

Oxidation chemistry and electrical activity of Pt on titania: development of a novel zeolite-filter hydrocarbon sensor

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Abstract

The change in resistance of semiconducting metal oxides upon exposure to gases is the basis for many gas sensors. Additives to the metal oxide provide a route to control selectivity and sensitivity for gas detection. Additives are often added to modify the chemical reactivity on the metal oxide surface. However, as the temperatures at which the sensing reactions are carried out increases, there is the possibility that the additive can also interact with the metal oxide and alter its electrical properties. In this paper, using Pt on titania as the model system, we examine how direct incorporation of Pt into TiO₂ alters the chemical and electrical properties upon CO and propane exposure as compared to Pt in a microporous zeolite dispersed in TiO₂. These results have allowed us to develop a novel Pt-zeolite filter-TiO₂ sensor that responds selectively to hydrocarbons in the presence of CO. We propose that the response to propane is from the water that is liberated as a result of the oxidation reaction, and this hypothesis is based on the observation that the resistance of TiO₂ at temperatures of 500–600 °C decreases upon exposure to water vapor.

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1. Introduction

There can be health and environmental damages due to the presence of carbon monoxide and hydrocarbons in the atmosphere. These gases are formed as a result of combustion processes emerging from automobiles and power plants. Accurate techniques exist for measurement of these gases, including optical spectroscopy and mass spectrometry, but these measurements usually employ bulky equipment which is fragile and expensive [1–3]. Metal oxide gas sensors offer the advantages of simple fabrication, low cost, and small size, but are often limited by their inherent lack of selectivity for determining a single component in a complex mixture of gases [4].

Our research group has examined titania-based sensors to detect gases at temperatures over 500 °C by correlating changes in resistance of titania to the interactions of the gas with the metal oxide [5,6]. It was shown that both CO and hydrocarbons cause changes in the sensor response due to oxidation on the oxide surface. A methodology was devel-

oped in which La₂O₃ and CuO were incorporated into the titania to fabricate a device which was selective to CO in the presence of CH₄.

In fact, when additives are included on metal oxide sensors, two major effects are likely [7]. First, the additive can alter the chemical reactivity of the gas on the oxide surface. Second, an electronic interaction can occur as the additives change the conductive properties of the oxide. Frequently, additives are employed to alter the chemical reactivity of the surface, however, these electronic interactions can also influence the sensor response. In the current work, platinum on titania was used as a model system to understand the influence of the chemical and electrical effects. The oxidation chemistry of hydrocarbons and CO and the change in electrical properties of the titania was examined. Undoped anatase was studied and compared to other titania samples that employed platinum. Several titania samples were fabricated with varying levels of platinum added in colloidal form. This set of samples is designed to show the effects that dopants can possess when incorporated into the metal oxide. In an alternate system, platinum within microporous zeolites was mixed with the titania, thereby isolating the metal particles from the titania. In the second set of samples, the catalytic ability of the platinum can still be manifested, while

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leaving the electrical properties of the titania relatively unchanged. Finally, based on the above results, a design for a selective hydrocarbon sensor that measures hydrocarbons in the presence of CO is proposed.

2. Experimental

2.1. Materials preparation

2.1.1. Anatase

Commercially obtained anatase (Aldrich, 99.9%+ purity) was milled with zirconia balls in isopropanol for 4 h. After the solvent was removed by evaporation, the resultant powder was heated at 800 °C for 6 h with a temperature ramping of 6 °C/min from room temperature. To prepare this powder for further use, it was combined with a glue (V-801 Heraeus), a solvent (5V-507 Heraeus), and dispersant (BYK Chemie) to make a thick paste which was then sonicated for an hour. A portion of this paste was then screen printed onto a 1.5 cm² alumina substrate which had gold interdigitated electrodes. The substrate with paste was subsequently heated at 200 °C for 2 h to remove the organic binders and then heated at 800 °C for 6 h.

2.1.2. Colloidal platinum/titania

Colloidal platinum stabilized with PVA was prepared by using a technique first described by Rampino and Nord [8] with slight modifications. Twenty-three milligrams of dipotassium tetrachloroplatinate was added to 2 ml of deionized water. A separate 2% PVA solution was made by adding 500 mg of polyvinyl alcohol in small amounts to 25 ml of stirred deionized water kept at 80 °C. Stirring and heating was maintained for 2–3 h until the solution was clear. Once the solution was cooled, it was filtered through glass wool. 12.5 ml of the 2% PVA solution was placed in a flask, stirred, and 11 ml of water added to it. To this new solution, 1 ml of the aqueous 0.5% Pt solution was added slowly in a dropwise manner under fast stirring. 0.4 ml of a 4% NaOH solution was added in a dropwise manner, and the solution heated to boiling for 5 min then cooled to room temperature. To this dark solution, 4 mg of sodium borohydride was added to reduce the dissolved platinum species to colloidal platinum and stirred overnight. A sample of titania with colloidal platinum was made by taking 0.8 g of titania and combining it with 4.2 ml of the PVA-Pt solution (resulting in 0.1 wt.% overall Pt). This suspension was then sonicated for an hour with periodic shaking in order to combine the layers thoroughly. After this was accomplished, the suspension was transferred to a flask, stirred, and heated briefly. Portions of this suspension were then added dropwise to the conventional 1.5 cm² alumina substrate, and underwent the same heating conditions as the anatase sample. Three samples with platinum loading of 0.006, 0.01 and 0.1 wt.% were synthesized using colloidal platinum.

