Selectivity of Catalytically Modified Tin Dioxide to CO and NH$_3$ Gas Mixtures

Artem Marikutsa *, Marina Rumyantseva and Alexander Gaskov

Chemistry Department, Moscow State University, Vorobyevy gory 1-3, Moscow 119991, Russia; E-Mails: roum@inorg.chem.msu.ru (M.R.); gaskov@inorg.chem.msu.ru (A.G.)

* Author to whom correspondence should be addressed; E-Mail: artem.marikutsa@gmail.com; Tel.: +7-495-939-5471; Fax: +7-495-939-0998.

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Abstract: This paper is aimed at selectivity investigation of gas sensors, based on chemically modified nanocrystalline tin dioxide in the detection of CO and ammonia mixtures in air. Sol-gel prepared tin dioxide was modified by palladium and ruthenium oxides clusters via an impregnation technique. Sensing behavior to CO, NH$_3$ and their mixtures in air was studied by in situ resistance measurements. Using the appropriate match of operating temperatures, it was shown that the reducing gases mixed in a ppm-level with air could be discriminated by the noble metal oxide-modified SnO$_2$. Introducing palladium oxide provided high CO-sensitivity at 25–50 °C. Tin dioxide modified by ruthenium oxide demonstrated increased sensor signals to ammonia at 150–200 °C, and selectivity to NH$_3$ in presence of higher CO concentrations.

Keywords: gas mixture analysis; selectivity; gas sensors; nanocrystalline tin dioxide; surface modification; carbon monoxide; ammonia

1. Introduction

Lack of selectivity is a major drawback of semiconductor metal oxide gas sensors. Nanocrystalline tin dioxide is one of the most utilized materials for such devices due to a combination of appropriate structural, adsorptive, and electrophysical properties [1]. The material, possessing several advantages, such as large active surface area and surface-to-volume ratio, result in high gas sensitivity, stability in
air, and low cost, makes it challenging to improve selectivity [2]. The problem of selectivity is complicated by the fact that most toxic gases (CO, NH₃, H₂S, volatile organic compounds) are the reducing ones. The sensor response to these gases is determined by the molecules oxidation on the material surface.

There are several tools to improve the sensitivity and selectivity of the detection of reducing gases. These include modulation of temperature regime of sensors operation, such as pulsed-temperature [3] or cycled-temperature regime [4]. Another approach is the modulation of the sensor measurement principle. For example, measuring voltage fluctuations instead of DC-resistance of nanocrystalline Pd₃WO₅-based sensors was shown to be hundreds of times more sensitive to the presence of ethanol vapor [5]. In environmental applications there is the need to selectively detect traces of reducing gases mixed in air, e.g., to discriminate toxic, fire alarming gases, food quality indicators, disease markers, etc. [6]. A promising tool to meet this challenge is the development of artificial olfaction systems (electronic nose). Such systems are based on a network of sensors operated in similar or different temperature modes. The treatment of multidimensional data from sensors networks requires a pattern recognition algorithm, such as principal component analysis [6]. In a recent review by Seifert et al., new mathematic algorithms for calibration and pattern recognition of sensor networks were demonstrated, the procedures being efficient for components concentration evaluation in gas mixtures composed of volatile organic compounds [7].

The operation temperature regime is also important in sensors networks: it was established that ammonia leakages could be selectively detected in the presence of water vapor, using commercial tin dioxide-based sensors operated in a linear heating–cooling mode [8]. On the other hand, in multisensory networks, it is reasonable to combine sensors with specific sensitivities to target gases. In this case, the “orthogonal” data from different sensors would be beneficial for the detection of various target gases and reliable discrimination of their mixtures. Thus, improving sensing materials’ selectivities is a challenge, not only for individual gas sensors, but also for sensor network systems.

