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Catalytic Membrane Sensors. A Thin Film Modified H₂ Resistive Sensor for Multi-Molecular Detection

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A so-called "catalytic membrane sensor" (CMS) is being developed to impart selectivity and reactivity to the surface of an existing sensor by modifying it with a series of thin films. The proposed "sandwich-type" modification involves deposition of a catalyst layer between two size selective sol-gel layers on a Pd/Ni resistive H₂ sensor. The role of the catalyst is to convert organic materials to H₂ and organic by-products by a dehydrogenation mechanism. The roles of the membranes are to impart chemical specificity by molecular sieving of the analyte and the converted product streams as well as to control access to the underlying Pd/Ni sensor. The "sandwich" modification will mediate the sensor response and avoid potential poisoning effects. Ultimately, an array of these CMS ele-

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ments encompassing different catalysts and membranes will further enable improvements in selectivity and specificity via pattern recognition methodologies. This report details the synthesis of the various thin film solutions (i.e., catalyst precursors, sol-gel solution), the generation of the catalyst through ion-exchange, a comparison of the double alkoxide versus standard catalyst precursors, and the processing required to generate a CMS. This paper also details the novel and surprising experimental data concerning the increased selectivity and durability observed for the sol-gel modified H_2 gas sensing resistors. The utility of the CMS component as a multi-molecular detector will be reported later.

INTRODUCTION

There continues to be significant interest in increasing the sensitivity of existing sensors while maintaining or even reducing their size. We are developing a method termed, a catalytic membrane-based sensor (CMS), that addresses this problem. The CMS modification of an existing sensor will be accomplished through the integration of a Sandia National Laboratories developed Pd/Ni-based hydrogen sensor^{1,2} with size selective gas separation membranes³⁻⁵ and ion-exchangeable hydrous metal oxide catalyst support⁶⁻⁹ overlayers. The basic constructs of the CMS are a catalyst layer, sandwiched between a top and bottom porous thin film SiO_2 membrane, deposited on a chemical sensor surface (Figure 1). The role of the catalyst is to convert organic materials to H_2 and organic by-products through dehydrogenation reactions. The roles of the membranes are to impart chemical specificity by molecular sieving of the analyte and the converted product streams as well as to control access to the underlying Pd/Ni sensor. This will mediate the sensor response and avoid potential poisoning effects. The actual CMS component has only been produced recently; therefore, this paper will only discuss the results obtained in production of the CMS component. Later reports will discuss the utility of the CMS modified sensor as a multi-molecular detection unit.

To produce the CMS prototype it was necessary to understand and develop new processing routes using sol-gel derived materials,³⁻⁵ synthesize novel¹⁰ and standard⁹ catalysts from hydrous titanium oxide (HTO) precursor solutions followed by ion-exchange, and testing of the functionality of the sensor at each interval. An existing high quality Pd/Ni H_2 resistive sensor was used as the platform to demonstrate the basic concepts of the CMS approach.¹¹ The sol-gel layers used in this

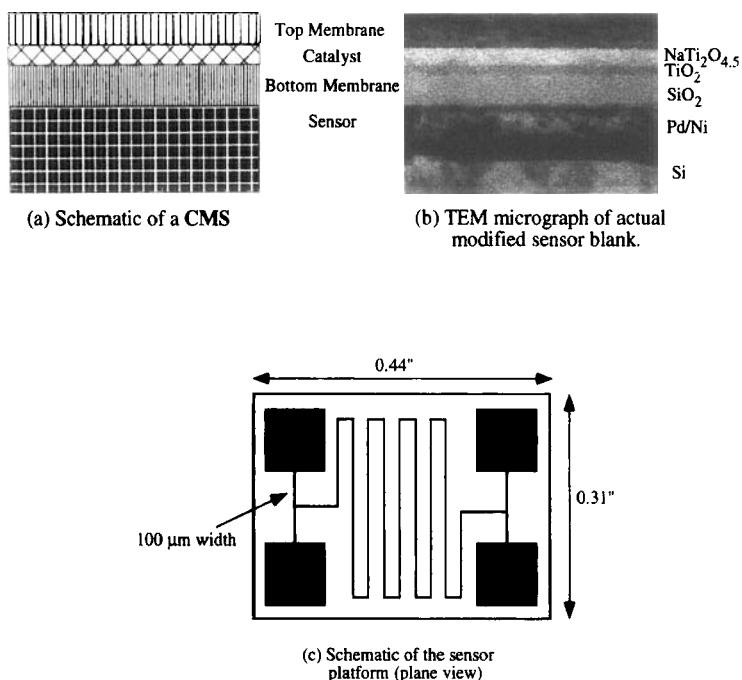


FIGURE 1 (a) Diagram of the basic constructs of a CMS component, (b) TEM micrograph of actual CMS component, (c) basic sensor design

project have been extensively studied at Sandia and little modification was required from literature reports.^{3,4} For the catalyst layer, we have isolated and characterized by X-ray crystallography several alkali metal alkoxides of general formula $[\text{ATi}(\text{OR})_5]_n$ ($A = \text{Li, Na, K}$; $\text{OR} = \text{OPr}^i$ (OCHMe_2),¹⁰ ONp (OCH_2CMe_3)¹²). The redissolved $[\text{NaTi}(\text{OPr}^i)_5]_\infty$ material was spin-cast deposited as a thin film and used for ion-exchange to generate a titania-supported Rh thin film catalyst. Since it is important to know the effect of each film on the sensor's ability to detect H_2 , we have investigated the sensor's H_2 response after each layer was added. The syntheses of various double alkoxide precursors, processing conditions of the spin-coat deposited films and the effect these layers have on the sensor's response will be reported.