2.1.3. Pt–Y

Platinum loaded zeolite–Y (abbreviated Pt–Y) synthesis has been described previously in the literature, and an adaptation of this technique was used [9,10]. One gram of Na zeolite–Y (LZY-52) was added to a solution of NaCl and the suspension centrifuged and washed repeatedly. A platinum concentration of 0.005 M was made by dissolving 0.175 g [Pt(NH₃)₄Cl₂] in 100 ml water and added to the dried zeolite and stirred well at room temperature for 24 h. The product was washed, centrifuged, and allowed to dry overnight. The dried product was then placed in a ceramic boat and subjected to calcination at 300 °C for 2 h in flowing air at ~50 ml/min. The material was then reduced at 500 °C in 5% hydrogen for 7 h in a flow of ~60 ml/min.

2.2. Materials characterization

Powder diffraction data were taken with a Rigaku Geigerflex X-ray powder diffractometer using Cu K α radiation.

SEM was performed with a XL-30 ESEM FEG using a pure sample of Pt–Y and also titania treated with colloidal platinum. Additional microscopy was conducted on a sample of Pt–Y mixed with titania with a Quanta 200 SEM. TEM was also performed using a Philips Tecnai TF20 with HAADF detector on the same samples.

Surface area measurements were taken with a Micromeritics instrument, Pulse Chemisorb 2700.

Additional surface studies were performed with an AXIS Ultra X-ray photoelectron spectrometer. A Mg source was used for all measurements made.

2.3. Electrical measurements

Our group and collaborators have previously described the physical setup used to measure electrical resistance, so only a brief summary will be presented here [5,6,11]. All measurements were performed at 600 °C in a background of 5% O₂/N₂. The sample was placed in a quartz cylinder housed within a tube furnace and attached via gold leads to either a 34401A HP multimeter or a 34970A HP multiplexer. The flow of gases was determined with digital mass flow controllers. Prior to the measurements, the mass flow controllers kept the atmosphere at 5% O₂/N₂ for 2 h.

2.4. Chemical reactivity

To better understand the ability of the platinum loaded species to oxidize CO and propane, analysis of product gases were performed with a GC-17A Shimadzu gas chromatograph with TCD detector. A Carboxen PLOT column from Supleco was used for separation of the gases. Using temperature programming, CO₂ evolved at approximately 5 min and propane eluted at 13 min. Once this was established, a calibration curve for CO₂ was constructed by performing separate injections with fixed amounts of Ar, O₂, and CO₂ in each.

Three powders were examined for their reactivity to CO and propane, heat-treated anatase, 5% Pt–Y in 95% anatase, and titania powder with 0.01 wt.% colloidal platinum. Samples were sieved with a poly-propylene mesh (350 μm holes) and placed in a quartz tube flow reactor (i.d. 1/8 in.) housed in a furnace. Each sample was preheated to its lowest temperature for testing (typically 400 °C) in a flow of 20% O₂/Ar and allowed to equilibrate for 20 min. After this occurred, 1.0% CO or propane was introduced (or 0.5% in the case of titania with colloidal Pt), and the O₂ level was changed to 5% in Ar. An injection was made when 10 min elapsed, and the gases present were analyzed by the gas chromatograph. Once this process was complete, the flow of CO or propane was stopped, the temperature increased to the next level, and the O₂ changed back to 20%. The entire process was then repeated as described before. The total flow rate of the test gases used for every step of these experiments was 50 ml/min. Calibration curves over a period of time indicate that the errors in our estimation of conversion is of the order of 10% and primarily arises from the flowmeters used to mix the gases.

2.5. Sensor design

Each sensor used in this study employed the same type of substrate, namely a 1.5 cm² square piece of alumina with gold, interdigitated electrodes spaced 0.25 mm apart. Gold leads were attached to these electrodes via gold paste which was fired at 850 °C.

For sensor preparation, Pt–Y was added to the titania in one of three ways. In the first method, the zeolite powder was first suspended in a few drops of 1-heptanol and sonicated thoroughly and added as a surface layer on the anatase substrate/interdigitated electrode assembly. In the second arrangement, the Pt–Y was used as a plug before the anatase substrate/interdigitated electrode assembly (plugs were either 20 mg or 100 mg). In the final system, samples were created by mixing appropriate amounts of Pt–Y and titania and adding isopropanol. This suspension was then sonicated for 20 min, after which the liquid was placed in a round bottom flask and evaporated to remove the solvent. The resulting powder was fairly homogeneous to visual inspection and 35 mg of it was added to seven drops of 1-heptanol and sonicated. This solution was then placed dropwise on a 1.5 cm² interdigitated alumina substrate.

3. Results

Gases such as CO, H₂, and hydrocarbons can be oxidized by reaction with a metal oxide surface. If the oxygen equivalents in this reduction process arise due to chemisorbed O_n^{m-} species on the oxide, then the electrons released upon oxidation can alter the resistance of the oxide. This is the basis for gas sensing using semiconducting oxides, such as SnO₂ and TiO₂. Metal particles added as dopants to semi-

conducting oxides can influence both the chemical and electrical properties of the oxide. Two systems involving platinum on anatase were examined in the present study so that the chemical and electrical effects of each variant could be more thoroughly understood. The first set of samples had intimate contact between the platinum and anatase and was prepared by mixing anatase with platinum colloids followed by thermal treatment. To provide a contrast for the experiments in which platinum is directly mixed with the titania, microporous zeolites loaded with Pt were examined. In this design, the platinum was in and on the zeolite, thus mostly isolated from titania, while still maintaining its chemical reactivity. The properties of both these systems are compared to anatase as reference.