An efficient approach to improve the selectivity of a gas sensing material is the chemical modification of a semiconductor oxide [2,9]. Catalytic additives of noble metals have been established as efficient modifiers, enhancing sensitivity and selectivity to reducing gases, e.g., to CO the efficient modifiers are Pd [10–13], Au [14,15], Pt [16]; to H₂S—CuO [17]; to NH₃—RuO₂ [18]; to LPG—Pd [19], Au [20]. However, the appropriate choice of a modifier is a non-trivial issue, since in the complex process of gas sensing not only the catalytic activity of clusters, but also their interference with the oxide surface sites, defines the sensor characteristics of modified material [21,22]. In our recent works, we demonstrated that nanocrystalline tin dioxide modification by palladium oxide increased sensor responses to CO at as low temperature as room temperature [23]; while introducing ruthenium oxide provided high responses to NH₃ at a raised temperature [24]. However, these studies dealt with individual gases. The specific sensitization to CO and NH₃ motivated an interest to appreciate whether the catalytic additives bring about enough selectivity to allow for distinguishing these reducing gases mixed together in a ppm-concentration level.

In the present work, the cross-sensing behavior of nanocrystalline SnO₂ modified by palladium and ruthenium oxides to CO + NH₃ gas mixtures in air was studied to estimate the selectivity.
2. Experimental Section

Nanocrystalline SnO₂, SnO₂/PdOₓ, and SnO₂/RuOᵧ materials were used for the study. Tin dioxide was synthesized using the aqueous ammonia-assisted sol-gel route [23]. 0.3 M solution of tin (IV) chloride in deionized water was obtained using SnCl₂-5H₂O (>99% pure, Sigma-Aldrich). 1 M ammonia solution was rapidly added until pH 6 was reached, after that, the deposit of α-stannic acid was left for 1 h at room temperature. Next, it was separated by centrifugation and washed several times with deionized water to remove chloride-ions (check by AgNO₃ solution). The washed SnO₂-nH₂O deposit was dried at 50 °C overnight and annealed in air at 300 °C for 24 h. Chemical modification of nanocrystalline tin dioxide by 1 wt.% of PdOₓ or RuOᵧ was performed via the impregnation of as-obtained SnO₂ powder by ethanol solution of noble metal acetylacetonate precursors. The impregnated samples, SnO₂/Pd(acac)₂ and SnO₂/Ru(acac)₃, were calcined at 225 °C and 265 °C, respectively, to decompose the modifier precursors at a sufficiently lower temperature [25,26].

The concentration of noble metal modifiers was measured by ICP-assisted analysis using a quadruple mass-spectrometer 7500c (“Agilent”). For this purpose, the powders were alloyed with zinc and then dissolved in nitric acid under heating. The measurements were performed for five isotopes of each modifier, and the signal were registered at mass numbers: for Pd at 104, 105, 106, 108, 110; and for Ru at 96, 98, 100, 101, 102. The micrographs of the nanocomposites were obtained using high-resolution transmission electron microscopy (HRTEM), high angle annular dark field scanning transmission electron microscopy (HAADF-STEM), and energy-dispersive X-ray (EDX) analysis with a Tecnai G2 transmission electron microscope operated at 200 kV. Characterization of the samples by X-ray diffraction (XRD), electron diffraction (ED), X-ray absorption spectroscopy (XANES and EXAFS), X-ray photoelectron spectroscopy (XPS), and electron paramagnetic resonance (EPR) were described in our previous publications [23–27]. The composition and microstructure parameters of the samples are summarized in Table 1.