EXPERIMENTAL

All of the compounds and solutions described below were handled with rigorous exclusion of air and water using standard Schlenk line and glove box techniques unless otherwise noted. The following solvents were distilled immediately prior to use: pyridine from CaO; THF, toluene, and hexanes from Na/benzophenone. The AOR compounds [A = Li, Na, K; OR = OPrⁱ, ONp] were isolated from the reaction of the appropriate AH and HOR in toluene and purified by sublimation.^{10,12}

Sensor Platform

The basic sensor investigated was a thin film meander line resistor of a Pd/Ni alloy which has previously been reported for use as a molecular hydrogen sensor under a wide range of partial pressures.^{1,2} The catalytic films were deposited through a shadow mask on device grade SiN on a Si wafer using a dual e-beam evaporator. The films were 100 nm thick and had 10 at. % Ni. An adhesion layer of Ti metal (10 nm) was used to increase the durability of the sensor. The substrate temperature was maintained at room temperature during the deposition at pressures $< 2 \times 10^{-6}$ Torr. The devices were annealed in a tube furnace using 2% H₂ in N₂ for 2 h at 350° C.

The mask design has four pads in the corners of a 1 cm² chip which were used for a four terminal resistance measurement. The design that was used is shown in Figure 1c. The spring loaded pogo pins that were used in this setup do not require wire bonding to obtain reliable resistance readings of the sensor films. Furthermore, the sensor could be removed and other processing performed (i.e., annealing or microscopy) without having to break any permanent electrical connections.

Adaptation of the silica-based membranes (*vide infra*) to the Pd/Ni sensor surfaces required development of a rigorous surface treatment procedure needed to both degrease the surface and remove a layer of residual oxide. This involved the following steps: (a) soap and water wash, (b) water rinse, (c) soaking in boiling acetone, (d) a water rinse with a nitrogen dry, (e) UV/ozone for 30 minutes at ~20°C and (f) hydrogen anneal for 2 hours at ~350°C.

Layer 1 and layer 3

Silica Sol-Gel (A2)³⁻⁵**

The synthesis of the inorganic membrane consisted of a two step acid catalyzed hydrolysis of $\text{Si}(\text{OEt})_4$ ($\text{OEt} = \text{OCH}_2\text{CH}_3$) which was reacted with $\text{HCl}/\text{H}_2\text{O}$ in HOEt , followed by heating and additional $\text{HCl}/\text{H}_2\text{O}$ additions. The final solution is referred to as A2** and used for both layers 1 and 3. For layer 1 only, $\text{Ti}(\text{OPr}^i)_4$ was layered on top of the A2** film to decrease pore size and therefore increase selectivity (referred to as A2**/Ti).⁵ A more detailed description of the synthesis and processing conditions of A2**^{3,4} and A2**/Ti⁵ can be found elsewhere.

Layer 2. Hydrous titanium oxide (HTO)

Standard⁹

To prepare standard bulk HTO ion-exchanger (referred to as ST-HTO) materials, NaOH was dissolved in MeOH (~10 wt.% NaOH solution), followed by addition of $\text{Ti}(\text{OPr}^i)_4$. The solution was stirred for 10 min. and then poured into an acetone/water mixture whereupon a precipitate of an amorphous sodium titanate HTO ion-exchanger immediately formed. The resultant powder was washed with more acetone and dried at room temperature under vacuum (75 – 130 mmHg) and used without further modification.

Synthesis of $[\text{ATi}(\text{OR})_5]_n$ ($\text{OR} = \text{OPr}^i$ { $A = \text{Li}$, $n = 2$; Na , $n = \infty$; K , $n = \infty$ }, ONp { $A = \text{Li}$, $n = 2$; Na , $n = 2$; K , $n = 2$ })

The alkali metal derivative of $\text{Ti}(\text{OPr}^i)_4$ ¹⁰ and $\text{Ti}(\text{ONp})_4$ ^{12,13} were prepared according to literature reports. The general synthesis involved the dissolution of $\text{Ti}(\text{OR})_4$ in toluene which was then mixed with the appropriate alkali alkoxide powder. After stirring for 12 hours, all of the volatile material was removed by rotary evaporation. Crystals of $[\text{ATi}(\text{OPr}^i)_5]_\infty$ were formed by rapid cooling of the reaction mixture.^{10,14} Crystals of $[\text{ATi}(\text{ONp})_5]_2$ were obtained by extraction with hot toluene and slow cooling.^{12,15} Approximate 5%w/w solutions of $[\text{NaTi}(\text{OPr}^i)_5]_\infty$ in THF were generated and used as stock solutions (referred to as DA-HTO) to produce catalyst precursor films.

Double Alkoxides

To prepare bulk HTO ion-exchangers from DA-HTO materials, 5 g of the $[\text{NaTi}(\text{OR})_5]_\infty$ (*vide supra*) were dissolved in 33.5 g of HOPr^i and hydrolyzed by pouring the resultant solution into a mixture of 2 mL H_2O in 20 mL of acetone. This results in the precipitation of the HTO ion-exchanger. After washing with acetone, the resultant powder was dried at room temperature under vacuum (75 – 130 mmHg) and used without further modifications.

Ion-Exchange of Bulk and Thin Films

Ion-exchange of Rh^{+3} was achieved by first acidifying an HTO/ H_2O slurry (nominally 1 g of the HTO precipitate:10 mL DI H_2O) to pH 4 using 10 wt.% HNO_3 , resulting in the exchange of a significant portion of Na^+ with H^+ . Subsequently, to prepare high weight loading (≥ 5.0 wt.% Rh) Rh/HTO samples, a concentrated (~ 10 wt.% Rh) $\text{Rh}(\text{NO}_3)_3$ solution was added in small (1–2 mL) aliquots to affect Rh^{+3} ion-exchange with H^+ or Na^+ . In the standard technique, enough $\text{Rh}(\text{NO}_3)_3$ was added to ensure a 50% excess beyond the total cation exchange capacity of the HTO, assuming exchange of one Rh^{+3} cation for three Na^+ ions on the HTO surface. Because of the extreme acidic nature (4–6 M excess HNO_3) of the concentrated $\text{Rh}(\text{NO}_3)_3$ solution (pH < 1), small (1–2 mL) additions of 0.6 M NaOH were required between aliquots to return the nominal slurry pH to the optimum value of ~ 4 . After completing the addition of the $\text{Rh}(\text{NO}_3)_3$, the reaction mixture was stirred for 1 h. at pH 4 (maintained by NaOH additions) to facilitate complete ion-exchange. This pH level was chosen to maximize the cation exchange capacity of the HTO support while avoiding precipitation of $\text{Rh}(\text{OH})_3$, which occurs at pH values > 4.5.¹⁶ After washing (with H_2O and acetone) and filtering, the catalyst was dried at room temperature under vacuum (75–130 mm Hg absolute pressure) for a minimum of 16 h.

