Abstract

The anatase form of TiO$_2$ has been examined for the sensing of CO and CH$_4$ at temperatures of 873 K. Though, there were differences in the sensitivity of the anatase sensor towards CO and CH$_4$, both gases showed considerable resistance changes. However, in the presence of lanthanum oxide and copper oxide (labeled as ALC sensor), the sensor showed minimal response towards CH$_4$, while still exhibiting sensitivity towards CO. The insensitivity towards CH$_4$ was also confirmed by measuring the sensor response in the presence of both gases. In order to understand the basis for selective CO sensing, diffuse reflectance infrared spectroscopy was carried out on the sensor materials at elevated temperatures. Lanthanum oxide was used to inhibit the anatase to rutile transformation. Infrared spectroscopic data strongly suggest that there is a layer of lanthanum oxide on the titania surface, which acts as a trap for the oxidation products of CO and CH$_4$. Upon oxidation of CO on ALC, carbonate species were detected, whereas the reaction of CH$_4$ produced negligible carbonate species. The insensitivity of the ALC sensor towards CH$_4$ is proposed to be due to its rapid oxidation by O$_2$ on the copper oxide. This efficient oxidation was responsible for lack of CH$_4$ reaction on the anatase surface, thus, producing minimal resistance change. CO oxidation also occurred partially on the CuO surface but significant reaction also occurred on the anatase surface and produced a change in resistance.

Keywords: Semiconducting oxide; Hydrocarbon sensing; Anatase; Oxygen sensing; Infrared spectroscopy

1. Introduction

In hydrocarbon-based combustion processes, the efficiency of the process is determined by the completeness of the conversion of hydrocarbons to H$_2$O and CO$_2$. High temperature combustion of hydrocarbons for energy generation is used in a wide variety of processes, including automobiles and power plants. An incomplete combustion process will lead to the formation of CO and unreacted hydrocarbons (HC). Monitoring these species should provide information useful for feedback control of combustion processes. The development of sensors with specific selectivity towards CO and HC as well as operation under harsh environments is necessary in this regard.

Commercial sensors for ambient monitoring of CO, driven primarily by the unhealthy, and sometimes deadly effects of CO exposure, are available [1]. Many of these sensors use semi-conducting metal oxides, such as SnO$_2$ [1–3]. Selectivity towards particular gases is usually accomplished by incorporating catalysts on these oxides. For example, Pd/SnO$_2$ is reported to have good sensitivity and selectivity towards CO [2]. For most of these sensors, though, the working temperatures are below 673 K [3].

Our research group has been interested in examining gas sensors that work at higher temperatures, preferably above 773 K. Towards that goal, we have examined the behavior of TiO$_2$ and have reported several studies on this material [4,5]. Like SnO$_2$, TiO$_2$ is non-stoichiometric at high temperatures and its resistance change upon gas exposure provides the basis for sensing. We have focused on metal oxides as catalysts for improving the selectivity of the sensor. The lower costs and selectivity that can be obtained with metal oxides make them attractive alternates for noble metal catalysts. Our earlier studies have included research on the sensing behavior of anatase and anatase doped with La$_2$O$_3$ and CuO towards CO in an inert environment [4]. Reasons for focusing on the anatase phase in this study is because it has been reported to be an excellent support in catalytic studies and far less is known about its sensing properties, as compared to the rutile phase of TiO$_2$ [4]. The choice of CuO as a catalyst was based on a study by Larsson et al. that found CuO/TiO$_2$ to be a more active combustion...
catalyst than cobalt, manganese and iron oxides on titania [6]. In the present study, we compare the sensing behavior of anatase towards CO and CH₄ in an oxidizing environment more typical of practical applications, and find that the presence of CuO produces a CO sensor that discriminates against CH₄. Infrared spectroscopic studies on the sensing materials at elevated temperatures have been used to develop a mechanism for the selective CO sensing behavior.

2. Experimental

2.1. Sample preparation

Samples of anatase, anatase/La₂O₃, anatase/La₂O₃/CuO and TiO₂/CuO were made by ball-milling commercial grade TiO₂ (anatase) with the desired weight percent of La₂O₃ and/or CuO in isopropanol for 4 h. After solvent removal by evaporation, the powders were heat treated at 1073 K for 6 h. The anatase/CuO sample was partially rutile/CuO after this treatment. Powders were then used to make sensing samples, or for characterization by diffuse reflectance infrared spectroscopy (DRIFTS).

