sensors and frequency subtraction or mixing.

Mesoporous Silica Thin Films

Sensitivity and selectivity of chemical sensors is determined by the properties of thin film surface layers. The high-temperature hydrocarbon sensor utilizes a sol-gel deposited surfactant-templated SiO_2 film. An alcoholic acid catalyzed silica sol is prepared with a pH near the isoelectric point of silica [2]. Cetyltrimethylammonium bromide (CTAB) surfactant is added to the sol in concentrations of 1.5 to 4.2 % by weight. After proper masking of the quartz resonator electrodes, the sol is spin-deposited on one surface. The films are then calcined at 400 °C for one hour (using a 1 °C/min ramp up and down) to burn out the organic template and access the porosity. Calcined films resemble the structure shown in Fig. 2. Films prepared using this

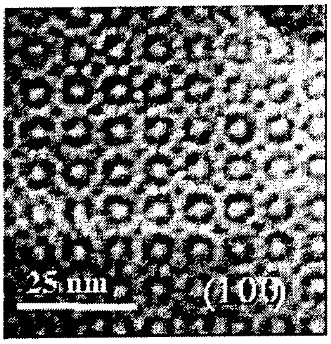

Fig. 2. A TEM image of the [100]-zone of a calcined fragment from a surfactant-templated mesoporous thin film. In this image, the pores have a diameter of ~ 3 nm and a spacing of ~ 8 nm. Choice of surfactant type and concentration determines pore modality and size. Typical film thicknesses are 150 to 200 nm.

technique have extremely high surface area (> 700 m^2/g), tunable pore diameters between ~ 2.0 and 3.5 nm, and 40-50% porosity. Spin-deposition is controlled to give film thicknesses between 150 to 200 nm. These thicknesses represent a good compromise between needed detection sensitivity and minimal loading and surface stress on the quartz resonator (see Fig. 1).

Gas selectivity is improved through ion-exchanging transition metals into the SiO_2 matrix to catalyze specific interactions. Sensors were prepared with Cu, Pd, Fe, V, Mo, and Cr ions by submersion in low-molarity metal-salt solutions for 5 to 30 minutes. Electron paramagnetic resonance (EPR) spectroscopy was performed on one of the $Cu:SiO_2$ devices which revealed a density of Cu^{2+} sites of approximately 0.1 atom percent. After a 400 °C anneal, the ion density was slightly reduced. None of the other ion-exchanged sensors were characterized for ion density, however, densities are expected to be on the same order as the $Cu:SiO_2$ device. Full optimization of the ion-exchange process for selective detection is now being performed.

Experimental Configurations

High-temperature evaluations of the metal:SiO_2-coated resonator sensors were performed in a specially-designed test cell. A photo of this test cell is shown in Fig. 3. The cell uses resistance

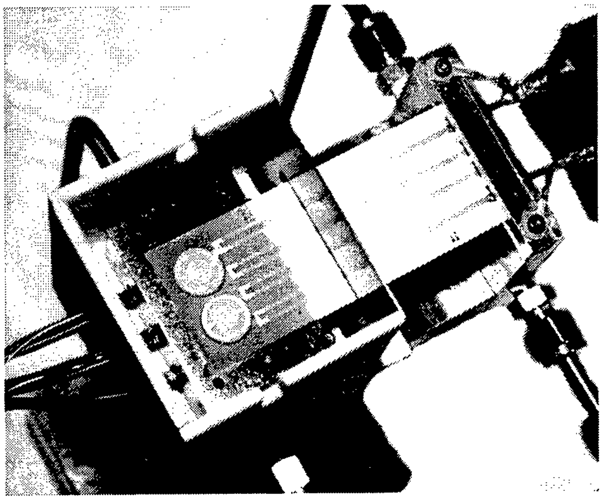

Fig. 3. *Interior view of the high-temperature test cell used for gas exposure of the surfactant-templated* SiO_2*-coated resonators. Two TSM resonators —one coated device, one uncoated reference device — are wire-bonded to ceramic striplines. Resistance heater control to 500 °C with ± 0.1 °C stability is possible using the fixture.*