Films

Films were either generated by standard dip- or spin-coating processes.¹⁷ Spin coating methods are the preferred technique due to the uniformity of the final films; however, acceptable films were also prepared

by standard dip-coating methodologies. Using ellipsometric analysis the appropriate spin speed and times to generate a 1000 Å film were determined to be 4000 rpm/30s. It was further found that the devices needed to be placed on a larger wafer to eliminate edge effects. The A2**/Ti membrane coatings on the sensor were thermally treated under an H₂/Ar gas mixture at 250°C following the A2** layer deposition and 100°C following the Ti(OPrⁱ)₄ modification. All of the porous coatings that have been tested, pass molecular hydrogen easily without poisoning of the sensor. The optimal processing temperature (i.e., the highest degree of gas separation) for H₂ selectivity was found to be 250°C (heating performed externally of the sensor testing chamber). Further testing to determine the failure temperature of the coated sensor revealed that 500°C was the upper limit; however, due to the setup of the testing chamber the actual sensor test can only be performed at 300°C. *Catalyst Precursor.* A 5 w/w % solution of [NaTi(OPr_i)₅]_∞ in THF was syringed onto a treated A2**/Ti modified sensor. This was allowed to sit for 5 minutes before spinning at 3000 rpm for 30 sec. This film was then ion-exchanged with Rh as described above and heated to 250°C. *Top Layer.* To the treated titania-supported Rh thin film catalyst another A2** layer was spin-cast deposited and fired at 100°C under H₂/Ar as before.

Testing

The sensors were mounted in a fixture that allows for up to six sensors to be exposed to gas mixtures at the same time and their four terminal resistances could be sequentially measured. The fixture was placed in an oven, (maintained at any temperature between 25°C to 110°C) which was inside a large hood so that toxic, explosive and corrosive gases could be studied. The gas flows were kept at one Standard Liter per Minute (SCM) by a bank of flow controllers. The sensors were tested by pulses of H₂/N₂ or other gases so that both the transient and steady state responses could be monitored.

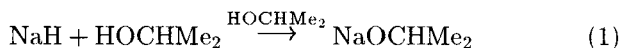
RESULTS AND DISCUSSIONS

Whenever possible existing systems were used to minimize the amount of development necessary for the construction of the CMS component. Little discussion on the sol-gel layers^{3,4} or the sensor^{1,2,11} are presented since the majority of this information has been previously published. The preparation of potential and the actual precursors used for the catalyst precursor layer, as well as the conversion to the titania-supported Rh thin film catalyst are described. A comparison of these new materials with existing hydrous titanium-supported Rh (ST-HTO) catalyst precursor solutions will follow. The final section covers the development of the CMS and the various results garnered from the deposition of the different film layers. The actual utility of the CMS device is currently under investigation.

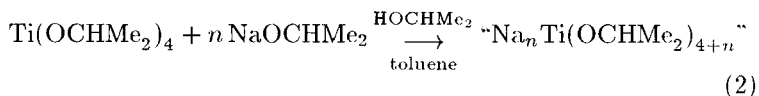
Synthesis

Double alkoxides of titanium alkali metals have been known for more than 5 decades;¹⁸ however, the solid state structures have only been recently been reported (see Figure 2a-c).¹⁰ It was thought that these would be good replacements for the HTO precursors due to their similar content and relative ease of preparation.

Due to the inherent sensitivity of these double alkoxides to ambient humidity, all synthesis described were handled under an inert atmosphere. $\text{Ti}(\text{OPr}^i)_4$ was freshly distilled to remove any potential hydrolysis side products. The alkali metal alkoxide powders "NaOR" are typically prepared from either the reaction of Na° or NaH and the parent alcohol, in this case HOPr^i , eq. 1. *Note:* This can be a very vigorous reaction and



the reaction vessel should be cooled in an ice bath. The resulting white powder was mixed with $\text{Ti}(\text{OPr}^i)_4$ in iso-propanol/toluene at the stoichiometric ratio ($n = 1$) to isolate the desired double alkoxides (eq. 2, Figure 2). These solutions were converted to a stock



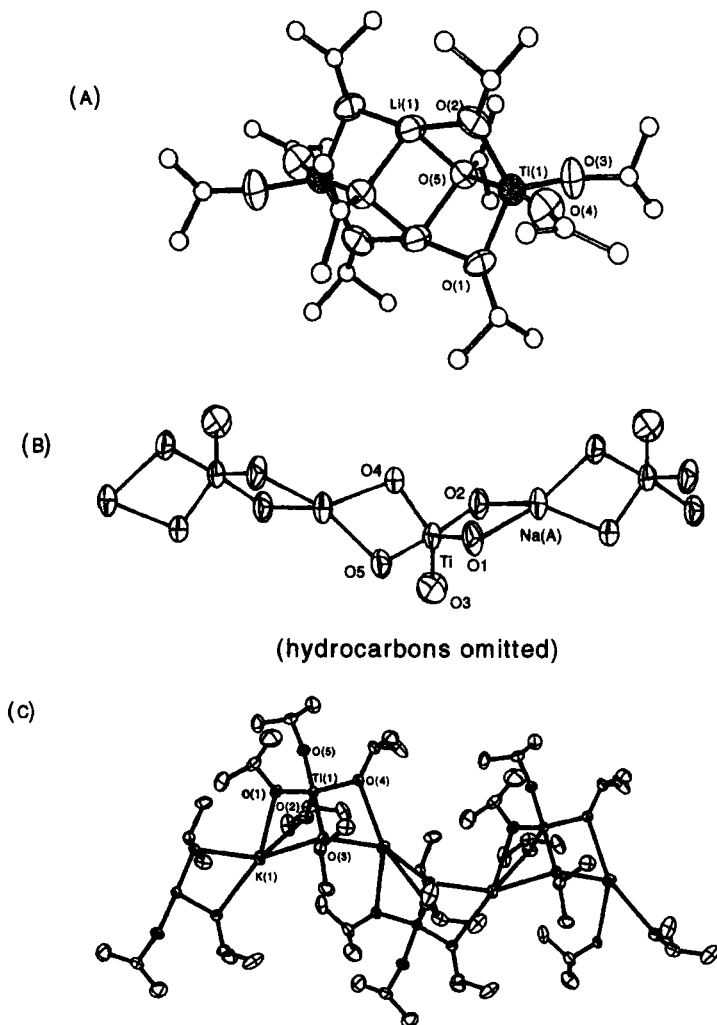


FIGURE 2 Thermal ellipsoid plot of potential catalyst precursor double alkoxides of $\text{Ti}(\text{OPr}^i)_4$: (a) $[\text{LiTi}(\text{OPr}^i)_5]_2$, (b) $[\text{NaTi}(\text{OPr}^i)_5]_\infty$ (c) $[\text{KTi}(\text{OPr}^i)_5]_\infty$