Sensor tests were performed by in situ measurements of the sensors’ DC-resistance at temperatures in the range of 25–250 °C and with controlled gas composition. To prepare the sensors, the sample powders were mixed with a binder (terpeniol). The paste was thick film-deposited onto alumina microelectronic hotplates, which provided vapor-deposited rectangular-shaped Pt contacts (0.3 × 0.2 mm) separated by a 0.2 mm gap and with embedded Pt-heaters. The sensing layer (5–7 micrometres thick) covered an area of 1.0 × 0.5 mm. The sensors were placed in the gas-purged (100 mL/min) chamber of a resistance-measuring device. Before measurements, the sensors were annealed at 200 °C for 14 h under purified air to remove the binder and to clean the surface from atmospheric impurities. Test gas was purged through the chamber in a pulsed regime: background gas–test gas–background gas. A purified air generator (model 1,2-3,5, “Himelectronica”, Russia) was used as the source of the background gas; the contaminations level is not exceeding: 10 ppm H₂O, 2 ppm CO₂, 0.1 ppm hydrocarbons. The test gas sources were certified gas mixtures (“Linde-Gas”, Moscow, Russia): CO (517 ± 12 ppm): N₂ and NH₃ (209 ± 8 ppm): air. Exposure time in test gas was 15 min, recovery time in air was 30 min. The cycled target gas exposure was performed three to four times for reproducibility. The concentrations of analytes were 2–50 ppm CO and 0.4–50 ppm NH₃ in the analyses of individual gases. The dilution of target gases in purified air was performed using mass-flow controllers (“Bronkhorst”). The sensor signal was defined as a ratio of sensor resistance in background gas (R_{air}) to that in test gas (R_{gas}):
\[ S = \frac{R_{\text{air}}}{R_{\text{gas}}} \]  

For selectivity tests, the mixtures of CO + NH\textsubscript{3} with component concentrations, varied in the range of 5–20 ppm in air, were prepared. Sensors were operated at constant temperatures, corresponding to the maximum sensitivity to individual gases: SnO\textsubscript{2} at 250 °C, SnO\textsubscript{2}/PdO\textsubscript{x} at 50 °C, and SnO\textsubscript{2}/RuO\textsubscript{y} at 200 °C.

3. Results and Discussion

3.1. Materials Composition and Microstructure

As was shown by diffraction techniques (Table 1), the samples contain one crystalline phase of cassiterite (SnO\textsubscript{2}), with an average crystallite size of 3–6 nm. Due to small concentrations, the additives could not be detected by XRD or ED. Using XPS, XANES, EXAFS, and EPR, the modifiers were shown to exist in the form of mixed-valence noble metal oxides, which could be formalized as PdO\textsubscript{x} and RuO\textsubscript{y}, respectively. The techniques allowed estimation of the fractions of different oxidation states of palladium and ruthenium in the nanocomposites (Table 1). The total concentration of Pd and Ru, measured by ICP-mass spectrometry, is close to the loaded amount of 1 wt.%. The additives could not be visualized on HRTEM images (Figure 1), presumably due to close atomic numbers with Sn, and, hence, close contrast with the support on the electronic micrographs. Using EDX-mapping with HAADF-STEM, the modifiers were observed in the form of clusters on the surface of agglomerated tin dioxide nanoparticles (Figure 2a,b). The size of PdO\textsubscript{x} and RuO\textsubscript{y} clusters were estimated at 1–5 nm, while those of aggregates of tin dioxide particles reached 20–80 nm. Previously, we demonstrated micrographs of PdO\textsubscript{x} clustered on SnO\textsubscript{2} crystallites with a size of more than 50 nm (tin dioxide annealed at 700 °C) that was detectable by HRTEM [27].

![HRTEM micrograph of SnO\textsubscript{2}/PdO\textsubscript{x} sample; inset—electron diffraction pattern.](image-url)
### Table 1. Materials composition and microstructure parameters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystalline Phase a</th>
<th>Modifier Content and Composition</th>
<th>Particle Size, nm</th>
<th>Modifier c</th>
<th>BET Area, m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SnO₂/PdOₓ</td>
<td>SnO₂</td>
<td>0.94 ± 0.05</td>
<td>3–6</td>
<td></td>
<td>95–100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Oxidation and Crystalline State b, at.% from Total Modifier Concentration</td>
<td>SnO₂ (d&lt;sub&gt;XRD&lt;/sub&gt;)&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td></td>
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<tr>
<td></td>
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<td></td>
<td>SnO₂ (d&lt;sub&gt;TEM&lt;/sub&gt;)&lt;sup&gt;d&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SnO₂/RuOᵧ</td>
<td>RuOᵧ</td>
<td>0.81 ± 0.05</td>
<td>3–5</td>
<td></td>
<td>90–95</td>
</tr>
</tbody>
</table>

a According to XRD and electron diffraction [23,24,26,27];
b from ICP-mass spectrometry analysis;
c estimated by XANES, EXAFS, XPS and EPR [23–25,27];
d from HRTEM;
e evaluated by HAADF-STEM and EDX-mapping.