heaters embedded in a metal housing above and below a flow cavity to control temperature. Maximum test temperatures were 500 °C with a control stability of ± 0.1°C. The resonators are wire-bonded to gold-plated alumina substrates which are configured as RF striplines for carrying electrical signals to the devices. The heated structure around the resonators forms a gas cavity of ~ 2.4 ml volume; an 8 cm long serpentine channel in the test cell cover preheats the gas before introduction into the cavity.

A vapor flow system provided the appropriate mixtures and flow rates for the target gases. Multi-component mixtures (up to three gases) along with a diluent and purge stream (nitrogen or air) were delivered by an array of mass-flow controllers and valves. Source gases were provided from calibrated bottles with desired concentrations or controlled flow through a bubbler (only water was mixed from a bubbler). Gas mixture concentrations using the flow system ranged from 10 ppm to 100%, while flow rates were controlled over the range 0.005 to 0.3 liters/min.

The quartz resonator sensors were configured as part of the Sandia-patented "lever" oscillator circuits that provide two signal outputs: the device resonance frequency (approximately 6 MHz) and a voltage proportional to the resonant resistance (related to the device quality factor or Q) [6]. Two resonators were mounted in the test cell: one coated device acting as the sensor, and an uncoated device acting as the reference. The frequency outputs from the two devices were mixed, providing a low frequency for measurement and a noise-rejection mechanism for operating in the difficult high-temperature environment (see difference frequency in Fig. 1).

A Windows-based computing system running code written in HPVEE and Visual Basic handled all sensor data acquisition, test cell temperature control, and vapor flow system control.

Results and Discussions

Several resonators coated with metal ion-exchanged, mesoporous SiO_2 thin films were evaluated for response to hydrocarbon vapors and cross-sensitivity to other gases present in the vehicle exhaust stream. To date, only one type of sensor — a resonator coated with a $Pd:SiO_2$ film — has shown good sensitivity for hydrocarbon detection. Figure 4 shows the measured frequency shift (in ppm) as this sensor is exposed to repeated intervals of 1 % by volume propylene gas in an oxygen-rich atmosphere at 490 °C. (Propylene or propene gas is used as one simulant for hydrocarbons in vehicle exhaust since it exists in a higher concentration than other non-methane organic gases and has one of the highest reactivity factors.) Maximum sensitivity at this temperature to propylene vapors is $\sim$ 0.44 (ppm-Δf)/(ppm-gas). Sensor response is rapid, $<$ 20 sec., however, adequate evaluation is limited by the 10 sec. data acquisition interval of the measurement system. The minimum detection capability for the $Pd:SiO_2$ sensor is $<$ 50 ppm propylene at 500 °C as shown in Fig. 5. Smaller propylene concentrations produce noticeable

