

Letter to the Editor

Abstract

The hypothesis that chemical reactivity of the surface for CO oxidation of a titania sensor impregnated with gold or copper oxide is related to the sensing behavior is tested. Results show that the mechanism of the oxidation reaction is more important to the sensing characteristics than the extent of reaction.

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Correlation of catalytic activity and sensor response in TiO₂ high temperature gas sensors

Optimization of combustion processes is essential for decreasing emissions and increasing fuel efficiency. Gas sensors with high sensitivity to combustion products, such as CO, hydrocarbons, NO_x, CO₂, along with rapid response and recovery times are necessary for combustion optimization. In addition, these sensors need to withstand the harsh environments of the combustion process, including high temperatures (>400 °C). Resistive metal oxide gas sensors have been used extensively for low-temperature applications, especially devices based on SnO₂. Typically, reducing species, such as CO reacts with chemisorbed oxygen species on the SnO₂ surface, thereby altering the bulk resistance of the material [1,2].

Our group has primarily focused on TiO₂ sensors with particular emphasis on CO sensing at temperatures above 400 °C [3–6]. Increasing the sensitivity of TiO₂ sensors is of considerable interest. Typical strategy for finding additives that increase the sensitivity of semiconductor sensors is to screen a large number of materials. In this letter, we test the hypothesis that the extent of chemical reaction, i.e. surface reactivity can provide a basis for discovering additives that increase sensor sensitivity. We have used as a model system TiO₂-based sensors with CuO and Au additives for CO sensing at temperatures spanning 430–700 °C. The experimental plan involved measurement of the extent of CO oxidation to CO₂ by gas chromatography and correlation of the chemical reactivity with changes in the electrical resistance.

The base material used in this study is anatase mixed with 10 wt.% La₂O₃ and heated to 800 °C. Henceforth, we refer to this material as AL. In previous studies, we and others have shown that the presence of La preserves the morphology of the anatase

particles (starting size ~ 100 nm) and inhibits the transformation of anatase to rutile even at temperatures as high as 800 °C, immaterial of addition of small amounts of other additives [3,7,8]. Thus, the presence of La ensures that the basic support material remains unaltered on introducing additives. Two materials were made from AL by adding 2 wt.% CuO (labeled ALC) and 2 wt.% Au (labeled AuAL). ALC was prepared by heating anatase with 2 wt.% CuO and 10 wt.% La₂O₃ at 800 °C. AuAL was prepared by addition of H₂AuCl₄·3H₂O to AL, followed by treatment with NH₃ to precipitate Au(OH)₃ onto AL followed by heat treatment at 800 °C for 6 h to generate Au particles [9].

Powder diffraction data for AL, ALC and AuAL show that the majority phase is anatase, with small peaks due to La₄Ti₉O₂₄, CuO, and Au, respectively. Electron microscopy studies show that the anatase morphology is similar in all three cases. Morphology of AL and ALC have been published [3] and Fig. 1 shows the TEM of AuAL particles, with anatase grains of the order of 100–200 nm with Au particles ranging from 5 to 55 nm and an average size of 31 nm.

The surface reactivity of AL, ALC, and AuAL for conversions of CO to CO₂ in a background of 5% O₂/N₂ balance at temperatures of 430, 500, 600 and 700 °C was measured with gas chromatography (Shimadzu GC/MS QP5050). The percent conversions (obtained with a calibration curve for CO₂ with a calibration error of ±5%) are shown in Fig. 2 comparing AL with ALC and AuAL, respectively. For AL, the dramatic increase in reactivity occurs between 400 and 600 °C. Introduction of CuO and Au increases surface reactivity at all temperatures tested, with conversions well over 90% in all cases.

Sensors were prepared by screen-printing AL, ALC and AuAL on alumina substrates with gold interdigitated electrodes, as previously described [3–5] and resistance was measured in the presence of 250 ppm CO in 5% O₂/N₂ balance at temperatures