3.1. Structural characterization

3.1.1. Titania samples with platinum

The diffraction pattern of all colloidal platinum loaded samples on titania was identical to pure anatase (Fig. 1). The microstructure as examined by SEM and TEM also resembled the starting anatase, with grains in the range of 100–200 nm (Fig. 2a–c). Although no distinct Pt particles were observed, energy dispersive analysis did show the presence of platinum. Surface area (BET) of the 0.01 wt.% colloidal Pt–TiO₂ sample was found to be 7.41 m²/g. Elemental analysis showed that the colloidal platinum sample synthesized to have a 0.1 wt.% Pt loading contained 0.094% Pt. XPS analysis did not show a signal due to the Pt even for the 0.1 wt.% Pt loaded sample.

3.1.2. Zeolite samples

The powder diffraction pattern of Na ion-exchanged zeolite Y (Na–Y) and Pt-loaded zeolite Y (Pt–Y) are compared in Fig. 3. The platinum loaded sample shows two new peaks at 39.6 and 46.1° (2 θ), which are typical of platinum. SEM was performed to examine the size and dispersion of the metal clusters and shown in Fig. 4a. Platinum agglomerates (100 nm) on the zeolite surface are clearly visible. TEM experiments show particles in the 5–10 nm range (Fig. 4b). Elemental analysis showed that Pt–Y contained 10.3 wt.% platinum. Surface area (BET) of Pt–Y was 443 m²/g, indicating the microporous nature of the zeolite.

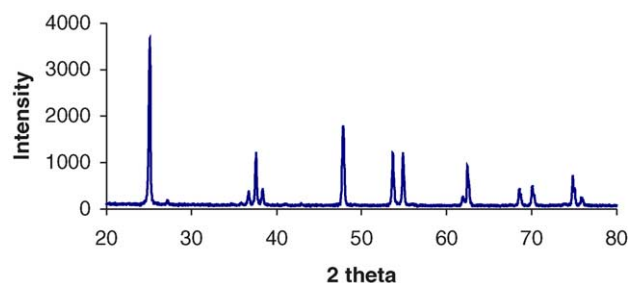


Fig. 1. X-ray diffraction pattern of titania with 0.1 wt.% colloidal platinum.

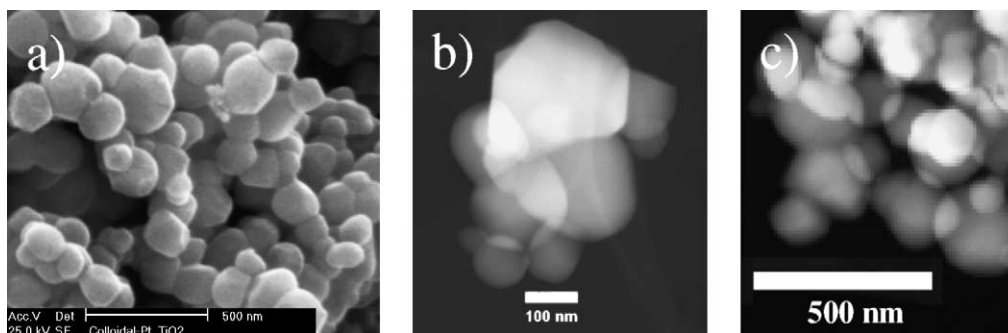


Fig. 2. (a) SEM and (b) TEM of titania with 0.01 wt.% colloidal platinum and (c) TEM of titania with 0.1 wt.% colloidal platinum.

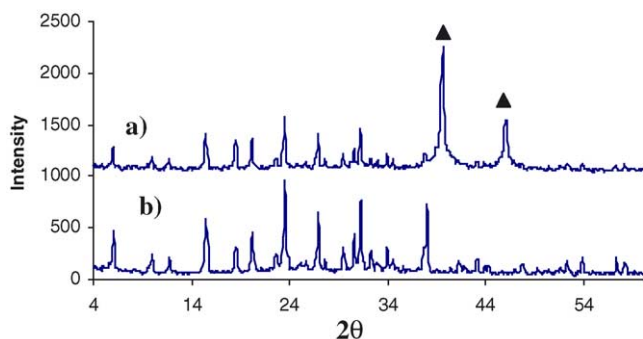


Fig. 3. X-ray diffraction pattern of zeolite (a) with and (b) without platinum. Triangles mark the peaks due to platinum.

3.1.3. Titania–zeolite mixtures

SEM was performed on a mixture of 20 wt.% Pt–Y/80 wt.% TiO₂ sample. This was done in order to examine the mixing between the two different particles. As Fig. 5 shows, the zeolites appear as large particles amidst the smaller ~100 nm sized anatase.

3.2. Chemical reactivity

Gas chromatography experiments were performed with the intention of studying the extent of CO and propane oxidation on the anatase surface. The first substance tested

Table 1
Catalytic ability of various materials to oxidize CO

Sample and gas concentration	Temperature (°C)	CO oxidized (%)
Anatase and 1% CO	400	62
	500	91
	600	92
0.01 wt.% Pt/TiO ₂ and 0.5% CO	400	97
	500	95
	600	97
Anatase/Pt–Y and 1% CO	400	87
	500	87
	600	88

Errors in estimation of percent gas oxidized is ~10%.

was anatase. The other materials were anatase doped with 0.01 wt.% platinum, and Pt–Y combined with TiO₂ (Pt–Y 5 wt.%/TiO₂ 95 wt.%). Tables 1 and 2 compare how effectively these solids oxidized a given amount of CO and propane, respectively. The data analysis was based on the amount of CO₂ that evolved. In addition, a sample GC trace for the oxidation of propane on Pt–Y/titania is provided in Fig. 6 to show that the only detected reaction products were water and CO₂.

