Catalytic and Catalytic Differential Calorimeter Gas Sensors

Fabrication and Evaluation

Introduction

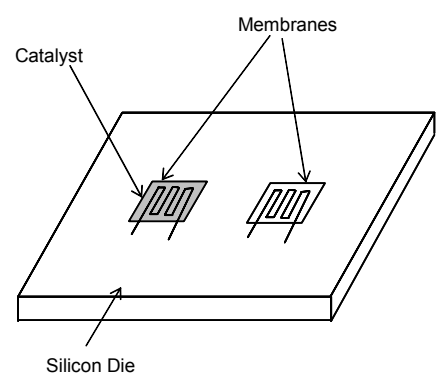
The Environmental Protection Agency and California Air Resources Board mandated on-board monitoring of the exhaust gas conversion efficiency of catalytic converters under its On-Board Diagnostic phase 2 (OBD-II) plan. A variety of exhaust gas constituent sensors were proposed in response to the need to meet OBD-II requirements. We focused on improving the sensitivity of the catalytic calorimeter sensors since calorimeter sensors are more stable and faster responding than semiconductor-type sensors.

In a catalytic calorimeter sensor combustible gases, e.g. hydrocarbons, CO, hydrogen etc., are oxidized with help of catalytic layer. The generated heat, measured as the increase in substrate temperature, results in an electrical output signal proportional to the amount of combustible gases present in the gas stream. These sensors typically operate in 250-500°C range and are suitable for automotive applications. We carried out this research to overcome the application-oriented limitations of existing sensors. We employed sol-gel processed alumina materials and organometallic compounds of precious metals (Pt, Rh, Pd etc.) to fabricate calorimeter sensors with improved sensitivity and durability.

Fabrication of Calorimeter Sensors

Calorimeter sensor device (Fig 1) was micro-machined so that there were two SiN_x membranes stretched across a Si frame. A platinum resistor, used to determine temperature changes, was deposited onto each membrane. An alumina layer is deposited on each membrane. A catalytic coating, to oxidize the combustible species in the automobile exhaust, was deposited on top of one of the two membranes. Temperature increases were measured on the catalytic membrane relative to the reference membrane. The increase in temperature was correlated to the total concentration of the combustibles in the exhaust gas.

Fig 1: Calorimeter Sensor



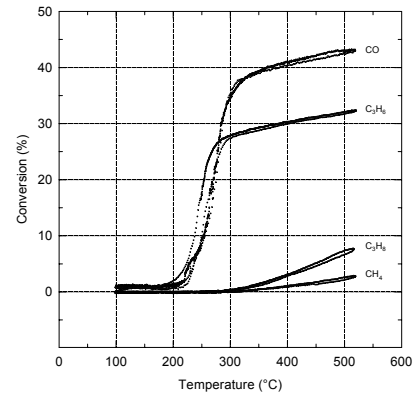
The alumina was deposited by a dip-coat method using alumina sol prepared from 2,4-pentanedione modified aluminum (2-propoxide). The overall thickness of the film was 600Å by profilometry. A microsyringing technique was used to apply precious metals (e.g. palladium from a 30g/L $Pd(DBA)_2$ in THF) onto a masked membrane. The catalyst coating was calcined in a two phase process starting at 4 hours at 80°C with a ramp rate of 1°C/min and 4 hours at 600°C with a ramp rate of 1°C/min.

Figure 2 shows conversion as a function of temperature for our sol-gel catalyst samples. In this experiment, the combustible species (1%CO or 1000 ppm HC) are mixed with oxygen at twice the stoichiometric combustion value (R=0.5) and diluted with N_2 to form a total flow of 250 sccm. The reactor furnace is ramped at 30°C/minute. The catalyst lights off at 270°C for CO and 250°C for C_3H_6 (cf. automotive catalyst lights off at about 175°C for CO and 225°C for C_3H_6 under our test conditions). For saturated hydrocarbons, CH_4 and C_3H_8, sol-gel catalyst is not as effective as automotive catalyst which shows considerable conversion for both species at 500°C. This is probably due to the lack of additive in our catalyst and the difference in the activity of Pd (our catalyst) and Pt/Rh (automotive catalyst).

These results suggest that our fabrication method has produced an optimum catalyst layer for CO and unsaturated hydrocarbons on calorimeter devices that is comparable to a fully formulated automotive exhaust reduction catalyst.

Evaluation

The calorimeter device was tested at 400°C, a gas flow rate of 250 sccm, and an operating redox ratio of 0.5. A 1 mA current was passed through the Pt resistors on the reference and active elements, and the output voltage (i.e. temperature) was measured while the test gas concentrations were varied. The results (Fig 3) indicate that the device response appears to be linear, and can produce temperature changes of 3°C per 1000 ppm of C_3H_6 and 0.85°C per 1000 ppm of CO. The device is not as responsive to the saturated hydrocarbons at 400°C. The sensor voltage operates as function of conversion efficiency, diffusivity, and heat of combustion, hence the difference in slope between the one and three carbon compounds.



Publications and Patents

This work was carried out in C.K. Narula's Laboratory at Ford Research by his group members and collaborators.

- Visser, J.H.; Narula, C.K.; Zanini-Fisher, M.; Catalytic Calorimeter Gas Sensor. U.S. Patent 5,707,148 Jan. 13, 1998.
- Visser, J.H.; Narula, C.K.; Zanini-Fisher, M.; Catalytic Differential Calorimeter Gas Sensor. U.S. Patent 5,813,764 Sept. 29, 1998.
- Nakouzi, S.R.; McBride, J.R.; Nietering, K.E.; Narula, C.K.; Sol-Gel Processed Alumina based Materials in Microcalorimeter Sensor Device Fabrication for Automotive Applications, Mater. Res. Soc. Symp., 431 (1996) 349-354.

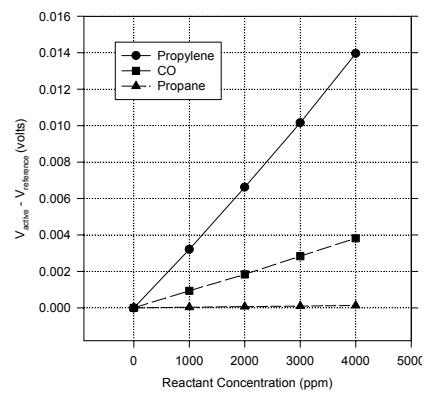


Fig 2: (upper) Light-Off Temperatures
Fig 3: (lower) Sensor Performance

Point of Contact:
Chaitanya K. Narula
Transportation Materials, M&C Division
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6066
Phone: 865-574-8445
FAX: 865-241-9844
E-mail: narulack@ornl.gov