powder by removal of all of the volatile material and redissolved in THF when HTO precursor solutions were required. These solutions are flexible in the amount and type of alkali metal that can be incorporated and

are amenable to standard dip coating processes which makes them ideal for generation of the CMS components. The mixed-metal double alkoxide precursor to the catalytic layer is shown in Figure 2b and has been previously characterized in the solid state as $[\text{NaTi}(\text{OPr}^i)_5]_\infty$; wherein, the alkali metal acts as a bridge between discrete, mononuclear, trigonal-bipyramidal, $\text{Ti}(\text{OPr}^i)_5$ moieties.¹⁰ This material was found to be dinuclear in toluene solutions.¹⁴ For this study we have concentrated on the $[\text{NaTi}(\text{OPr}^i)_5]_\infty$ complex (DA-HTO) due to its similarity to the ST-HTO catalyst ion-exchange material.

Other alkali metal OPr^i derivatives have also been isolated as $[\text{LiTi}(\text{OPr}^i)_5]_2$ (Figure 2a) and $[\text{KTi}(\text{OPr}^i)_5]_\infty$ (Figure 2c).¹⁰ Recently we have isolated a new titanium alkoxide characterized as $[\text{Ti}(\mu\text{-ONp})(\text{ONp})_3]_2$ (Figure 3a).¹³ Attempts to generate double alkoxides from this precursor have lead to the isolation of $[\text{LiTi}(\text{ONp})_5]_2$ (Figure 3b) and $[\text{KTi}(\text{ONp})_5]_2$ (Figure 3c).^{12,15} Each of these can be utilized as a catalyst precursor. Alternative catalyst precursors are also being investigated including “ $\text{AZr}(\text{OR})_5$ ” (HZN) ion-exchange compounds for higher temperature processing and pre-mixed “ $\text{RhTi}_6(\text{OR})_{26}$ ” or “ $\text{RhZr}_6(\text{OR})_{26}$ ” precursor solutions to eliminate the ion-exchange step. All of the above materials have been generated as films and powders and are currently being investigated/compared to ST-HTO precursors and catalysts.

Catalyst

Initial work on the double alkoxide catalyst layer has focused on comparing the DA-HTO to the ST-HTO ion-exchange precursors. Ion-exchange experiments, using a Rh^{+3} controlled ion-exchange procedure,⁶ were performed using three DA-HTO powders (Na:Ti molar ratios of 0.5, 1.0, and 2.0), in addition to a Na:Ti (0.5:1) material prepared using the ST-HTO process (see Experimental Section) to determine the extent of the Rh^{+3} loading that could be realized. To allow a fair comparison of the various Na:Ti stoichiometries prepared in this study, enough Rh^{+3} was added to ensure a 50% excess beyond the total cation exchange capacity of the HTO, assuming one Rh^{+3} cation was exchanged for three Na^+ ions on the HTO surface. In this manner, it could be determined if the DA-HTO with higher Na:Ti stoichiometries offered any advantages in terms of preparing high metal loading catalyst materials.

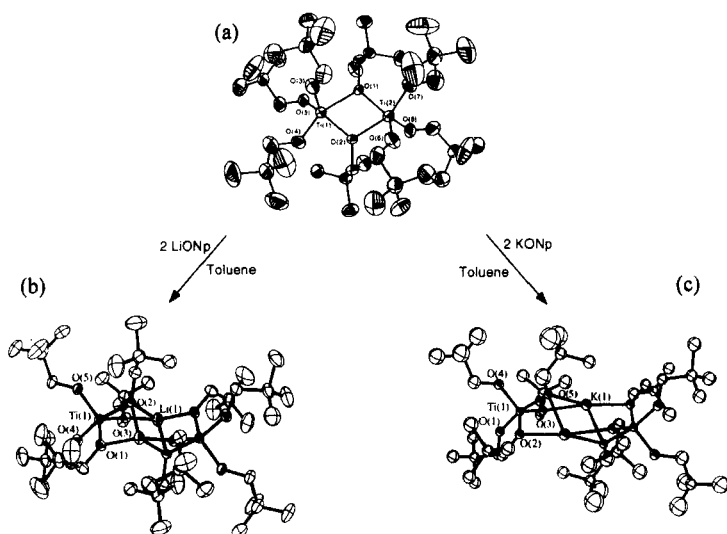


FIGURE 3 Thermal ellipsoid plot of potential catalyst precursor double alkoxides of (a) $[\text{Ti}(\mu\text{-ONp})(\text{ONp})_3]_2$, (b) $[\text{LiTi}(\text{ONp})_5]_2$, and (c) $[\text{KTi}(\text{ONp})_5]_2$

TABLE I Comparison Between Bulk Powders of DA-HTO $[\text{Na}_n\text{Ti}(\text{OPr}^i)_{4+n}]$ and ST-HTO before and after Rh^{+3} Exchange

<i>Na:Ti Ratio^a</i>	<i>Initial Wt. % Na^b</i>	<i>Wt. % Rh^c</i>	<i>Wt. % Na^c</i>
DA-HTO (0.5) ^a	7.85	9.75	0.03
DA-HTO (1.0)	13.3	7.93	0.03
DA-HTO (2.0)	19.9	7.18	0.05
ST-HTO (0.5)	9.10	8.50	0.04
ST-HZO(0.5) ^d	---	7.28	0.04

^aThe number in parentheses refers to the stoichiometry of Na to Ti in the initial solution. 100% incorporation is assumed.