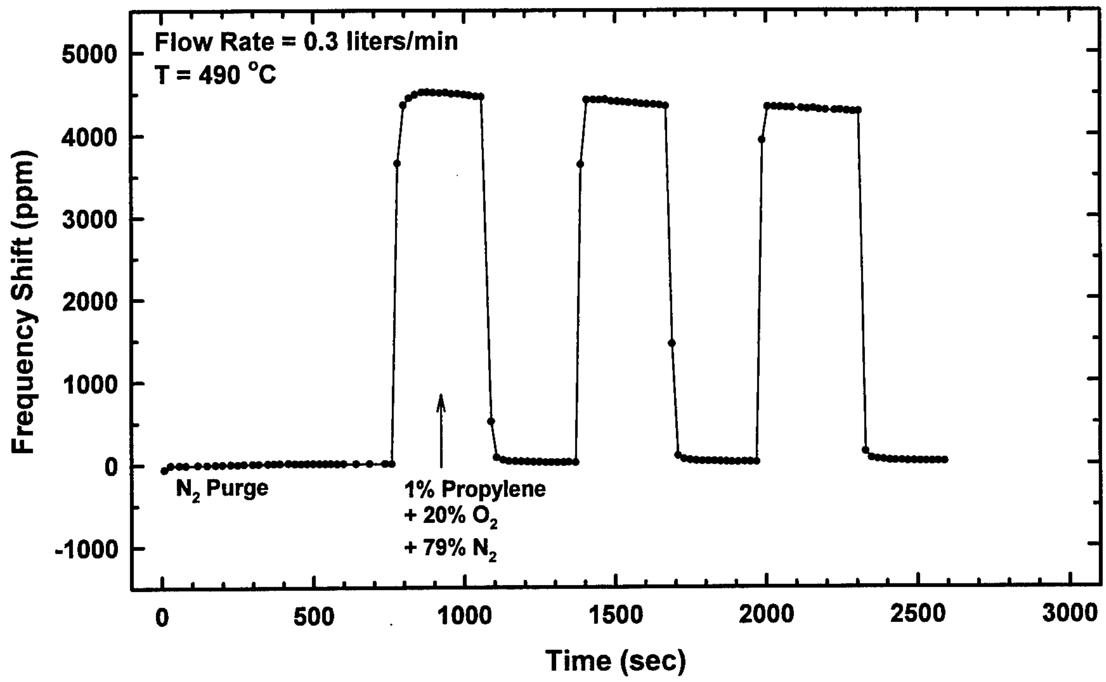

Fig. 4. Measured frequency shift vs. time for one Pd:SiO_2-coated TSM resonator when exposed to repeated intervals of 1% propylene gas mixed with 20 % oxygen.

