MULTIFUNCTIONAL (NO_x/CO/O₂) SOLID-STATE SENSORS FOR COAL COMBUSTION CONTROL

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ABSTRACT

The composition and microstructure of the sensing electrode are the key parameters that influence the sensing mechanism, and hence key sensor performance parameters: sensitivity, selectivity and response time. During this reporting period we investigated the effect of microstructure and the fundamental heterogeneous gas solid interactions of our NO sensor electrode material.

In order to optimize the sensor electrode microstructure, powders were prepared using four different powder synthesis routes, resulting in different particle sizes distributions and BET surface areas. Different electrode processing conditions, e.g. screen-printing slurry composition, sintering schedule, etc. were also applied. In this report we demonstrate that the microstructure of electrodes, synthesized with the same composition, has a dramatic effect on both sensitivity and response time of potentiometric NO sensors.

A quartz reactor and a tube furnace were built for the catalysis experiments. The installation of a quadrupole mass spectrometer (QMS) and a multi gas controller were completed. Moreover, the system for the temperature-programmed reaction (TPR) and desorption (TPD) were completed by combining the equipment. We used this heterogeneous catalysis system to determine the adsorption characteristics of O₂, NO, CO, CO₂, and their mixtures, on the electrode material using TPD, and related the results to sensor performance.

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INTRODUCTION

There is a tremendous environmental and regulatory need for the monitoring and control of NO_x emissions from coal, natural gas and oil combustion sources. Solid oxide electrochemical O_2 sensors are inexpensive and have been well demonstrated in harsh high-temperature combustion exhaust environment. If modified to selectively measure NO_x and CO concentrations this type of sensor can be used to further improve combustion control, resulting in improved fuel utilization and reduced emissions.

We have developed solid-state sensor technology that can provide an inexpensive, rugged, small, solid-state device capable of measuring the concentration of multiple species (such as NO, NO_2 and CO) in coal, natural gas and oil combustion exhaust. Our sensor technology is similar to that used in conventional automotive O_2 sensors and thus can be used directly in high temperature exhaust. However, both the sensing and reference electrode are in the same gas stream, significantly reducing fabrication costs. These small ($<1 \text{ cm}^2$) simple potentiometric (voltage output) sensors are sensitive to each of these gasses and can be readily combined on a single chip to provide a multifunctional (NO_x , CO, O_2) sensor (Fig. 1). This technology is the basis for a low cost, simplified way to meet emissions monitoring regulations as well as to improve combustion control, thus, improving fuel utilization and reducing emissions from coal, natural gas and oil combustion sources.

Figure 1. Multifunctional NO_x , CO, O_2 sensor.

The key scientific issue that must be addressed for this type of sensor to effectively measure NO_x and CO concentrations in coal, natural gas and oil combustion exhaust gas streams is the

selectivity of the electrode(s) for discrimination between gaseous NO_x and CO vs. O_2 . Specifically, the sensors must exhibit a highly selective response to ppm levels of NO_x and CO in the presence of percent levels of O_2 . Not only must the sensor exhibit a selectivity factor of, for example, 1000:1 NO/O_2 , based on the typical concentration differences between NO and O_2 , but the sensor must be insensitive to large changes in the O_2 concentration associated with variations in combustion conditions.

We have developed an innovative scientific approach "Differential Electrode Equilibria" (described below), and demonstrated that this approach provides the necessary selectivity to measure for example ppm levels of NO with high sensitivity in lean-burn (13-17% O_2) exhaust gas unaffected by variations in O_2 concentration. Since we have already demonstrated this approach works for NO the objectives of our proposed research are to: advance the fundamental understanding of this approach, apply it to the development of selective NO_2 , CO and O_2 electrode elements; fabricate and test a multifunctional (NO_x , CO, O_2) sensor; and develop a miniature low-cost multifunctional (NO_x , CO, O_2) sensor prototype for evaluation by commercial/industrial companies. In achieving these objectives we will both advance the science of solid-state electrochemical sensors, including the education and training of students, and bring closer to commercialization a device that will result in both improved fuel utilization and reduced emissions from coal, natural gas and oil combustion.