^bAfter bulk HTO synthesis via hydrolysis.

^cAfter controlled Rh^{+3} ion-exchange procedure (as-prepared basis).

^d See Ref No. 22.

Atomic absorption spectrometry (AAS) analysis of the precipitated bulk HTO ion-exchangers is shown below in Table I. It is clear from the

increasing initial wt.% Na in the hydrolyzed product with increasing Na:Ti ratio that the increased Na levels in the DA-HTO materials have been successfully incorporated into the precipitated bulk HTO ion-exchangers. The data in Table I show that each of the final Rh/HTO catalyst precursor materials has nominally the same Rh loading, in the range of 7–10 wt.% on an as-prepared basis, while Na has been completely removed. The fact that the final Rh loadings were not significantly higher for the HTO materials with the higher Na:Ti ratios indicates that once a Na:Ti ratio of 0.5 has been exceeded, the excess Na is easily exchanged and lost during the acidification process. This fact is consistent with previous work associated with Ni^{+2} ion-exchange with $\text{Na}_{1.0}\text{Ti}$ materials prepared via double alkoxides.¹⁹

Therefore, blanks (substrates which had identical make-up (Pd/Ni) as the sensor but without the resistors present) of a thin film of the $[\text{NaTi}(\text{OR})_5]_\infty$ double alkoxide were generated by spin coating techniques. A 0.4M solution of $[\text{NaTi}(\text{OR})_5]_\infty/\text{THF}$ onto Si/SiO₂ wafers was used to determine the speed and time for generation of the optimal 1000 Å thick films. It was found that films processed in air, developed swirls due to the hypersensitivity of the $[\text{NaTi}(\text{OR})_5]_\infty$ to ambient atmosphere. Setting up a spinner under inert atmosphere eliminated this problem. The films were successfully ion-exchanged to generate titania-supported Rh thin film catalysts. A successfully ion-exchanged $[\text{NaTi}(\text{OR})_5]_\infty$ film, on a silicon wafer, was analyzed by XPS, Auger electron spectroscopy (AES), and secondary ion mass spectrometry (SIMS) depth profiling. The surface analysis results are essentially identical with those obtained from analysis of the thin film Rh/ST-HTO materials. Rh to Ti intensity ratios as measured by AES and XPS, as well as Rh depth distribution as measured by SIMS, all exhibit values in good agreement with those measured for the Rh/ST-HTO films. These results strongly supports the proposition that the ion-exchange properties of the NaTi films with respect to Rh exchange closely mimic those found for HTO films.⁶

To verify this idea, bulk supported Rh catalyst prepared from both DA-HTO and ST-HTO ion exchangeable supports were tested for catalytic activity using n-butane hydrogenolysis, a known structure-sensitive reaction.^{20–22} The different catalysts (ST-HTO vs. DA-HTO) were examined following two types of activation treatments in H₂ (results shown in Table II). First, a low temperature (150°C) activation treatment was performed, followed by a higher temperature (300°C) activa-

tion treatment, for various times, to monitor changes in catalyst performance. Previous experience with high weight loading Rh/ST-HTO catalysts has shown that the catalyst activity is optimized for low temperature activation conditions. Increases in activation temperature result in sharp decreases in catalyst activity due to strong metal-support interaction (SMSI) phenomena that cause the formation of reduced TiO_x species. These molecules migrate to, and block, active sites on the supported metal particles.

TABLE II *n*-Butane Hydrogenolysis Activity Results for Rh/HTO Catalysts Prepared Using Different Synthesis Techniques

<i>Ion-Exchanger</i>	<i>Wt.% Rh</i>	<i>150°C/H₂ Activation 1 h Rate Data^b</i>	<i>300°C/H₂ Activation 1 h Rate Data</i>	<i>300°C/H₂ Activation 32 h Rate Data</i>
ST-HTO	8.5	0.106 (1.243)	1.28×10^{-6}	2.0×10^{-7}
DA-HTO (0.5) ^a	9.8	0.164 (1.677)	3.22×10^{-5}	1.2×10^{-6}
DA-HTO (1.0)	7.9	0.167 (2.109)	NA	NA
DA-HTO (2.0)	7.2	0.057 (0.789)	NA	NA
ST-HZO (0.5) ^c	7.3	0.050 (0.690)	0.1440 (1.9778)	0.1202 (1.6518)

^aThe number in parenthesis refers to the stoichiometry (*x*) of the double alkoxide solution $[\text{Na}_x\text{Ti}(\text{OR})_{4+x}]$

^bUnits for reaction rate data are $\mu\text{moles n-butane reacted}/(\text{g raw catalyst } \Sigma \text{ s})$. For data included in parentheses, units are $\text{mmoles n-butane reacted}/(\text{g Rh } \Sigma \text{ s})$. All reported *n*-butane hydrogenolysis rates correspond to a reaction temperature of 150°C. NA = Not applicable. Testing not performed.

^cSee Ref No. 22

Table II shows that all of the catalysts have relatively high *n*-butane hydrogenolysis activity after low temperature activation. The scatter observed in the data is not statistically significant. Table II also shows the sharp drop-off in catalyst activity upon exposure to higher temperature activation conditions. The large drop in activity (4–6 orders of magnitude) observed for both ion-exchanged catalysts is consistent with the SMSI phenomena described above. From these activity tests, we can conclude that the bulk titania-supported Rh catalysts derived from the DA-HTO and the ST-HTO precursors behave in a nearly identical manner. The DA-HTO material is 10 times better than the ST-HTO material after a 300°C heat treatment (these have been extrapolated from higher

temperature reaction rate data using calculated Arrhenius parameters). The loss of activity at higher temperatures in the presence of H_2 can be avoided by the use of hydrous zirconia (ST-HZO) supports (see Tables I and II). These materials were synthesized in a similar manner as described for the titania supports, wherein $Ti(OPr^i)_4$ was replaced with $Zr(OEt)_4$ (details are supplied elsewhere²²).