All sensors were prepared by depositing the mixed oxide powders on alumina substrates with screen-printed gold interdigitated electrodes. Powders were sieved with 70 μm fluorocarbon mesh, weighed to 25 mg, suspended in several drops of n-heptanol and dropped by pipette onto the sensing substrate surface. The substrate was dried in an oven at 100°C to evaporate the solvent, leaving a compact film on the surface. The sensor was then fired at 1073 K for 6 h in air to ensure bonding of sample film to alumina surface.

2.2. Electrical measurements

Sensing measurements were done at 873 K in a background gas of 5% O₂/N₂ balance. The apparatus used for these measurements has been described previously [4]. The sensor is placed within a quartz tube that is contained within a tube furnace. Gases are passed through the quartz tube, their concentrations controlled by digital mass flow controllers. Data is acquired by computer via Hewlett-Packard Data Acquisition/Switch Unit (HP 34970A). Prior to starting sensing measurements, sensors were kept at 873 K and 5% O₂/N₂ for 2 h to allow for sample equilibration. Additional sensing measurements were made after the sample had been at 873 K and 5% O₂ for an additional 24 and 48 h.

2.3. Sample characterization

Infrared spectroscopy was done with Bruker Instruments IFS-66s Fourier Transform Infrared Spectrometer, with a Spectra-Tech Collector/Environmental Chamber which allows the sample to be heated and exposed to gas phase analytes during the infrared measurement. Sample powder is placed on a sample post that can be heated to various temperatures. A dome containing two KBr windows, through which incident light is directed onto and reflected light is collected from the sample, isolates the sample from the ambient. The sample is exposed to different gas concentrations by flowing gas mixtures through the dome. Prior to measurements, samples were heated to a temperature of 873 K (setting on the heater assembly of the infrared cell) for 2 h under a flow of N₂. A background measurement was made under a flow of 5% O₂/N₂, first at a 1073 K, and then at room temperature. The sample gas (either CO, CO₂ or CH₄) was introduced at a concentration of 0.5% and measurements were made at room temperature, 1073 K and then room temperature. Due to thermal conductivity losses from the sample holder and the powdered samples, actual surface temperatures were typically much lower than the temperatures set on the heater assembly. At a heater setting temperature of 873 K, the temperature of the sample cup was measured to be 598 K, and the top of the sample surface was between 493 and 553 K. For the 1073 K heater setting, the sample cup temperature was measured at 686 K, and the sample surface ranged from 673 to 753 K. It should also be noted that the thermocouple only measures the temperature at a single spot on the sample surface, and that the packing of the powder was loose. Because of the variation in sample temperature, throughout the text, we have referred to the temperature that was set on the heater assembly. Infrared measurements were made on the sensing samples and on La₂O₃ in KBr, La₂O₃/CuO in KBr and TiO₂/CuO to clarify some aspects of the AL and ALC spectra.

All the infrared data are reported in Kubelka Munk units: \[ KM = \frac{(1 - r)^2}{2r} \], where \( r \) is the relative reflectance (\( r/r_0 \)). The reference reflectance (\( r_0 \)) is the single channel reflectance of a sample under a flow of 5% O₂/N₂ (at room temperature or 1073 K) and the sample reflectance, \( r_s \), is that of the powder in a gas stream containing either CO or CH₄. In diffuse reflectance spectroscopy, it is important that the ratio \( r_s/r_0 \) be less than one. Changes in the sample reflectivity due to the heating and cooling cycles can result in ratios less than one. To account for these overall reflectance changes, single channel spectra were often multiplied by a correction factor, similar to a method described by Brimmer and Griffiths [7].

3. Results

3.1. Sensing behavior

TiO₂ can exist in several crystalline modifications, the most common forms being anatase and rutile [8]. In the present paper, the focus is on the anatase form of TiO₂ and the role of CuO as a catalyst for promoting selective gas sensing. We have shown earlier that the use of CuO leads to the transformation of anatase to rutile under the conditions of sensor fabrication and testing and that to avoid this transformation, La₂O₃ needed to be added to the anatase/
CuO [4]. The three samples that form the focus of the present investigation are anatase (A), anatase/La$_2$O$_3$ (AL) and anatase/La$_2$O$_3$/CuO (ALC). The powder diffraction pattern indicates that for the ALC sample, the anatase phase is indeed preserved even after extended heat treatments at 1073 K [4] and, thus, all sensing measurements reported here at 873 K are occurring on the anatase form of TiO$_2$.