Differential Electrode Equilibria

A difference in electrochemical potential between two electrodes exposed to the same environment (Differential Electrode Equilibria) will occur if one or both of the electrodes does not achieve thermodynamic equilibrium. In a potentiometric sensor this non-Nernstian response produces a voltage that depends on the concentration of one or more of the species present.

Semiconducting resistive sensors have been investigated¹ for many years for detection of gases. Sensor characteristics depend on the microstructure of the material and geometrical configuration of the sensor element. However, most of these sensors lack in the ability to

selectively detect the concentration of individual gases. For instance, it is difficult to monitor NO under varying O₂ concentration in combustion exhaust.

Traditional potentiometric sensors operate² on the principle that a voltage arises at the surface between two similar electrodes, fabricated on two opposite faces of an electrolyte material, when exposed to different environments. The voltage is proportional to the log of the P_{O₂} difference.

In contrast, our sensors operate with two dissimilar electrodes exposed to the same environment. The differential electrode equilibria³ created between the gas molecules and the dissimilar sensor electrode surfaces give rise to a potential gradient between the electrodes, resulting in a voltage response. Semiconducting oxide electrodes combined with platinum reference electrodes on YSZ substrates are sensitive and selective to NO with negligible response to O₂ or CO. Due to its principle of operation; microstructure plays an important role in performance. The gas solid interaction is highly dependent on the microstructure and morphology of the sensing electrode. A higher surface area with a porous electrode improves the adsorption sites and enhances the equilibrium (or non-equilibrium) process. This in turn, gives rise to a faster response time and higher sensitivity of the sensor element. In this investigation, an effort was made to make powders through different synthesis technique to generate sensing electrodes of different morphologies and compare the response characteristics using them.

EXECUTIVE SUMMARY

The composition and microstructure of the sensing electrode are the key parameters that influence the sensing mechanism, and hence key sensor performance parameters: sensitivity, selectivity and response time. During this reporting period we investigated the effect of microstructure and the fundamental heterogeneous gas solid interactions of our NO sensor electrode material.

In order to optimize the sensor electrode microstructure, powders were prepared using four different powder synthesis routes, resulting in different particle sizes distributions and BET surface areas. Different electrode processing conditions, e.g. screen-printing slurry composition, sintering schedule, etc. were also applied. In this report we demonstrate that the microstructure of electrodes, synthesized with the same composition, has a dramatic effect on both sensitivity and response time of potentiometric NO sensors.

A quartz reactor and a tube furnace were built for the catalysis experiments. The installation of a quadrupole mass spectrometer (QMS) and a multi gas controller were completed. Moreover, the system for the temperature-programmed reaction (TPR) and desorption (TPD) were completed by combining the equipment. We used this heterogeneous catalysis system to

determine the adsorption characteristics of O₂, NO, CO, CO₂, and their mixtures, on the electrode material using TPD, and related the results to sensor performance.

SENSOR FABRICATION AND TESTING

EXPERIMENTAL

Sensor Fabrication

To synthesize powders of different particle size distribution and surface area, the electrode material was prepared through three different powder preparation techniques: auto-ignition⁴, Pechini⁵ and co-precipitation⁶, which lead to sensor electrodes of the same composition but with different microstructures and surface areas.

In the auto-ignition process, nitrate salts of constituent elements were dissolved and citric acid added in appropriate proportion and subsequently heated with thorough mixing forming a gel, which was burnt to ash. The nature of burning depends on the citrate-nitrate ratio, and is the key parameter in determining the powder morphology. Depending on citrate-nitrate molar ratio γ , the nitrate and citrate ions in the gel will undergo a redox reaction under stoichiometric condition at $\gamma=0.277$. Excess citric acid in the gel ($\gamma>0.277$) presents a fuel-rich condition while lower concentrations produce a fuel-lean condition. Such conditions are expected to produce perovskite powders with different properties and varying particle characteristics. So two different ratios were adopted to produce powders which are named as auto-ignition fuel-lean ($\gamma=0.098$) and auto-ignition fuel-rich ($\gamma=0.50$), respectively.

In the co-precipitation process, aqueous 1:1 metal stoichiometric solutions of the metal nitrates were prepared in distilled H₂O. The metals were precipitated as hydroxides by slowly adding 10% excess of a basic solution of tetra-methyl ammonium hydroxide in 25% methanol. The precursor metal-hydroxide powders were recovered, rinsed, and air dried at 110°C overnight.