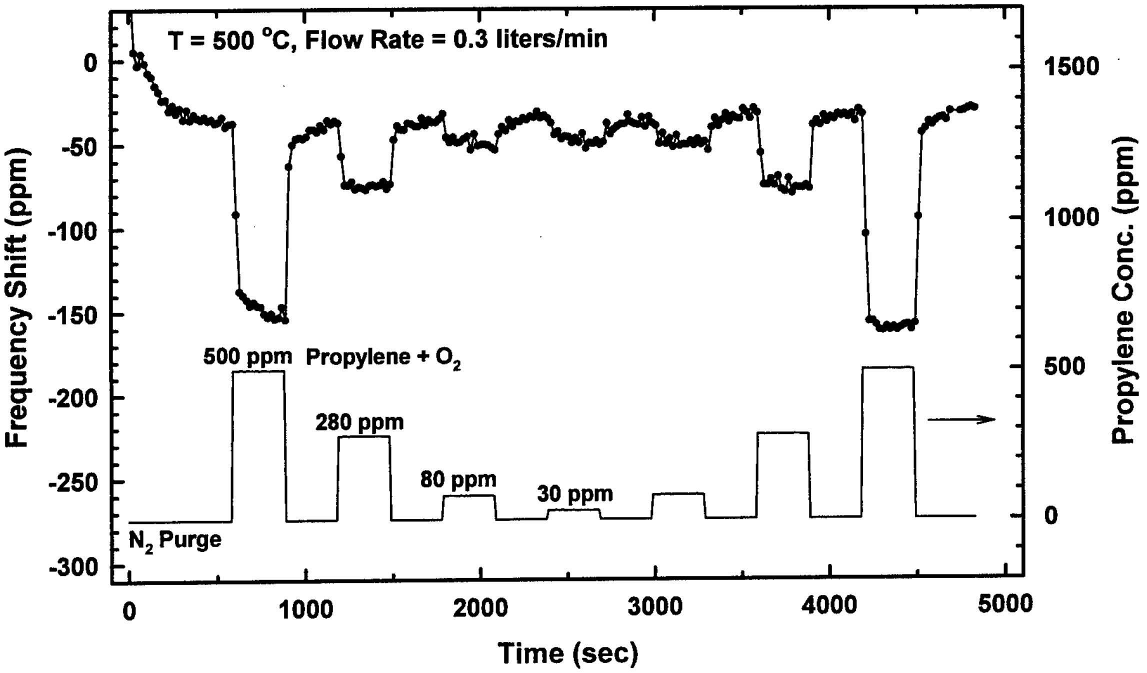

Fig. 5. Measured frequency shift vs. time for a Pd:SiO_2-coated sensor when exposed to low concentrations of propylene in an oxygen-rich atmosphere. Signal detection is possible below 50 ppm. Negative frequency shifts are seen in this figure (compared to Fig. 4) due to frequency mixing with a reference device.

deviations in frequency response, but it is not certain what fraction of this response is thermal noise created by slight flow rate changes as the vapor delivery system toggles between the target and purge gases.

This sensor functions much like a typical calorimeter or combustible gas detector [7-9]. Figure 6 shows that measured responses increase with higher temperature for all the test gases: propylene, ethylene, propane, methane, and hydrogen. This is due to increases in both the gas enthalpy and the quartz resonator response coefficient as the temperature rises. The response magnitude also increases as expected with number of gas molecule carbon atoms as evidenced by the propylene (C3) and ethylene (C2) responses. In Fig. 7, the measured response to propylene gas is shown to decrease as the oxygen atmosphere becomes leaner, going to zero in the absence