At temperatures above 500 °C, CO oxidation proceeds readily (≥90%) on all three samples. Introduction of Pt into the system either directly doped or indirectly via the zeolite

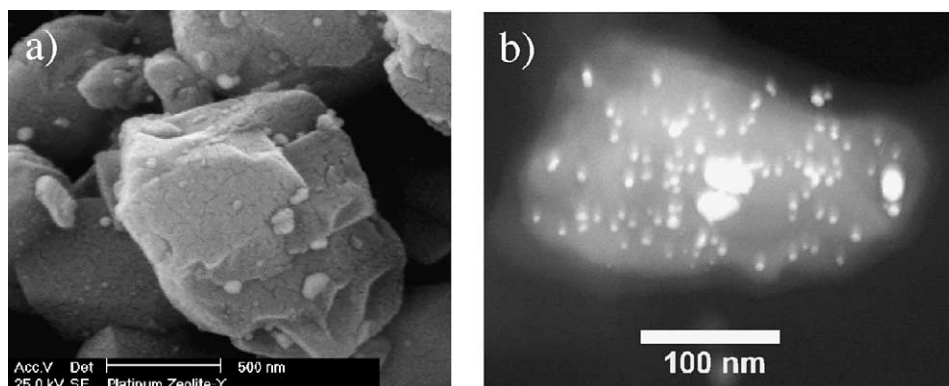


Fig. 4. (a) SEM and (b) TEM of Pt–Y.

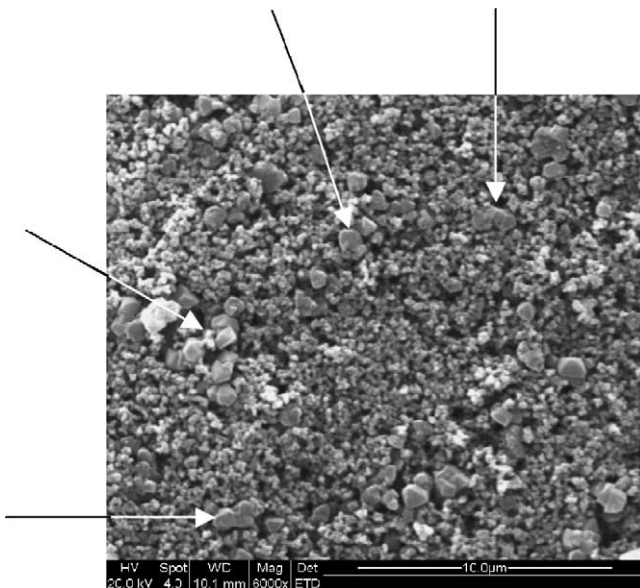


Fig. 5. SEM of a sample comprised of 20% Pt-Y and 80% anatase. Arrows indicate the position of some zeolite particles.

Table 2

Catalytic ability various materials to oxidize propane

Sample and gas concentration	Temperature (°C)	Propane oxidized (%)
Anatase and 1% propane	400	15
	500	24
	600	33
0.01 wt.% Pt/TiO ₂ and 0.5% propane	400	12
	500	16
	600	20
Anatase/Pt-Y and 1% propane	400	70
	500	77
	600	80

Errors in estimation of percent gas oxidized is ~10%.

lowers the barrier to CO oxidation such that efficient oxidation is observed even at 400 °C. The extent of propane oxidation was considerably lower than CO for all samples. However, for the sample in which Pt-Y is combined with anatase, propane oxidation is increased, e.g. at 500 °C, the percent conversion increased from 24 to 77%, on changing from anatase to Pt-Y/anatase.

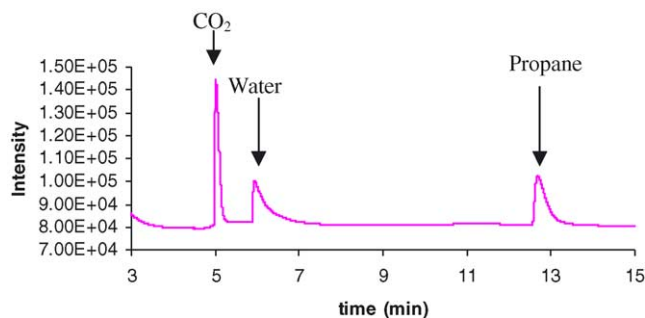
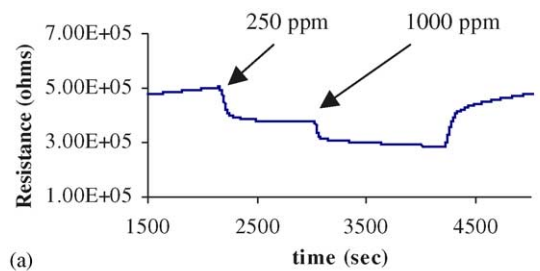
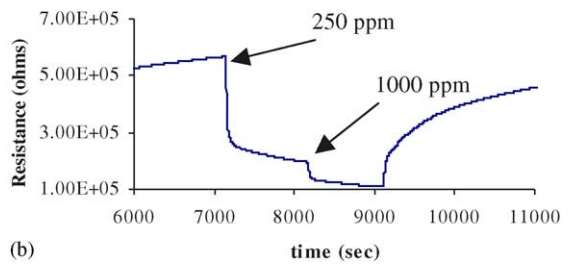


Fig. 6. Gas chromatogram showing the products of propane oxidation from exposure to anatase at 600 °C.