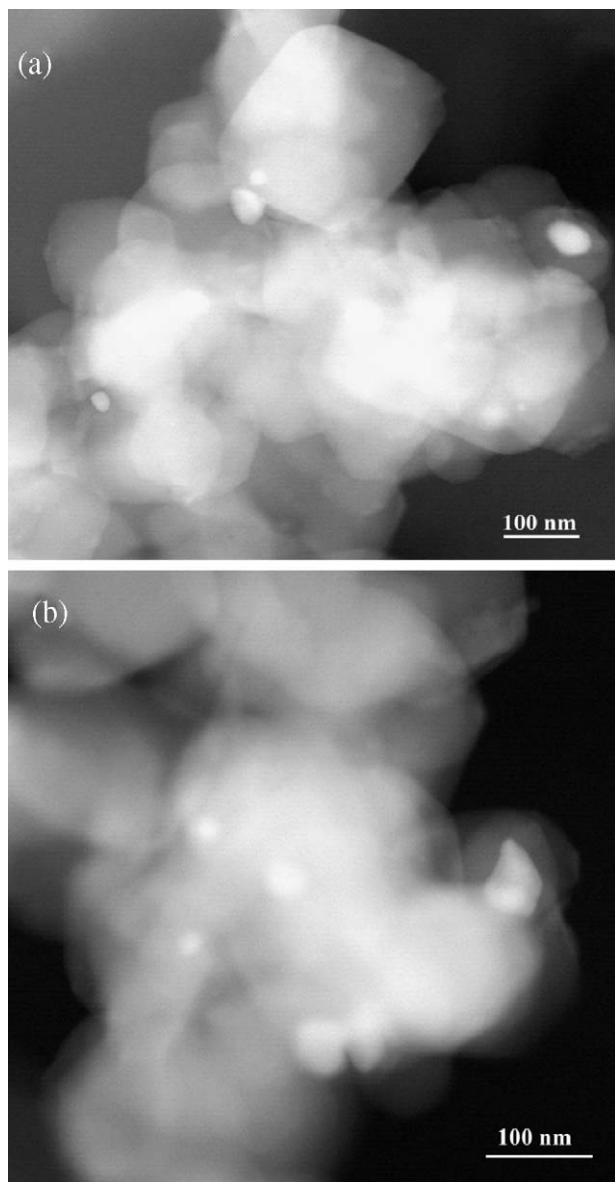


Fig. 1. STEM images of Au dispersion on AuAL: (a) and (b) show different regions of the same sample.

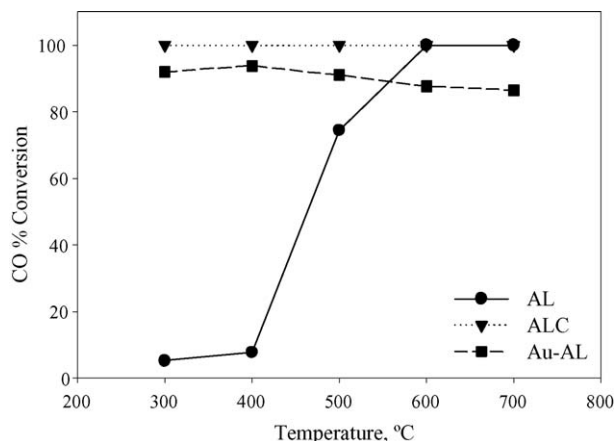


Fig. 2. CO₂ production with AL, ALC and AuAL for 0.5% CO and 5% O₂/N₂ at various temperatures.

of 430, 500, 600 and 700 °C. The sensor response, defined as R_0/R , where R_0 is the resistance in background gas (5% O₂/N₂) and R in presence of 250 ppm CO is compared for AL, ALC and AuAL in Fig. 3. The choice of 5% O₂ in the background was made based on the fact that in high temperature combustion processes, the O₂ content is typically between 2 and 10%. For ALC-based sensors, there is a slight improvement in sensitivity at 430 and 500 °C and comparable response at 600 and 700 °C to AL-based sensors. With the AuAL-based sensors, there is significant improvement in response to 250 ppm CO over AL-based sensors at 430, 500, and 600 °C.

With both chemical reactivity and sensor response of AL, ALC and AuAL available, correlations can be drawn. For AL, there is an increase of conversion of CO from 10% at 430 °C to 80% at 500 °C, yet the sensor response is barely altered. With increase in temperature, the O_m^{n-} (O₂⁻, O⁻, O²⁻) species chemisorbed to the AL surface is also altered, changing the barrier to electronic conduction between grains [10]. With both reactivity and oxygen adsorption changing, it is difficult to compare sensitivities at different temperatures. Given that information, it is better to focus on a particular temperature. Also considering that the base material in all three sensor cases is AL, the O_m^{n-} adsorption properties should be similar at a fixed temperature and sensor response as a function of surface reactivity can be examined. If we compare the three sensors at any of the temperatures in the 430–600 °C range, the sensitivity follows the order AuAL > ALC ≈ AL, though chemical reactivity is AuAL ≈ ALC > AL. Thus, dramatically increasing the CO to CO₂ conversion by adding CuO, especially at temperatures below 500 °C does not translate to improvement in sensor response, whereas, addition of Au does improve both conversion and sensitivity.