Sensor

Design

As mentioned in the introduction a “sandwich” of thin films consisting of a catalyst layer in-between two sol-gel size selective membranes (Figure 1a) is the basic design of the CMS. A multi-layer structure that mimics the intended sensor/membrane/catalyst architecture was prepared by successive sol-gel spin-coat procedures onto a “blank”, shown in Figure 1b. The bottom membrane was prepared by spin-coating a mixture of $A2^{*3-5}$ onto a cleaned “blank” followed by processing at $250^\circ C$. A $Ti(OPr^i)_4$ layer was then added to further reduce the porosity and heat treated at $250^\circ C$ to generate the first layer H_2 selective membrane.⁵ Double alkoxide solutions (*vide supra*) were generated by spin-coat deposition of the redissolved $[NaTi(OPr^i)_5]_\infty$ powders in THF followed by an ion-exchange to generate the catalytic layer.²⁰⁻²² The cross-sectional TEM micrograph shown in Figure 1b clearly illustrates the successful integration of the sensor membrane and catalyst layers consistent with the intended idealized microstructure shown in Figure 1a. Ion-exchange was successfully undertaken to remove the Na ions and replace them with Rh (3:1 exchange). The ion-exchanged film was heated to $250^\circ C$ to convert the metallo-organic species to the finely divided metallic and ceramic components. Finally the top sol-gel layer was added by spin-coating methods, thereby, completing the “CMS-blank”.

After successful generation of the “CMS-blank”, a working sensor (Figure 1c) was used as the substrate for film deposition. An identical layering process used to generate the “CMS-blank” was undertaken to produce the working CMS component. Throughout the various layer additions, the sensor was tested to insure that H_2 could still be detected. Several unusual and exploitable observations were noted, especially after the first layer was added.

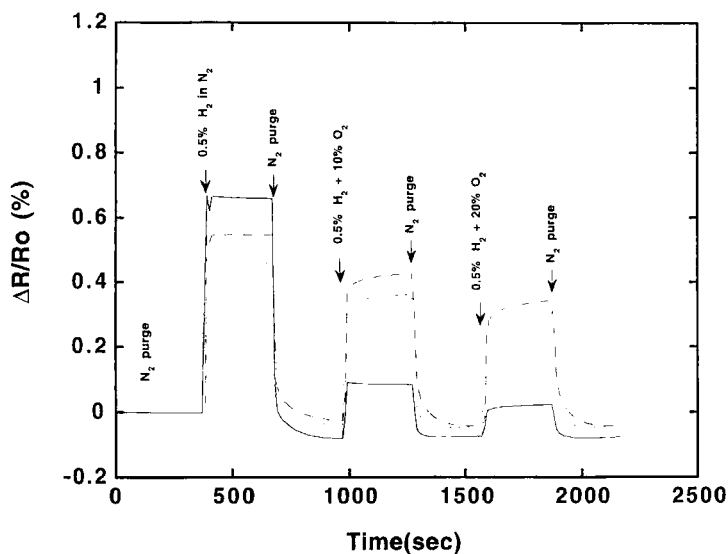


FIGURE 4 The resistance change of three Pd/Ni sensors to pulses of the mixtures indicated. Flow rate is always one SLM, with N_2 as the make-up gas. Sensor HTR 16.3 has the silica coating. The sensor temperatures are all 80°C and sensors 16.3 and 9.4 had both received a 150°C anneal

Layer 1 (A2** Sol-Gel)

The sol-gel coated Pd/Ni resistive hydrogen sensor was annealed from 100°C to 400°C at 50°C intervals, in a 2% hydrogen ambient atmosphere. The response of an uncoated versus a coated sensor at 50°C sensor temperature are shown in Figure 4. The sensor was able to respond to hydrogen gas or mixtures of hydrogen and oxygen gases throughout the various heat treatments. A smaller signal with respect to an uncoated Pd/Ni resistor from mixtures of hydrogen and oxygen were measured at anneals between 150 – 250°C . At 300°C , a distinct change in the sol-gel coated sensor's response to both hydrogen and mixtures of hydrogen and oxygen occurs. At the present time, this complex response is not completely understood, but a compression of the pore size in the sol-gel coating is suspect. At anneals higher than 300°C , the measured signals are similar for both 10% and 20% oxygen mixtures with 0.5% hydrogen. These results show with this arrangement there is significant poten-

tial for blocking the influence of oxygen with respect to hydrogen and oxygen mixtures and, using different sol-gel solutions, the potential of deriving the individual molecular concentrations in mixtures by pattern recognition.

Characterization of the porosity of membranes deposited on Pd/Ni sub-layers was begun using a cantilever beam molecular probe technique developed at Sandia.^{23,24} Briefly, this technique involves measuring the deformation of a very thin wafer coated with a film upon exposure to a series of gases. If there is no intercalation of gas into the film, the bend of the wafer will remain constant. Initial experiments indicated that the membranes processed at 500°C had no porosity accessible to water, establishing the pore size as less than about 0.38 nm. TEM experiments performed on similarly processed samples revealed substantial interaction of the Pd/Ni and membrane layers consistent with the observed loss in porosity. This idea would be consistent with the destruction of the Pd/Ni film observed for the high temperature processed sol-gel modified sensors. Lower temperature (<300°C) processing revealed intercalation of H₂O into the film and this was used as the processing temperature for the A2** films.

H₂/O₂ Sensing

Some interesting behavior in the sensing of hydrogen for the A2** coated sensors was noted when the H₂ gas was mixed with other gases. On bare sensor surfaces, O₂ competes with H₂ for adsorption sites, which usually causes the sensor to give a signal which would be characteristic of a lower partial pressure of H₂ in an inert atmosphere (i.e., the sensor detects less H₂). Little difference in the time response of a coated versus an uncoated sensor was observed. It was thought that the nanoporous coating would reduce the amount of O₂ and give an H₂ signal independent of O₂ partial pressure. This did not occur. Two different partial pressures of O₂ were investigated while holding the partial pressure of H₂ constant and the results are shown in Figure 4. For the coated sensors, the activity of O₂ actually *increased* as determined by a decrease in the amount of H₂ detected; however, it is of note that the H₂ signal was not obscured completely. If the very small pores in the A2** silica reduced the amount of O₂ that reached the Pd/Ni surface, the resulting H₂ signal should be independent of O₂ partial pressure. Not only did this not occur, but the amount of H₂ signal recorded for the coated sensor is

smaller than on the uncoated sensors. This indicates that not only are the molecules of H_2 and O_2 gases being detected but the O_2 is preferentially observed. One would expect this result for a very clean Pd/Ni catalyst surface, as in ultra high vacuum when there is an excess of O_2 . The O_2 is more catalytically active on a clean surface than a contaminated one (relative to H_2); therefore, in spite of the thick overlayer, the coated sensor acts more like a clean surface! This result was reproducible for many repeated exposures on the same sensor if there were no further high temperature anneals.