(a)



(b)

Fig. 7. Change in anatase resistance to (a) propane and (b) CO at 600 °C in a balance of 5% O₂/N₂.

3.3. Electrical behavior

3.3.1. Titania samples with platinum

The change in resistance of an anatase sample as well as those doped with increasing amounts of colloidal platinum was examined in the presence of CO and propane. Fig. 7 shows typical resistance traces for anatase exposed to CO and propane. Table 3 displays the relative resistance changes for each of these samples (defined as R/R_0 where R and R_0 are the resistances in the presence of either CO or propane and background gas, respectively). If the magnitude of R/R_0 is 1, then no change in resistance has occurred upon exposure to the reducing gas and from a sensor point of view, would be a poor sensor. Thus, R/R_0 is also considered to be an indication of the sensitivity. In addition, the recovery times after exposure to 1000 ppm of each gas are also listed (defined as t_{90} which refers to the duration required for the sample to return to 90% of its baseline resistance).

Trends become apparent when reviewing the data in Table 3. The resistance changes observed for anatase are

Table 3

The normalized resistance changes and recovery time of Pt-titania samples in varying concentrations of CO and propane

Gas mixture	R/R_0			
	Anatase	0.006 Pt-TiO ₂	0.01 Pt-TiO ₂	0.1 Pt-TiO ₂
CO (250 ppm)	0.41	0.41	0.48	0.96
CO (1000 ppm)	0.26	0.26	0.34	0.88
Propane (250 ppm)	0.71	0.7	0.83	0.95
Propane (1000 ppm)	0.50	0.54	0.68	0.87
R_0 (MΩ)	1.5	0.4	1	0.3
t_{90} CO (min)	>30	>30	>30	6
t_{90} propane (min)	>30	>30	13	7.5

Table 4
The normalized resistance change and recovery times of Pt–Y mixed with anatase to varying concentrations of CO and propane

Gas mixture	R/R_0		
	Anatase	10% Pt–Y/TiO ₂	20% Pt–Y/TiO ₂
CO (250 ppm)	0.41	0.7	0.99
CO (1000 ppm)	0.26	0.43	0.91
Propane (250 ppm)	0.71	0.68	0.77
Propane (1000 ppm)	0.50	0.49	0.65
R_0 (M Ω)	1.5	3.5	3
t_{90} CO (min)	>30	8	8
t_{90} propane (min)	>30	7	6

lower with propane as compared to CO. There is a decrease in sensitivity to both CO and propane as the amount of platinum is increased. In addition, there are variations in the baseline resistance among the different samples. For the anatase sample, the baseline resistance is around 1.5 M Ω . When platinum is introduced, however, a decrease in resistance to ≤ 1 M Ω is observed. With regards to recovery time, the increase in metal loading leads to faster recovery.

3.3.2. Pt–Y/titania mixtures

Table 4 compares the change in resistance of films made by directly mixing Pt–Y into anatase (the first with 10% Pt–Y, the second having 20% Pt–Y). The sample which contained 10% Pt–Y exhibited a reduced sensitivity with CO, but the propane sensitivity was similar to anatase. Increasing the Pt–Y levels to 20% only facilitated this process by nearly eliminating any resistance change with CO, while lowering the propane response only slightly. In addition, all of the samples that used Pt–Y had their recovery times diminished for both CO and propane relative to anatase.

4. Discussion

Resistance changes occur in titania when the amount of $O^-_{(ads)}$ varies. If CO or hydrocarbons react with the adsorbed surface oxygen species and the products depart, there is a subsequent release of electrons into the bulk material. Thus, it would be reasonable to predict that increasing reactivity of CO and propane should lead to greater resistance changes and increase in sensitivity. In the case of CO oxidation at 600 °C (Table 1), the temperature of resistance measurements, the percent conversion to CO₂ remains high (~90%) and relatively unchanged between anatase, Pt/anatase, and Pt–Y/anatase. However, the normalized resistance changes (R/R_0) approach the value of 1 upon introduction of Pt, leading almost to complete loss of sensitivity for 0.1 wt.% Pt/TiO₂ and 20 wt.% Pt–Y/TiO₂ for 250 ppm CO. Note that closer R/R_0 is equal to 1, it is an indication that the resistance is unaltered upon exposure to the reducing gas. For propane, on the other hand, at 600 °C, the extent of oxidation decreases from anatase (33%) to Pt/TiO₂ (20%),

but increases markedly in Pt–Y/TiO₂ (80%). The normalized resistance changes increase for propane on Pt/TiO₂, whereas it remains relatively unchanged for Pt–Y/TiO₂. The discussion below focuses on explanation of the trends of sensitivity versus reactivity and concludes with a proposed design and demonstration of a hydrocarbon (propane) sensor that shows minimal interference from CO.

4.1. Platinum on titania

Compared to anatase, Pt/TiO₂ shows a decrease in baseline resistance. Microstructure studies show no evidence of colloidal Pt in the platinum doped samples, though elemental analysis clearly demonstrates the presence of Pt.