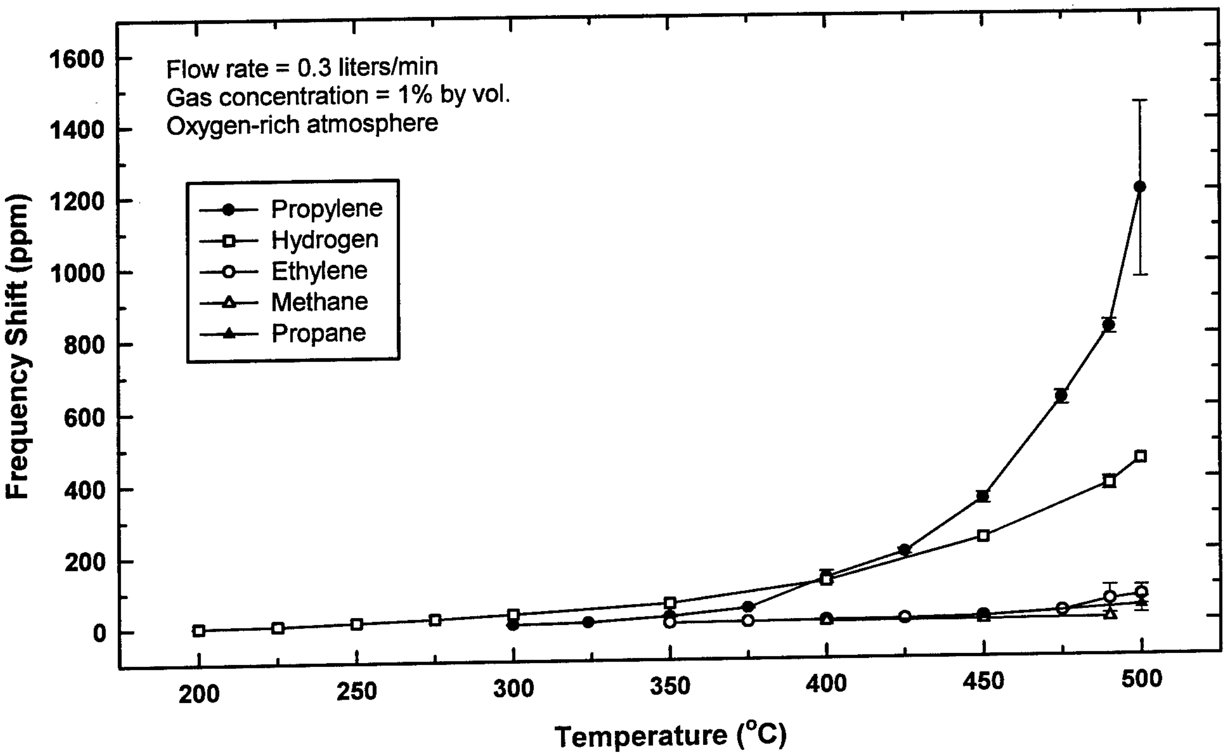

Fig. 6. Measured frequency shift vs. temperature for a Pd:SiO$_2$-coated sensor exposed to 1% concentrations of propylene, ethylene, propane, methane, and hydrogen gases mixed with oxygen.

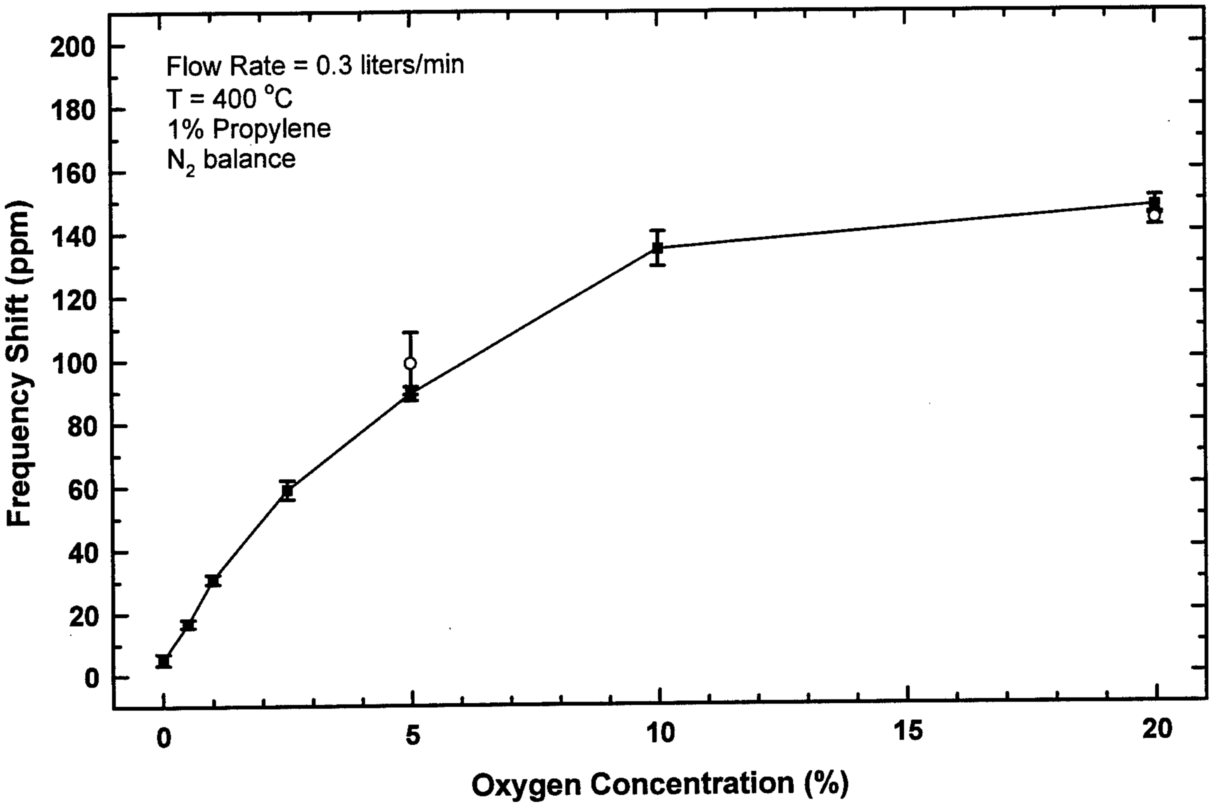

Fig. 7. Measured frequency shift vs. oxygen concentration for 1% propylene gas flowing across a Pd:SiO$_2$-coated sensor. No response occurs for hydrocarbons in an oxygen-deficient atmosphere. The different plotted points (open circles and filled squares) represent values from two separate tests.

of oxygen, and to saturate in high concentrations of oxygen. Again, this behavior is typical of calorimetric sensors.