In the Pechini process, a solution was formed from citric acid, ethylene glycol and cation nitrate salts. The solution was heated forming a gel which was subsequently burnt.

For the fabrication of the sensing electrode material, semiconducting oxides, prepared in the laboratory, were ball-milled for 24 hrs with ethyl alcohol as a solvent and polyethylene glycol as a dispersing agent. The mixed slurry was heated at 60°C for 10 hrs for complete evaporation of

the solvent alcohol and screen-printed on one face of the YSZ substrates (Fig. 2). Tape cast YSZ substrates of dimension (20 mm × 10 mm × 0.15 mm) were used for sensor fabrication. Pt paste was screen-printed on the other side of the substrate. Thin platinum wires were connected to both electrodes using Pt paste for ohmic contact. Finally, after drying of the printed electrode slurry, the sensor electrodes were sintered at temperatures ranging from 700°C - 1050°C.

Figure 2. Configuration of the sensor element (a) front view and (b) side view.

The fabricated sensors were systematically evaluated in a simulated combustion environment, O₂-3%, CO₂-16%, NO₂-100ppm, CO-100ppm, saturated H₂O (3%) and balance N₂. Sensing experiments were carried out with a computer controlled gas-flow system connected to a quartz tube sample holder inside of a temperature controlled furnace. The sensors were exposed to 50, 100, 200, 400 and 650 ppm NO step changes, in the simulated combustion environment, at a total flow rate of 300 ml/min., in the temperature range between 400 and 700°C. Electromotive force (e.m.f.) measurements were performed between the two electrodes of the sensors using a Keithley digital voltmeter. During the e.m.f. measurements the oxide electrode was always kept at the positive terminal of the electrometer and both electrodes were exposed to the same gas environment.

Powder and Electrode Characterization

X-ray diffraction patterns (e.g. Fig. 3a) of powders prepared by the different synthesis techniques showed that the minimum calcination temperature for complete phase formation is 600°C (10hrs) for the auto-ignition powders while at least 650°C (10hrs) was necessary for the co-precipitated and Pechini processed powders, and even at 650°C the Pechini powders were not

phase pure. BET surface area analysis (Fig. 3b) show the highest surface area was obtained with the auto-ignition fuel-rich process.

Figure 3. Characterization of electrode powders prepared through different synthesis routes.

High resolution Field Effect Scanning Electron Micrograph (FESEM) pictures of powders prepared through the different techniques are presented in Fig. 4. The average particle size ranges between 50-200 nm depending on the synthesis technique, which were estimated from the micrographs and presented later in Table 1. Typical agglomerated structures of the respective powders are shown in the low magnification figures inside a box within individual pictures. The morphologies of the agglomerated systems after calcination are dependent on the method of powder synthesis. In powders prepared through auto-ignition rich-combustion, the submicron particles join together to form a net-like structure. In co-precipitation net-like agglomerates are also formed, but from larger particles. In auto-ignition lean-burn, the nature of agglomeration is different from the net-like structure of the Rich-burn process. Whereas in the Pechini process, the agglomerated microstructure is entirely different – forming solid lumps of particles joined strongly together. Typical agglomerate sizes are also presented in Table 1. During sintering the agglomerated structures results in different microstructure development resulting in different morphologies of the sintered electrodes.

Figure 4. Field Emission Scanning Micrograph of calcined powders.

Average particle size was determined from analysis of FESEM micrographs of the calcined powders. Among the more open net-morphology agglomerates, the lowest particle sizes were obtained from the powders prepared through the auto-ignition fuel-rich technique. The lower particle size of the auto-ignition powders must be due to an inherent characteristic of the synthesis process.

The Pechini prepared powders appear to have the smallest particle size, however, the higher packing density of these agglomerates makes quantitative assessment of particle size by this approach more difficult. Moreover, the BET results indicate that the Pechini processed powders should have the larger particle size. These results are summarized in Table 1.

Table 1. Characteristics of powders prepared through different processing techniques.