**Figure 2.** HAADF-STEM images of (a) SnO₂/PdOₓ and (b) SnO₂/RuOᵧ samples; inset—EDX maps of selected areas (blue—Sn, yellow—noble metal).
S. Sensing Behavior to Individual CO and NH₃ Gases

The influence of PdOₓ and RuOᵧ catalytic clusters on the sensitivity of nanocrystalline tin dioxide to CO and NH₃ was compared from the sensing tests to individual gases. Figures 3 and 4 illustrate the dynamic resistance response of SnO₂, SnO₂/PdOₓ, and SnO₂/RuOᵧ sensors to 50 ppm of CO or NH₃ at variable operating temperatures of 25–250 °C. The highest responses to CO were observed for PdOₓ-modified tin dioxide in the whole temperature range (Figure 3). At a lower temperature region (25–50 °C), the sensitivity of SnO₂/PdOₓ increased, however, the response kinetics were poor: the recovery time, i.e., time needed to reach 90% of resistance value in air ($R_{air}$) when the target gas is switched off, increased from $τ_{90} \sim 10$ min at $T = 200$ °C to $τ_{90} \sim 25$ min at room temperature.

![Figure 3](image1.png)

Figure 3. Dynamic resistance response of SnO₂, SnO₂/PdOₓ, and SnO₂/RuOᵧ sensors to the pulses of 50 ppm CO in air at different temperatures.

![Figure 4](image2.png)

Figure 4. Dynamic resistance response of SnO₂, SnO₂/PdOₓ, and SnO₂/RuOᵧ sensors to the pulses of 50 ppm NH₃ in air at different temperatures.
The response of SnO$_2$/PdO$_x$ to 50 ppm NH$_3$ was low and unstable, especially at low temperature (Figure 4). Low responses with long response ($\tau_{90} > 10$ min) and recovery ($\tau_{90} > 25$ min) time were characteristic for all the sensors when detecting NH$_3$ at $T = 25$–$50$ °C. Raising the operating temperature resulted in the increase of sensitivity to NH$_3$, most prominently for SnO$_2$/RuO$_y$ sensor (Figure 4). Corresponding sensor signals to 50 ppm of CO and NH$_3$, calculated via Equation (1), are plotted in Figures 5 and 6, respectively, as a function of operating temperature. SnO$_2$/PdO$_x$ demonstrated the highest sensor signals to CO compared to other samples, with the maximum at $T = 25$–$50$ °C (Figure 5). SnO$_2$/RuO$_y$ was characterized by superior signals to ammonia, with the maximum at $T = 200$ °C (Figure 6). Since the samples are characterized by quite close particle sizes and BET area values (Table 1), the sensitization effects are due to the influence of catalytic modifiers on the interaction of materials’ surfaces with target gas molecules, rather than their affecting the materials’ microstructure. Recently, we reported on the specific promoting effect of PdO$_x$ and RuO$_y$ clusters on the active sites on the surface of nanocrystalline tin dioxide [28]. This should be an important factor controlling the specificity of materials’ interaction with gases.

Figure 5. Temperature dependence of sensor signals of nanocrystalline SnO$_2$, SnO$_2$/PdO$_x$, and SnO$_2$/RuO$_y$ samples to 50 ppm CO.