However, based on the limited sensor measurements for these few test gases, the Pd:SiO$_2$ sensor response is somewhat atypical for a calorimeter. The olefins (represented by propylene) produce significantly larger frequency shifts than the paraffins (propane), ~ 20 times greater as seen in Fig. 6, and hydrogen sensitivity is relatively large compared to the hydrocarbons. Combustible gas detectors will also show some response to carbon monoxide in the presence of oxygen. But this sensor shows no reaction (although in an oxygen-deficient atmosphere at the highest temperatures, CO strips oxygen from the SiO$_2$ matrix, producing a small, but measurable, mass shift).

The palladium in the matrix obviously modifies the gas sensitivity and selectivity giving it an enhanced catalytic activity. Figure 8 shows the response of two sensors, one having only a surfactant-templated mesoporous SiO_2 thin film and the other with an identical SiO_2 film with palladium introduced in the matrix, exposed to a 1% propylene gas mixture. The virgin SiO_2 device shows a small reaction at the highest temperatures due to the large surface area of the porous film, but its response is much lower than that of the Pd:SiO_2-coated sensor. The exact dependence on the metal ions exchanged in the SiO_2 films is still under investigation, but from limited work it is known that V, Cu, or Fe in the matrix exhibit no favorable hydrocarbon or hydrogen catalytic reactivity and often have responses no larger than those for the SiO_2 film