Powder Preparation Routes	Calcination Temp. (phase formation)	Agglomerate Size (mm)	Average Particle Size (nm)	Morphology (appearance)	BET Surface Area (m²/g)
Auto-ignition, Rich	600°C / 10hrs.	24 ± 8	75 ± 25	Flakes	16.7
Auto-ignition, Lean	600°C / 10hrs.	19 ± 5	85 ± 50	More spherical	7.57
Co-precipitation	650°C / 10hrs.	35 ± 5	140 ± 50	Net-like	9.15
Pechini Process	650°C / 10hrs.	17 ± 2	62 ± 12	Spherical	3.7

The electrode microstructures obtained from powders prepared through these techniques, were studied to identify the morphology of the sensing surface. SEM micrographs of sensor surfaces, for samples fired at the same sintering temperature of 800°C, are compared in Fig.5. Powders prepared through the fuel-rich auto-ignition process show the finest microstructure (Fig. 5a) with an average particle size of ~0.15 µm and a flakey microstructure, while the fuel-lean

(a) Auto-Ignition Rich, 800°C / 10hr

(b) Auto-Ignition Lean, 800°C / 10hr

(c) Co-Precipitation, 800°C / 10hr

(d) Pechini Process, 800°C / 10hr

Figure 5. Morphology of sintered sensing electrodes from powders fabricated through different techniques.

conditions produced a comparatively coarser microstructure (Fig. 5b) with an average particle size of $\sim 0.29 \mu\text{m}$. The co-precipitation (Fig. 5c) and Pechini (Fig. 5d) processed powders similarly resulted in $\sim 0.29 \mu\text{m}$ grains, but with some differences in microstructure.

The effect of sintering temperature was studied with the co-precipitated powders. SEM micrographs of co-precipitated powders sintered at four different temperatures are presented in Fig. 6. The figure shows a limited increase in grain size between 700°C and 800°C , whereas there is dramatic increase in grain size beyond 800°C . At 1050°C the grains are very large, more joined together, and have a large reduction in contact angle between grains.

Figure 6. Variation of microstructure of Co-precipitated sensing electrode material sintered at various temperatures: (a) $700^\circ\text{C}/10\text{hrs}$, (b) $800^\circ\text{C}/10\text{hrs}$, (c) $900^\circ\text{C}/10\text{hrs}$, and (d) $1050^\circ\text{C}/10\text{hrs}$.

Similar variations in microstructure with sintering temperature were observed for powders produced through the other three different synthesis routes. Some of the microstructures are presented in Fig. 7, showing variation of morphology with sintering temperature and time.

Figure 7. Variation of microstructure of electrode material sintered at various temperatures and processes. Auto-Ignition Fuel-lean (a) 700°C/10hrs and (b) 900°C/10hrs; Auto-Ignition Fuel-rich (c) and 700°C/10hrs; (d) 800°C/18hrs; and Pechini (e) 700°C/10hrs and (f) 800°C/18hrs.

Powders prepared through other techniques also have a limited grain growth up to 800°C as can be observed comparing Figs. 7c (700°C/10hrs.) and 5a (800°C/10hrs.) for auto-ignition rich powders, and relatively large grain growth at 900°C and above. The effect of sintering time is less of an issue, although there is some grain growth between 10 hrs and 18 hrs of sintering at

800°C as presented in Fig. 5a (800°C/10hrs.) and Fig. 7d (800°C/18hrs.) for auto-ignition rich powders, and Fig. 5d (800°C/10hrs.) and Fig. 7f (800°C/18hrs.) for Pechini powders. Based on all these observations, the temperature of sintering was selected to be 800°C for 10 hrs yielding small sized uniform distribution of grains and pores.

Results and Discussion

The sensor response for samples prepared through these preparation techniques are compared in Fig. 8 at 450° and 500°C. The auto-ignition powders showed the sharpest response at lower

Figure 8. Response for NO sensors fabricated through Pechini, Auto-ignition Lean, Auto-ignition Rich and Co-precipitation processes, at 450°C and 500°C in simulated exhaust.

temperature of operation. This may be due to the flaky grains having higher available surface area (Fig. 5a) for the gas species. Samples prepared from Pechini powders showed the highest sensitivity (~20mV at 650ppm of NO) whereas co-precipitated powders showed the lowest

sensitivity (~13mV at 650ppm of NO) at 450°C. However, at 500°C co-precipitation and auto-ignition lean exhibited the greatest sensitivity.