Kirner et al. [12], found that upon heating Pt/TiO₂(1 1 0) single crystals to 1170 K in air, the peak for platinum in the XPS spectrum broadened and decreased. It was proposed that these lines reflected the formation of platinum oxides which were entering into the TiO₂ bulk. Under these conditions, the diffusion of Pt into the interstitial sites as Pt²⁺ and Pt⁴⁺ results in donation of electrons to the conduction band [12]. We observe a decrease in resistance of the anatase sample upon heating with Pt colloid (Table 3), consistent with the electron donation model. This would also clarify the decrease in sensitivity observed in these samples as well (Table 3), because charge injection due to gas oxidation (e.g. CO) would not cause the same net change in electrons in the anatase had the platinum been absent.

Thus, for the Pt/TiO₂ samples, the controlling feature is the incorporation of Pt into the TiO₂, which influences the carrier density and thereby modifies the sensitivity of the reacting gases, although the chemical reactivity of the oxide surface remains high. Clearly, addition of dopants to control chemical reactivity can have electrical effects and unintended consequences.

4.2. Systems with Pt–Y and titania

The microporous Pt-loaded zeolite sample was an alternate route to get high levels of Pt into the TiO₂ sample, with minimal incorporation of Pt into the TiO₂ lattice. As compared to the anatase samples with baseline resistances of around 1.5 M Ω , the Pt–Y/TiO₂ samples had resistance of 3 M Ω , indicating that Pt incorporation into the TiO₂ framework is not occurring. The Pt loading in the zeolite samples was 10 wt.%, so the overall Pt in the 20 wt.% Pt–Y/TiO₂ sample is of the order of 2 wt.%, considerably higher than the 0.1 wt.% Pt/TiO₂ sample. The microporous nature of the zeolite makes it possible to carry out the high Pt loading. Although Fig. 4 shows that there is Pt on the zeolite surface, it is known that significant fraction of the of the Pt is inside the zeolite pores [13].

The Pt–Y was mixed directly into the titania at different amounts. The sample which contained 10% Pt–Y in titania showed a decrease for CO sensitivities by about a factor of 2 compared to the anatase sample. The sensitivity to propane;

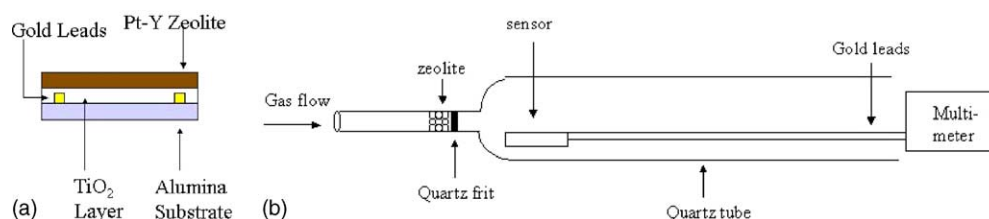


Fig. 8. Sensor designs incorporating Pt–Y with a titania sensing layer. (a) One device has the Pt–Y layer directly on the titania; and (b) the second has the Pt–Y as a plug in front of the titania.

however, was not affected much after this addition. When adding a greater amount of Pt–Y into the titania (i.e. the 20% mix), the sensitivity to CO was virtually eliminated, and the propane response was slightly reduced. Thus, it is evident that in the presence of Pt–Y, a resistance change is observed in anatase upon introduction of propane, but not so in case of CO. Chemical studies show that propane is converted to CO₂ and water when Pt–Y is present while CO is oxidized to CO₂. The gas molecules can react with Pt on the zeolite surface, but, considering the high internal surface area (~450 m²/g), it is more likely that most of the chemical reactivity resides within the zeolite. Thus, in the reaction of propane, CO₂ and H₂O formed in/on the zeolite is released and can contact the surrounding anatase. In the case of CO, it is only CO₂. Our previous studies have shown that CO₂ does not influence the resistance of titania, and thus it is not surprising that presence of Pt–Y leads to a total loss of sensitivity for CO.

We propose that in the Pt–Y/titania system, the resistance change in the presence of propane is due to the interaction of the reaction product water with the anatase surface. In order to establish the validity of this hypothesis, we removed the Pt–Y from the anatase and employed it as a plug isolated spatially from the anatase, as shown in Fig. 8b. The amount of zeolite used was 100 mg, resulting in a plug of several centimeters. Table 5 compares the sensitivity. There is no sensitivity to CO, but with propane, the signal remained unchanged. From gas chromatography experiments, we know that increasing the amount of catalyst increases propane oxidation. We expect that all the propane is oxidized which confirms that the anatase is interacting with the water vapor rather than hydrocarbon gas.

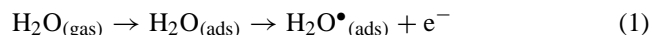
Table 5

The normalized resistance changes of Pt–Y-based sensors to varying concentrations of CO and propane

Gas mixture	R/R_0	
	Pt–Y film on TiO ₂	100 mg Pt–Y plug
CO (250 ppm)	1	0.99
CO (1000 ppm)	0.83	0.94
Propane (250 ppm)	0.72	0.66
Propane (1000 ppm)	0.6	0.63
R_0 (MΩ)	6	13
t_{90} CO	>20	16.5
t_{90} propane	7.5	9

Final confirmation of the hypothesis is provided by examining resistance changes of anatase upon direct introduction of H₂O vapor as shown in Fig. 9. This system was created by exposing the anatase sensor to a dry environment of 5% O₂/N₂ for several hours in order to establish a stable baseline. After this was accomplished, the dry gas was passed through a plug of hydrated zeolite–Y which was heated to facilitate the liberation of water. Upon this change, the resistance of the sensor dropped significantly and remained at that level for the duration of the water exposure. When the system was reverted to the dry 5% O₂/N₂, the resistance rose to the original baseline. These resistance changes are consistent with that observed with the propane experiments with the devices utilizing Pt–Y.