Figure 6. Temperature dependence of sensor signals of nanocrystalline SnO$_2$, SnO$_2$/PdO$_x$, and SnO$_2$/RuO$_y$ samples to 50 ppm NH$_3$. 
3.3. Sensing Behavior to CO + NH₃ Gases Mixtures

To estimate the selectivity of the catalytically-modified tin dioxide sensing test to gas mixtures of CO + NH₃ was performed. The upper plot in Figure 7 shows the dynamic resistance responses of the sensors to target gas mixtures with different component concentrations. During the measurements, the sensors were operated at temperatures appropriate for the specific detection of corresponding molecules, which were chosen based on the above-discussed temperature profiles of sensor signals (Figures 5 and 6). SnO₂/PdOₓ was operated at 50 °C to detect CO in the mixture, SnO₂/RuO₂ at 200 °C for specific NH₃ sensing. Blank SnO₂, the sensitivity of which unselectively increased with temperature, was operated at 250 °C as a reference sensor. The experiment was carried out so that, firstly, CO (20 ppm) pulses were purged through the chamber. Subsequently, an increasing concentration of NH₃ (5–10–20 ppm) was admixed to the test gas containing 20 ppm CO. Finally, NH₃ concentration was fixed at 20 ppm and CO content was decreased step-by-step to 10–5–0 ppm. Corresponding sensor signals to test gas mixtures were calculated using Equation (1) and are plotted in the lower part of Figure 7.

![Figure 7](image-url)

**Figure 7.** Upper plot: dynamic resistance response of SnO₂ (1), SnO₂/PdOₓ (2), and SnO₂/RuO₂ (3) sensors to the pulses of CO + NH₃ mixtures in air. The component concentrations in the test gas mixture are shown in the middle table. Operating temperature of sensors: SnO₂—250 °C, SnO₂/PdOₓ—50 °C, SnO₂/RuO₂—200 °C. Lower plot: corresponding sensor signals to the test gas mixtures.
As can be seen in Figure 7, the \( \text{SnO}_2/\text{RuO}_x \) sensor displayed extremely low responses to 20 ppm CO. However, introducing a lower concentration of NH\(_3\) (5 ppm) to the test gas mixture resulted in a drastic sensor signal growth, increasing further with the increase of NH\(_3\) concentration. Decreasing the concentration of CO affected, neither response behavior, nor the sensor signal values of \( \text{SnO}_2/\text{RuO}_x \) (Figure 7). Hence, \( \text{SnO}_2/\text{RuO}_x \) is selective to ammonia in comparison with CO when the gases are mixed in a ppm-concentration level with air. Previously, the additive of RuO\(_x\) was found to promote oxygen spillover and dissociation on the surface of \( \text{SnO}_2/\text{RuO}_x \) to a larger extent than on \( \text{SnO}_2 \) or \( \text{SnO}_2/\text{PdO}_x \) [27]. This resulted in the highest promotion of oxygen species on the surface of \( \text{SnO}_2/\text{RuO}_x \), comparing to other samples [28]. These oxygen species could be the active sites for ammonia oxidation at raised temperatures. However, since surface oxygen species are unselective to reducing gases, the main reason for \( \text{SnO}_2/\text{RuO}_x-\text{NH}_3 \) selectivity should be the specific catalysis of ammonia oxidation. In a recent work, we established catalytic role of RuO\(_x\) clusters in deep NH\(_3\) oxidation to nitrogen oxides as the main feature reflecting increased sensitivity of \( \text{SnO}_2/\text{RuO}_x \) to ammonia at raised temperatures [24]. In contrast to that, ammonia is likely oxidized to \( \text{N}_2 \) on the surface of PdO\(_x\)-modified or blank \( \text{SnO}_2 \).