The temperature dependence of sensor response for the samples prepared from the different powders is shown in Fig. 9. Among these, sensors prepared from Pechini processed powders have the strongest temperature dependence. The results also show that the sensitivity increases at lower operating temperatures. The lower limit of operating temperature is limited by the response stability and auto-ignition rich prepared electrodes were the only ones that had reasonable stability down to 400°C. Response stability is our qualitative assessment of the rise and fall of sensor voltage with each concentration step. Deviation from a rapid vertical rise (or fall) followed by a 90° transition and flat plateau is an indicator of a less than stable response. An example of this are the overshoots of the 400°C data in Fig. 5a.

At lower measurement temperature the sensitivity at lower gas concentration also increases. The range of maximum sensitivity for detection of NO gas concentration is also dependant on powder synthesis route. The auto-ignition rich samples are highly sensitive between 0-50ppm whereas samples prepared from the Pechini process are more sensitive at higher ppm ranges. Correlating these results with microstructures (Fig. 5) of corresponding samples, it may be concluded that higher resolution at lower ppm can be achieved with finer microstructural features.

(a) Auto-Ignition Rich

(b) Auto-Ignition Lean

(c) Co-Precipitation

(d) Pechini Process

Figure 9. Sensor response at varying measurement temperatures, for powders prepared through different processes (all sintered at 800°C/10hrs).

(a) Sensitivity at 450°C

(b) Sensitivity at 500°C

(c) Response time at 450°C

(d) Response time at 500°C

Figure 10. Sensitivity and response time of sensors fabricated from powders prepared through different techniques (all sintered at 800°C/10hrs).

The mean values of response for the four (up and down) measurements, calculated from Fig. 9, at each NO gas concentration are plotted in Fig. 10 (a) and (b). The standard deviations are presented as error bars. At 450°C, auto-ignition lean and Pechini prepared electrodes exhibit higher voltage responses. The dependence of voltage response on NO concentration (sensitivity)

is non-linear for auto-ignition lean and co-precipitation prepared electrodes. At 500°C, the auto-ignition lean and co-precipitation samples are most sensitive and the sensitivity is more linear.

The response time was taken to be the time to reach 90% of the stable value. At 450°C, response times range from 10 to 80 sec and is faster at higher NO concentrations. For auto-ignition rich, response time is nearly constant. At 500°C average response time is decreased to 10 to 40 sec and the response time dependence on NO concentration is relatively small. The auto-ignition rich exhibits the fastest and most stable response at both 450°C and 500°C.

Table 2. Correlation between synthesis techniques and response of fabricated sensors.

Synthesis Technique	Powder Surface Area ^a (m ² /g)	Electrode Grain Size ^b (μm)	Sensitivity (mV/decade)		Response Time ^c (sec)	
			450°C	500°C	450°C	500°C
Auto-Ign. Rich	16.7	0.146 ± 0.055	9.59	2.88	13.2 ± 2.2	16.8 ± 5.8
Pechini	3.7	0.292 ± 0.110	10.99	4.49	47.4 ± 19.1	23.0 ± 8.2
Auto-Ign. Lean	7.6	0.292 ± 0.100	6.81	9.70	28.0 ± 15.0	25.0 ± 6.8
Co-precipitation	9.2	0.285 ± 0.111	5.71	7.99	36.0 ± 20.0	29.8 ± 1.4

^a B.E.T. surface areas measured on as-calcined powders.

^b Grain size measurements of sintered electrodes from SEM micrographs.

^c Average value of response times for five different ppm ranges, based on 90% criteria.

A comparison of the response time and overall sensitivity as a function of powder surface area and electrode grain size, due to the different powder preparation techniques, is presented in Table 2. The overall sensitivity is defined by the slopes of the curves in Fig. 10 (a) and (b) over the total gas concentration range investigated, even though they deviate from linearity. At 450°C Pechini powders have the highest sensitivity and co-precipitation powders have the least. At 500°C auto-ignition lean powders have the highest sensitivity and auto-ignition rich powders have the least. These results show that microstructure plays a role in sensitivity, however, no direct correlation can be made between microstructure and sensitivity. Further analysis of sensitivity over specific concentration regions and temperatures may elucidate a relationship.