Our present explanation of this observation is that it represents a radical example of the "spill-over" effect.²⁵ "Spill-over" is said to occur when a catalytic reaction (i.e., H_2 and O_2 reacting to become H_2O) occurs at an atomic location, distant from the catalytic metal atom, in this case Pd. The Pd/Ni resistive sensor does not measure the reaction products directly, but only the equilibrium between the bulk of the Pd/Ni film and the metal surface. The word "surface" becomes a little obscure when a 1000 Å sol-gel (or glass) film is strongly bonded to that surface. Nevertheless, the presence of the glass film has little effect on the equilibrium bulk concentration of $H\cdot$ with the partial pressure of H_2 external to the film. It would be difficult to distinguish a coated and uncoated sensor with this experiment. However, when the oxidant O_2 is added to the mixture, the difference becomes readily apparent. Glass films annealed at 150°C have more O_2 catalytic activity than uncoated sensors.

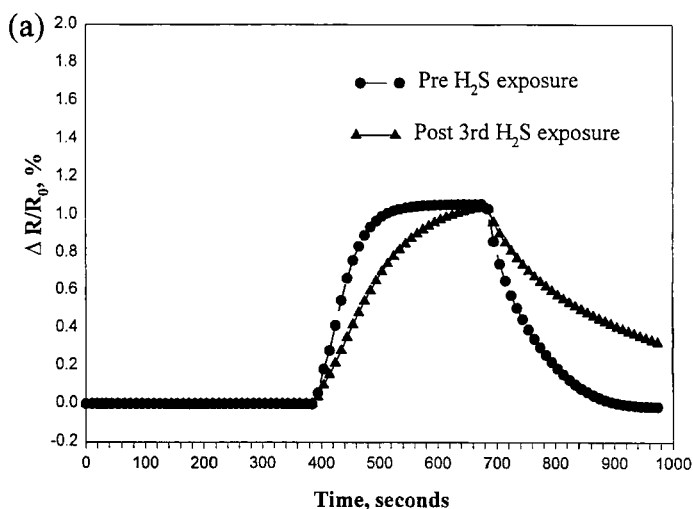
Though unexpected, this result can be exploited through the use of pattern recognition to derive the individual concentrations of H_2 and O_2 in a mixture where both are unknown. This determination is especially important when explosive mixtures are suspected. For example, a mixture of 4% H_2 and 20% O_2 can be detonated, causing physical damage, whereas a mixture of 3% H_2 and 10% O_2 will burn, but not detonate when an ignition source is present. Thus it is important to have accurate measurements of the concentrations in this range. For much higher concentrations of H_2 (> 10%), the sensor signals are not strongly effected by O_2 and the pattern recognition will fail to give accurate results for the O_2 concentration. In any case, such high concentrations are very dangerous and should be acted on whether O_2 is present or not. For very low H_2 concentrations (< 0.1 %) the resistive sensor is not accurate.

A second type of sensor based on the same Pd/Ni type film is called a Field Effect Transistor (FET) sensor²⁶ and it will measure partial pres-

tures of H_2 down to as low as 10 parts per million in 20% O_2 . We are exploring FET sensors with the same coatings as reported in the article. These devices are more difficult to fabricate than the resistors reported here, but will be important when molecules that are not detected on uncoated devices and exposed to CMS catalytically active coated sensors.

Poisoning by H_2S

In catalytic sensors (e.g., the Pd/Ni resistors under discussion), sulfur poisoning is revealed as a slow response to a pulse of H_2 of a given partial pressure (but the signal size is not reduced). Due to the interesting response to H_2/O_2 mixtures, tests were undertaken to determine the amount of protection the glass film imparts to the Pd/Ni surface against poisoning by H_2S . The results are depicted in Figure 5. Six sensors were tested simultaneously by exposure to 1000 ppm of H_2S in N_2 at $34^\circ C$ in three separate tests. The coated sensors showed no meaningful change in response upon exposure to the H_2S gas under the conditions investigated; however, some of the uncoated sensors failed to detect hydrogen by the third exposure and the other was notably slowed.