The \( \text{SnO}_2/\text{PdO}_x \) sensor demonstrated highest responses to 20 ppm CO when there was no ammonia in the test gas (Figure 7). The addition of as little as 5 ppm NH\(_3\) resulted in a sensor signal decrease, despite the persistence of a CO concentration (20 ppm). This effect increased as a higher concentration of ammonia was added to the gas mixture. A similar behavior was observed for blank \( \text{SnO}_2\)-based sensor, but the NH\(_3\)-induced sensor signal depression was less prominent in this case (Figure 7). It suggests that interaction of tin dioxide with CO, and the sensitization provided by PdO\(_x\) clusters at low temperatures, proceed via a different mechanism in comparison to the \( \text{SnO}_2/\text{RuO}_x-\text{NH}_3 \) interaction at raised temperatures. Direct CO oxidation by surface OH-groups on the surface of \( \text{SnO}_2/\text{Pd} \), facilitated by the catalytic additive, was discovered in the works of Barsan et al. [21]. We proposed that CO interaction with surface hydroxyls is responsible for increased \( \text{SnO}_2/\text{PdO}_x \) sensitivity to carbon oxide at temperatures as low as room temperature [23]. Moreover, it was PdO\(_x\) that, to the largest extent, promoted tin dioxide surface hydroxylation by increasing the concentration of different hydroxyl species, including reactive ones, such as Brønsted acid sites, paramagnetic OH\(_{-}\), and hydrogen-bonded OH…OH groups [28]. In this respect, the inhibition of \( \text{SnO}_2/\text{PdO}_x \) sensitivity to a fixed (20 ppm) CO concentration by adding even a smaller concentration of ammonia (5 ppm) can be attributed to blocking surface OH-groups by chemisorbed ammonia. Furthermore, the low operating temperature of the \( \text{SnO}_2/\text{PdO}_x \) sensor (50 °C) is favorable for the adsorption of basic NH\(_3\) molecules on Brønsted acid sites, i.e., on surface hydroxyl species.

In this context, the sensors’ operation at low temperatures has limited applicability for environmental monitoring. Moreover, ambient humidity would block the active sites for CO oxidation, as well as ammonia gas in the above-discussed situation with \( \text{SnO}_2/\text{PdO}_x \) and \( \text{SnO}_2 \). However, we believe that the specific sensitivities of the studied materials might be advantageous for the use of the sensors (as a future prospect) in multisensory devices. In the work of Frank et al., it was shown that using sensor networks, based on tin dioxide with different additives (palladium oxide, cobalt oxide, copper oxide, etc.), the realization of the selective analysis of hydrocarbons gas mixtures could be achieved [29]. Perhaps, the selectivity of CO and ammonia detection in gas mixtures could benefit from the strong distinction of the temperature dependence of sensitivity in the \( \text{SnO}_2/\text{PdO}_x-\text{CO} \) (Figure 5) and \( \text{SnO}_2/\text{RuO}_x-\text{NH}_3 \) systems (Figure 6). The issue of sensor surface poisoning at low temperatures could be overcome by an
appropriate modulation of the operating temperature, e.g., pulsed heating to desorb impurities or applying a temperature gradient to the sensing layers [4,29]. However, this is a matter for further research with these materials.

4. Conclusions

Modification of nanocrystalline SnO$_2$ using palladium and ruthenium oxides results in gas sensitivity increase to CO at low temperatures (25–50 °C) and to NH$_3$ at a raised temperature (150–200 °C), respectively. A selectivity test for the detection of CO + NH$_3$ gas mixtures with air revealed that SnO$_2$/RuO$_2$ is selective to NH$_3$ in the presence of higher CO concentrations. The selectivity is supposed to arise from RuO$_2$-catalyzed oxidation of NH$_3$ to nitrogen dioxide. CO sensing by PdO$_x$-modified tin dioxide at low temperatures is likely to involve target molecules oxidation by surface OH-groups, which are promoted by the modifier. CO sensitivity of SnO$_2$/PdO$_x$ is suppressed by lower ammonia concentrations in gas mixtures due to the inhibition of active surface hydroxyls by NH$_3$ chemisorption, favored by low operating temperatures.

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Author Contributions

Artem Marikutsa and Marina Rumyantseva contributed equally to the experimental work and discussion of the results. Alexander Gaskov contributed greatly to the concept, purposing of the work, and discussion of the results.

Conflicts of Interest

The authors declare no conflicts of interest.

References


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