It is apparent however, that the highest surface area powders, from auto-ignition rich processing, resulted in the finest grain size and that these electrodes resulted in the fastest response time at both 450° and 500°C. All three of the other techniques resulted in significantly lower surface area powders and almost identical larger grain sizes in the sintered electrode microstructure. Further, all three had essentially the same response time (within the statistical significance of the data). Hence, it may be concluded that starting powders with large surface

areas generate a porous morphology with smaller grain size, and that smaller grain size results in a sharper response and faster response time.

CONCLUSIONS

Powders prepared through different synthesis routes have different specific surface areas, which lead to different morphologies of the sintered sensing electrode element. This variation in morphology has a large effect on sensor response and modifies the sensitivity and range of detection of NO gas. With sintered electrode elements having finer grain distribution, higher resolution at low gas concentrations and faster response times were obtained. The temperature dependence of stability, sensitivity and response time was determined. It was shown that stability improves with increase in operating temperature and stable response was not observed at temperatures below 400°C. Faster response time was observed at higher operating temperature as the system comes to equilibria much quicker. However, it was observed that sensitivity decreases significantly at temperature above 550°C. So, depending on the morphology of the electrode, the sensor may be operated at sufficiently high temperature (450-500°C), for significant stability and fast response time, without sacrificing much sensitivity.

EVALUATION OF SENSING ELECTRODE MATERIALS BY HETEROGENEOUS CATALYSIS TECHNIQUES

EXPERIMENTAL

TPD/TPR System Fabrication

A catalytic reactor was fabricated using quartz tubes and a frit. As shown in Figure 11, the reactor was constructed by welding the two quartz tubes around a semiporous frit to isolate the sample. To minimize the dead volume between the reactor and the quadrupole mass spectrometer (QMS), a tube with small inner diameter (ID) = 1 mm was used at the gas effluent end. A thermocouple (type-K) contained in a concentric quartz tube to prevent direct contact to the sample, was placed just above the sample to monitor the temperature. The reactor was sealed gas-tight using Ultra-Torr fittings. Input gas entered from the top, reacted with the sample, and exited out through the bottom to the QMS.

Figure 11. Quartz reactor.

A small tube furnace was built using Kanthal wire (nickel-chrome alloy, 0.4 mm thickness) coiled inside a cylinder and packed with ceramic wool. The heated inner volume is 20 mm wide and 150 mm long. A QMS was installed, which includes an ABB 150-QC QMS, a power supply, an Extrel Merlin automation QMS controller, and Pfeiffer vacuum pump unit. A MKS eight channel mass flow programmer/display (Model 647C8RON) and six mass flow controllers (MFC) were purchased, manifolded, and calibrated. The complete system is shown in Figures 12 and 13.

Figure 12. Complete system for TPR and TPD experiments.

Figure 13. Picture of the complete system.

Sample Preparation and TPD Experiments

The electrode material was synthesized by the fuel-lean auto-ignition method. A mixture of metal nitrates, and Citric acid was dissolved in deionized water, where the molar ratio of citrate and nitrate, $M_{\text{citric acid}} / M_{\text{total nitrate}} = 0.25$. The mixture was kept on the hot plate (~ 80 °C) under constant stirring until transparent gel and later dark brown precipitate was formed. The ignition product was calcined for 10 hr at 800 °C with heating and cooling rates of 5 °C/min. The specific surface area of the calcined sample was ~ 2 m²/g.

TPD experiments were performed to investigate the adsorption characteristics of exhaust gases such as NO, CO, O₂, CO₂, and their mixtures on ≈ 0.033 g of the electrode material (total BET surface area ≈ 0.066 m²). TPD experiments start from the adsorption of a particular gas at elevated temperature. The reactor is then cooled down to 50 °C and subsequently purged with the He gas containing 1 % Ar for internal calibration. Temperature was increased from 50 to 800 °C under flowing He 20 cc/min while measuring the concentration of effluent gases with the QMS. We scanned $m/e = 12$ (C), 14 (N), 28 (CO or N₂), 30 (NO), 32 (O₂), 44 (CO₂ or N₂O), and 46 (NO₂) during the TPD measurements. The $m/e = 12$ and 14 peaks are due to internal mass spectrometer cracking fractions of C and N containing compounds, respectively. They are monitored to determine if, for example, an $m/e = 28$ peak is due to CO or N₂.