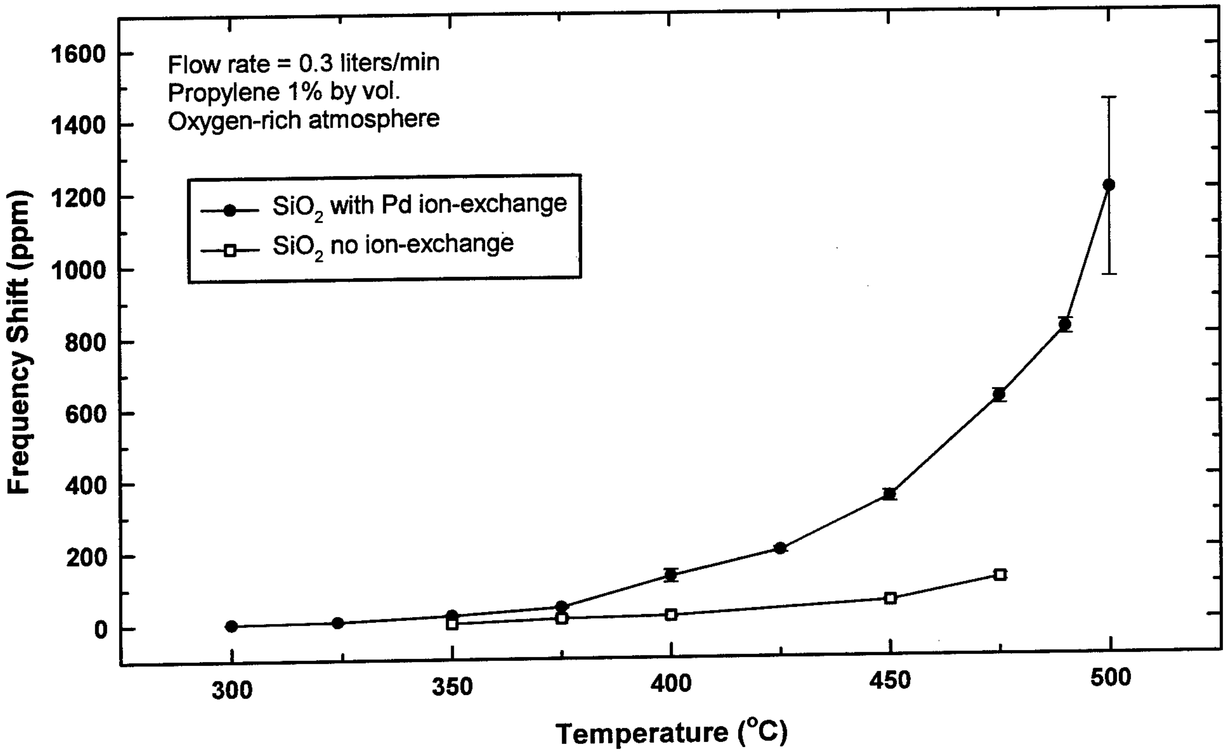

Fig. 8. Measured frequency shift vs. temperature for a propylene-oxygen mixture comparing the sensitivity enhancement due to Pd ion-exchange in the mesoporous SiO_2 thin film coatings.

alone.

From measurements using the Pd:SiO_2-coated resonators, it appears that sensitivity to hydrocarbon detection may be greater than for other types of calorimeters. It is postulated that catalyzed combustion (and the associated temperature increase) in the porous films stress the resonator surface, producing a frequency shift greater than that for an equivalent temperature shift in the bulk quartz (as illustrated in Fig. 1).

Utility of the surfactant-templated mesoporous silica sensors for vehicle exhaust monitoring depends on discrimination in the presence of other gas constituents. The Pd:SiO_2 devices exhibit no measurable response to NO or NO_2 at concentrations up to 9000 ppm, levels several times higher than expected in the exhaust stream. CO_2 illicits a small response (~ 20 ppm-Δf at 15% by volume concentration at 450 °C) due to a much larger heat capacity than the other test gases. Since CO_2 concentration in vehicle exhaust is usually near the values tested, it could interfere with detection of low levels of hydrocarbons. Water vapor, when exposed individually to the sensors, does not illicit a response. However, when water vapor is mixed into a propylene-oxygen stream at high temperatures (> 300 °C), a significant reduction in measured frequency shift (~ 2 times for 3 % H_2O) occurs. This reaction is unexpected as the difference in gas thermal conductivity alone does not account for such a large shift in response from a small concentration of water. Some of the shift in response magnitude could be an anomaly of the measurement system, and the phenomenon is still being studied. If proved real, the interference from water vapor could prove detrimental to eventual sensor implementation.

A comparison of relative responses for the Pd:SiO_2-coated resonators when exposed to all the test gases is given in Table 1.

Table 1. Comparison of Pd:SiO_2-coated resonator response for various gases at a specified temperature and concentration.

Gas	Temp (°C) / Conc. (%)	Sensitivity (ppm-Δf/ppm-gas)	Comments
Propylene (C_3H_6)	450 / 1	5.4×10^{-2}	due to catalytic combustion in O_2
Ethylene (C_2H_4)	450 / 1	2.4×10^{-3}	"
Propane (C_3H_8)	450 / 1	2.1×10^{-3}	"
Methane (CH_4)	450 / 1	$< 5 \times 10^{-4}$	too small to quantify
Hydrogen (H_2)	450 / 1	3.8×10^{-2}	due to catalytic combustion in O_2
Carbon Monoxide (CO)	450 / 1	$\sim 1 \times 10^{-3}$	only in oxygen-deficient atm.
Carbon Dioxide (CO_2)	450 / 15	2.7×10^{-4}	due to higher specific heat
Nitric Oxide (NO)	450 / 0.5	none	
Nitrogen Dioxide (NO_2)	500 / 0.9	none	
Water Vapor (H_2O)	400 / 3	$< 5 \times 10^{-5}$	anomalous response in mixtures

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