Thus, there appears to be no direct correlation between chemical conversion and sensor response. In the oxidation of CO to CO₂, there are two relevant oxygen species on the metal oxide surface: O_{ads} and O_{ads}ⁿ⁻

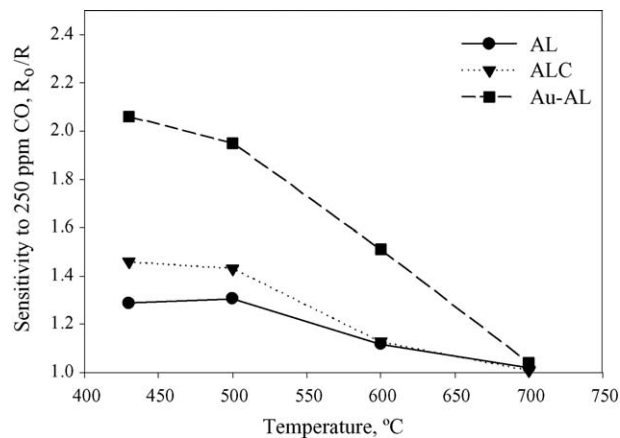


Fig. 3. Relative response (R_0/R) of AL, ALC and AuAL sensors to 250 ppm CO in 5% O₂/N₂ at various operating temperatures (R_0 is resistance in background gas).



Resistance changes will only occur when CO reacts with $\text{O}_{\text{ads}}^{n-}$, while catalytic mechanisms do not distinguish between the types of adsorbed oxygen species, O_{ads} or $\text{O}_{\text{ads}}^{n-}$.

The catalysis literature provides insight regarding the mechanism of CO oxidation. In the case of supported CuO, enhanced CO oxidation is proposed to involve redox phenomena on the surface involving formation of Cu_2O [11,12]. Adsorption sites of CO are proposed to occur at oxygen vacancies on the CuO, and CO_{ads} can react with O_{ads} on the CuO without specific contributions from the $\text{O}_{\text{ads}}^{n-}$ on the AL surface. Thus, despite significant increase in chemical reactivity of ALC over AL, especially at 430 and 500 °C, there is only marginal improvement in sensor response since O_{ads} is primarily on the CuO surface. For Au particles on supports, the proposed mechanism involves adsorption of CO on Au, with TiO_2 providing a reservoir of reactive adsorbed oxygen species, with the reactions occurring at the Au– TiO_2 interfaces [13,14].

For any particular surface, e.g. AL, at a certain temperature, both reactions (2) and (3) are occurring. It is expected that at higher temperatures (>700 °C), the extent of (3) is decreased and sensor response is negligible. At a particular temperature, the ratio of $\text{O}_{\text{ads}}/\text{O}_{\text{ads}}^{n-}$ on AL is comparable for AL, ALC and AuAL, primarily being controlled by the nature of the AL surface. At both the Au and CuO interface with AL, there will be a distribution of adsorbed oxygen species. In case of AuAL, these interface oxygen species are involved in CO oxidation and not in the case of ALC. Thus, as a function of dopants, mere chemical reactivity of CO oxidation will not provide information regarding sensor performance and the mechanism of the oxidation reaction needs to be taken into account.

Mechanisms of several CO oxidation catalysts supported on TiO_2 have been reported in the literature and based on our results with ALC and AuAL, predictions about sensor response can be made. In particular, Pt, Pd, Ag and Ir supported on TiO_2 have been examined as CO oxidation catalysts, though primarily at low temperatures. Because of the inability of Ag to adsorb and activate CO, it is expected that Ag/ TiO_2 would be a poor sensor [15]. For Pt/ TiO_2 , the $\text{CO} + \text{O}_2$ reaction is proposed to occur on the Pt surface and would be comparable to the ALC sensor [16]. Similar behavior is expected for Pd/ TiO_2 , where enhanced oxidation was proposed to arise from CO activation via adsorption at the defect sites and reaction with O_{ads} , with the support playing a minimal role [17]. The Ir/ TiO_2 system is most comparable to AuAL, with Ir spread over TiO_2 as a thin surface layer with iridium oxide at the metal– TiO_2 interface and is predicted to have good CO sensor performance [18].

Acknowledgements

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