RESULTS AND DISCUSSION

O₂ TPD results are presented in Figure 14. After exposure to 2 % O₂ in He, the main O₂ desorption peak occurred at 300 ~ 380 °C and the evolution of bulk lattice oxygen occurred at >700 °C.

Figure 14. O₂ TPD

Figure 15 shows the NO TPD curves after a 1 % NO adsorption step. Broad, probably doublet, NO and N peaks appeared at 300 ~ 420 °C, indicating two different adsorption states for NO. This was followed by an intense lattice oxygen peak above 700 °C, as was detected in the O₂ TPD.

Figure 15. NO TPD

For CO TPD experiments, the sample was initially exposed to 1 % CO in He. As shown in Fig. 16, strong CO₂ and CO peaks appeared at 500 ~ 800 °C. These are probably due to

carbonate decomposition. No evolution of bulk oxygen was observed, most likely because lattice oxygen was consumed in carbonate formation from absorbed CO.

Figure 16. CO TPD

The CO_2 TPD is shown in Fig. 17. After cooling with 1 % CO_2 in He and then heating under 1 % Ar in He, CO_2 exhibited a maximum at ~ 290 °C. A smaller peak, most likely due to

Figure 17. CO_2 TPD

physisorption, was also observed at ~ 140 °C. The maximum peak was very broad, covering from 200 °C to 600 °C. As was the case for O₂ and NO TPD, a significant peak due to the release of bulk oxygen appeared at >650 °C.

When NO was co-adsorbed with O₂ (0.67 % NO and 0.67 % O₂), the NO desorption occurred at the same temperature region as the pure NO TPD curve but the lower temperature peak increased indicating greater NO adsorption with O₂ for this desorption state, as shown in Fig. 18. Also the O₂ co-desorption at ~ 420 °C was more prevalent at the higher temperature desorption state indicating it may be an adsorbed nitril type species. No NO₂ desorption was observed. Bulk O₂ desorption at >650 °C was still observed.

Figure 18. NO and O₂ TPD

When the sample was exposed to mixture of 0.5 % NO and 0.5 % CO, the position of the NO doublet was shifted to lower temperature, 100 ~ 350 °C (Fig. 19). In addition, both the intensity and separation of the peaks increased. No C species desorption was observed. Interestingly, an N₂ peak appeared at ~ 680 °C.

Figure 19. NO and CO TPD

CONCLUSIONS

The NO_x sensors were tested in the simulated exhaust gas environment containing N₂, CO₂, H₂O, O₂, CO and NO_x. As previously explained, when NO was present, asymmetric electrodes (Pt and metal oxide) produced large e.m.f. changes. The sensor showed high selectivity toward NO_x, and NO sensitivity (voltage response) increased with decreasing temperature, from 600°C to 400°C. However, at the lower temperatures, sensing response was limited by slow unstable heterogeneous kinetics, thus limiting sensor operation to >400°C.

As shown in Fig's 15, 18 and 19, NO does not fully desorb from the surface of metal oxide until >400°C. Therefore, the instability of sensor response at low temperature can be explained, using the TPD results, by saturation of the metal oxide surface with NO. That is at <400°C the rate of NO adsorption is greater than the rate of NO desorption. The sensing mechanism is dominated by adsorbed NO species that are not in full equilibrium with the gas phase composition, most likely by a semiconducting response (change in Fermi level) rather than heterogeneous kinetics (Mixed Potential). At >400°C, the rate of NO desorption is greater than

the rate of NO adsorption. Any surface NO species are now directly proportional to the gas phase composition.

The lack of any NO₂ from co-adsorbed NO and O₂ (Fig. 18) would tend to indicate that the sensor voltage is not due to the conventional Mixed Potential theory. This will be explored further in the near future by:

1. TPD experiments of NO₂ and NO₂-containing gas mixtures on the electrode material.
2. TPR of NO/NO₂/O₂ gas mixtures on the electrode material.

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