In fact, examples exist in the literature which describe the phenomena associated with water adsorption on metal oxides and subsequent change in electrical properties. Water vapor has been noted for its ability to alter sample resistance in the presence of other gases such as CO and CH₄ [14,15] as well as causing a decrease in resistance when introduced alone [16]. During one study in particular by Giber et al. [17], Ga₂O₃ was heated to 923 K in a nitrogen atmosphere and its response to water vapor was studied. It was proposed that an initial sharp decrease in resistance accompanied the adsorption of water on the sample surface due to the following reaction (1):



Other postulates concerning the changes in surface conduction due to water come from Heiland and Kohl [18]. The first mechanism proposes that the liberation of an electron occurs when gaseous water adsorbs and causes the forma-

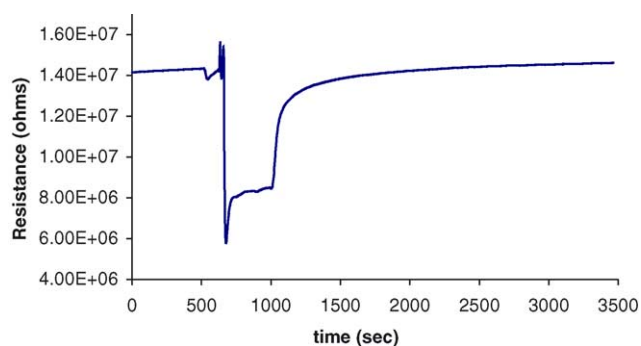
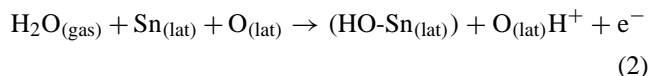


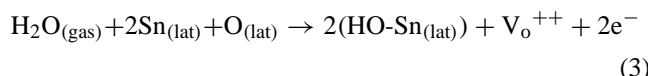
Fig. 9. Response of anatase titania sensor at 600 °C to water evolved from zeolite.

tion of a hydroxyl group with oxygen coming from the lattice as in reaction (2) shown for SnO₂:



In this scenario (HO-Sn_(lat)) represents a hydroxyl group that is isolated through a linkage to lattice tin, while O_(lat)H⁺ is group that is made with lattice oxygen.

The second mechanism states that the hydrogen atom from water reacts with the lattice oxygen, and the resulting hydroxyl group binds to tin. The oxygen vacancy produced in this reaction will ionize and produce electrons as shown in the following Eq. (3):



The mechanism by which the resistance of TiO₂ changes upon exposure to water is not yet determined. However, spectroscopic studies of the variations in the anatase surface during hydration has been studied. Morterra investigated the changes of a hydrated titania sample during heat treatment under reduced pressure [19]. It was reported that after a brief evacuation at ambient temperature, nonspecific hydrogen bonded species present around 3300 cm⁻¹ had been mostly removed, while the OH stretching region contained two distinct regions. The first of these regions, the 3600–3800 cm⁻¹ range, was attributed to surface hydroxyl groups, and the second, between 3350 and 3500 cm⁻¹ was assigned to the ν_1 and ν_3 stretching modes of un-dissociated water. The initial stages of heating ($T = 420$ K) caused a decrease in the intensity of the 3350–3500 cm⁻¹ region, but no changes were seen in the 3600–3800 cm⁻¹ series, which experienced a complex change of relative intensities. Further heating causes the hydroxyl region to develop as many as seven different peaks, which the author attributes to the heterogeneous nature of the polydispersed oxide species. The correlation of spectroscopic properties with sensing behavior needs to be elucidated.

4.2.1. Development of a hydrocarbon sensor

Based on the above discussion, it is clear that in the presence of Pt–Y, a resistance change is observed in the case of propane, but not so in case of CO, and can be the basis of a selective hydrocarbon sensor. Upon incomplete combustion, both hydrocarbons and CO are present, and considerable interest exists in detecting hydrocarbons without interference from CO. Most of the strategies in creating selective sensors are to add catalysts to the sensing material that selectively oxidizes interfering gases while leaving the gas of interest relatively unchanged [20,21]. From the experiments described in this paper, it is obvious that the addition of platinum to titania while encapsulated in a zeolite enhances selectivity to hydrocarbons over CO, but not because the hydrocarbon is left unreacted, but due to its conversion to

Table 6

The normalized resistance changes and recovery times of Pt–Y-based titania sensors to varying concentrations of CO and propane

Gas Mixture	R/R_0			
	Anatase	Pt–Y film on TiO ₂	100 mg Pt–Y plug	20% Pt–Y/TiO ₂
CO (250 ppm)	0.41	1	0.99	0.99
CO (1000 ppm)	0.26	0.83	0.94	0.91
Propane (250 ppm)	0.71	0.72	0.66	0.77
Propane (1000 ppm)	0.50	0.6	0.63	0.65
R_0 (M Ω)	1.5	6	13	3
t_{90} CO (min)	>30	>20	16.5	8
t_{90} propane (min)	>30	7.5	9	6

water. This idea can be used to design a selective hydrocarbon sensor that discriminates against CO. Several designs are possible. Two of these have already been discussed, the Pt–Y can be mixed into the zeolite (Fig. 5), it can be applied as a filter plug ahead of the sensor (Fig. 8b), and a third design where Pt–Y is applied directly onto a layer of titania (Fig. 8a). Although each of these designs exhibited significant selectivity of propane over CO, there are differences in the sensitivity as is evident from the data summarized in Table 6.