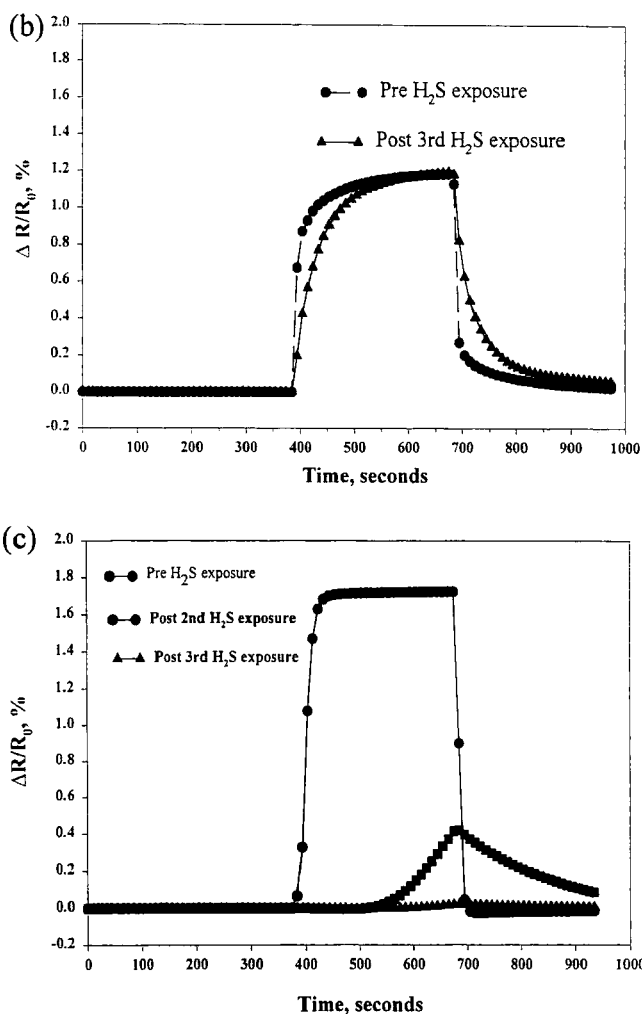


FIGURE 5 The effect of H₂S poisoning on coated versus uncoated films: (a) an uncoated sensor exposed to a pulse of 0.5 % H₂ before and after exposures to H₂S (1000ppm). The sensors were held at 34°C for both poisoning and testing. The size of the response is not effected but the rates for both pulse and purge are notably lowered for the uncoated sensor (9.3); (b) a coated sensor (16.1) of the same design as (a) in which the H₂S exposure has only a small effect; (c) another type of uncoated sensor wherein the H₂S exposure has a much more damaging effect. For the post 3rd exposure, almost no response can be noted on this time scale

Layer 2

The resulting titania-supported Rh thin film catalyst prepared from the DA-HTO powder were found to be ion-exchangeable and demonstrate similar activity as found for the ST-HTO Rh/HTO catalyst. The double alkoxide approach is greatly simplified in comparison to the ST-HTO synthetic route. Attempts to bypass the $\text{Ti}(\text{OPr}^i)_4$ layer by depositing the $[\text{NaTi}(\text{OR})_5]_\infty$ directly onto the A2** layer resulted in complete shut down of a working sensor. Therefore, the A2**/Ti/ $[\text{NaTi}(\text{OR})_5]_\infty$ modified sensor was produced and tested (see Figure 6a). Upon modification of the DA-HTO by ion-exchange to form a titania-supported Rh thin film catalyst, there is little change in the response of the sensor versus the “ $\text{NaTi}(\text{OR})_5$ ” coating.

Layer 3

The final layer was deliberately deposited as a highly porous material and therefore had no further effect on the sensor. This layer completed the production of the CMS and tests are currently underway to determine the selectivity of this component. Figure 6b shows the response of the CMS component.

Conclusion

We have clearly proven that the individual components of the CMS are integratable. The addition of the sol-gel A2** layer has yielded some surprisingly beneficial results. Sensors are often required to operate in chemically hostile environments for extended periods of time and we have quite unexpectantly found that the initial A2** coating imparts poison resistance and protection from other hazards like condensed water and dust, while not degrading its performance. Furthermore, the large difference in response of the A2** coated and uncoated sensors allows us to employ a pattern recognition scheme to classify mixtures of H_2/O_2 and to extract the individual concentrations where both are unknown.

The generation of the double alkoxide $[\text{NaTi}(\text{OR})_5]_\infty$ solution involves a much less demanding solution synthesis in comparison to existing HTO catalyst precursors but has demonstrated similar catalytic

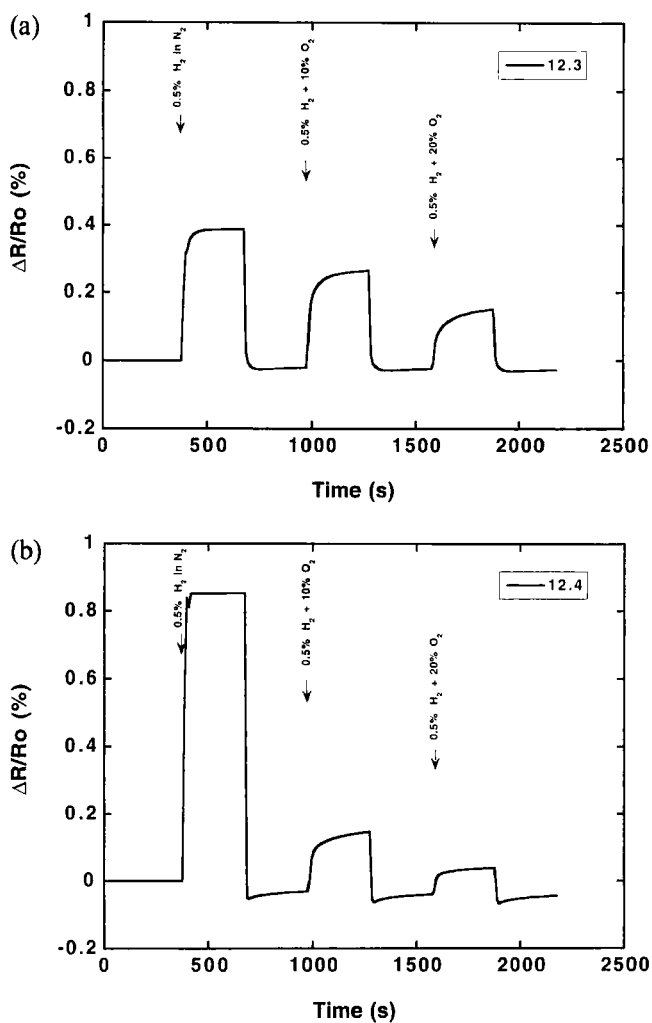


FIGURE 6 Response of Pd/Ni sensor to H_2/O_2 mixtures for : (a) A2**/Ti/catalyst layered sensor (12.3) and (b) A2**/Ti/catalyst/A2** layered (actual CMS component, 12.4). The sequence of exposures is the same as those noted for Figure 4. The data presented is typical of a post 150°C anneal where the sensor in 6b shows the most catalytic activity for O_2 . This behavior was reproducible in several runs for one week before higher temperature anneals

behavior. The application of this layer to the A2**/Ti modified coating reduces the sensitivity of the sensor but does not shut it down. Further modifying the NaTi film by ion-exchange to make the titanium-supported Rh thin film catalyst does not further diminish the sensitivity of the sensor. The porous top layer also has little effect on the sensing ability of the Pd/Ni sensor.

Currently we are pursuing the functionality of the CMS component discussed above as a molecularly selective catalytically activated sensor. Initial attempts to selectively reduce an organic species will focus on dehydrogenation catalytic reactions.

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