Pt–Y as a filter directly onto an anatase surface has a measurable effect on the CO response. When examining the CO sensitivity, the response to 250 ppm is almost entirely eliminated by addition of the zeolite layer directly to the substrate. The Pt–Y/titania mixture and the isolated plug experiments showed equal efficiency in this process. When increasing the CO content to 1000 ppm; however, we observe a difference. When the surface film method is used, the response to CO is still present (with a relative resistance change of 0.83), whereas in the other two devices, the resistance change is considerably lower (0.91 and 0.94). For propane, all three sensors give comparable results.

The isolated zeolite plug eliminates the possibility of the interfacial effects from the Pt–Y on the sample surface or mixed into the titania. Another advantage is that by making the holder holding the Pt–Y narrow, longer pathlengths can be obtained. Thus, for example, with Pt–Y as a plug, the CO sensitivity was reduced to 0.94. Comparable amount of Pt–Y as a filter on the top of the anatase film had a sensitivity of 0.83. The diffusion length of the gas is important. For example, the CO needed to penetrate ~ 100 μm of Pt–Y in the samples which had a zeolite layer directly on the sample surface. In comparison, when using the plug configuration, the filter layer was over 1 cm long.

Furthermore, Fig. 10 shows the transient plots upon exposure of a Pt–Y plug design (Fig. 8b) to mixtures of CO and propane. The sensor begins in a background of 5% O₂ in a balance of nitrogen. After equilibration was allowed to occur, 250 ppm propane was introduced, and a subsequent drop in resistance followed. CO (250 ppm) was then flowed into the reaction vessel in addition to the propane, but the

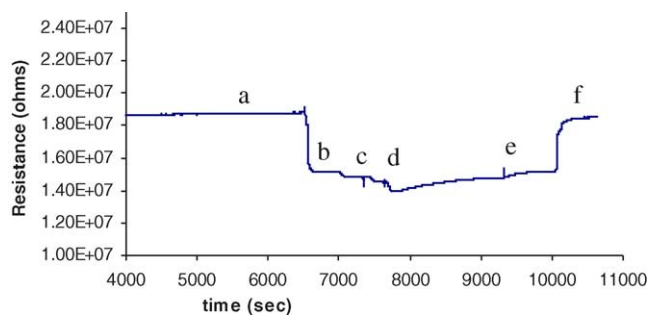


Fig. 10. The response of a device having a titania sensing layer with a 20 mg plug of Pt–Y held before it. The initial conditions were (a) 5% O₂/N₂ at 600 °C, but then (b) 250 ppm propane was introduced, followed by (c) the addition of 250 ppm CO, then (d) 1000 ppm CO. Finally (e) the CO was removed and only the propane remained, then (f) the propane flow was stopped.

resistance remained unchanged. The CO was then increased to 1000 ppm, which caused a slight decrease in resistance, but the sensor recovered back to the resistance dictated by the propane. The CO was then removed and, again, the resistance was constant, and when the propane was removed, the sensor recovered back to the conditions given by the 5% O₂/N₂ baseline. Clearly, the presence of Pt–Y zeolite functions to make a selective hydrocarbon sensor in the presence of CO gas.

In addition to reviewing the sensor response to this water formation, it is also interesting to note that the recovery times associated with the sample using a Pt–Y filter in contact with titania are different than pure anatase TiO₂ devices. With propane, the device with Pt–Y on the surface exhibits a markedly faster recovery time compared to pure anatase titania (7.5 min as opposed to over 30 min). The sluggish recovery times for anatase titania are thought to occur because the adsorption of O₂ onto the titania is a difficult process when propane covers the surface after testing [22]. If water is causing the sensor response instead of propane, it is more easily displaced from the surface upon being removed from the gas stream, thus allowing oxygen to adhere to the sensor surface at a faster rate.

Since the basis for the sensing of propane is the water interaction with the anatase surface, such a sensor design would have interference from humidity in the gas stream.

5. Conclusion

Additives are commonly used to modify the chemical reactivity of metal oxides in order to achieve desired sensor characteristics. It was discovered that an anatase-based semiconducting oxide sensor could have both its chemical activity and its electrical response altered when colloidal platinum is introduced on the anatase. Undesired effects on chemical sensing was observed due to the incorporation of

platinum into the metal oxide lattice at high temperatures, resulting in lower baseline resistances and decreased sensitivities. To prevent this electrical effect from occurring in the anatase sensor while still utilizing the catalytic abilities of platinum metal, platinum was introduced into zeolite–Y in considerably larger amounts and added to the anatase. The Pt–Y powder converts CO into CO₂ and hydrocarbons into CO₂ and water. Because the anatase sensor is not sensitive to CO₂, the devices only showed an electrical response to the water from hydrocarbon oxidation. Thus, a selective hydrocarbon sensor can be designed with a Pt–zeolite filter.

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