Fig. 1 compares the relative resistance change (defined as $R/R_0$, where $R$ and $R_0$ are the resistances in the presence of the sensing gas and background gas, respectively) of A, AL and ALC film sensors (~100 µm thick) upon exposure to CO and CH$_4$ in the presence of 5% O$_2$/N$_2$ at 873 K. In the case of A and AL samples (Fig. 1a and b), the resistance change upon exposure to both CO and CH$_4$ is significant. The addition of La$_2$O$_3$ does not alter the sensing properties, except for the change in baseline resistance which increases from ~1.5 MΩ for the anatase sensor to ~2 MΩ for the AL sensor. With the addition of CuO to the sample, there is a dramatic change in the sensing behavior (Fig. 1c). The overall sensitivity of the sample is lower than the A and AL sensors towards both CO and CH$_4$. However, since the ALC sensor response remains close to a $R/R_0$ value of 1 for CH$_4$ levels between 0 to 1000 ppm, a CO selective sensor is obtained. The baseline resistance of the ALC sensor is ~1.5 MΩ. The bars in Fig. 1c indicate the results from three different ALC sensors, and provides information on the extent of reproducible fabrication of these sensors.

The A, AL and ALC sensors were kept at 873 K for a total of 48 h, and the sensor responses were re-examined. A drift in the resistance was noted for all samples. The percent change in the relative resistance (for CO) was of the order of ~12% for A, +37% for AL, and +12% for ALC. However, even after extended aging, the response to CH$_4$ for the ALC sensors remained essentially unchanged. The 90% recovery in resistance upon turning off the CO took about ~10 min for A and AL sensors, and 0.5 min for the ALC sensor. These times serve as a good comparison between the three samples, but should not be judged on an absolute basis, since the dead volume of the sensing system is 350 ml.

Fig. 2 shows the change in relative resistance for the ALC sensor at a fixed concentration of CO (500 ppm) with varying concentrations of CH$_4$ in the gas stream. The resistance change appears to be relatively independent of methane, confirming the CO selectivity of the ALC sensor.

Fig. 3 shows the change in relative resistance at a fixed concentration of sensing gas (750 ppm CO or CH$_4$) as a function of oxygen content in the gas stream for the A and ALC sensors. On the anatase sample, both CO and CH$_4$ sensing data indicate an increase in sensitivity with decreasing oxygen levels. However, for the ALC sensor (Fig. 3b), while increased sensitivity is observed for CO sensing with decreasing O$_2$, for CH$_4$, the resistance remains mostly unchanged with O$_2$. These data demonstrate that for the ALC sensor, CH$_4$ sensing is insensitive to O$_2$ over a wide range of O$_2$ concentrations.

### 3.2 Adsorption of CO and CH$_4$ on the sensor surface

The infrared (IR) spectroscopic measurements in this study were done under conditions of constant gas flow at...
atmospheric pressures and should provide a realistic idea of what species are being produced and adsorbed under typical sensing conditions. Additionally, the background gas was always a mixture of oxygen and nitrogen, conditions similar to those used during sensing. Most of the data presented here are in situ IR spectra obtained with a heated diffuse reflectance cell at heater settings of 1073 K (see Section 2 for details on sample temperature).

The characteristic IR band of gas phase CO occurs at 2143 cm$^{-1}$ and for CH$_4$ at 1304 and 3016 cm$^{-1}$, with both molecules exhibiting rotational structure [9,10]. For all the samples, gas phase IR bands were observed upon introduction of CO or CH$_4$ into the spectral cell. As the temperature was raised, the peaks due to the gas phase molecules decreased in intensity and were accompanied by the formation of gas phase CO$_2$, as confirmed by the doublet around 2345 cm$^{-1}$.

Since our interest was to correlate the chemistry on the solid surface with the sensing behavior, we examined the IR spectra of the samples upon adsorption of gases at heater settings of 1073 K. No infrared peaks, characteristic of chemisorbed CO or CH$_4$, were observed on any of the samples. The lack of chemisorbed species at the high temperatures is consistent with previous studies [9]. Infrared bands due to chemisorbed CO have been observed on anatase surfaces at room temperature and below on heavily reduced surfaces and under vacuum conditions [9,11]. However, we found that if the samples were exposed to CO at heater settings of 1073 K, brought back to ambient temperature and the IR spectra examined after the CO was replaced with background gas, bands due to chemisorbed species were observed. Fig. 4 compares the IR spectra in the CO stretching region for A, TiO$_2$/CuO and ALC (note same y-axis scale). A weak band around 2100 cm$^{-1}$ (Fig. 4a) is observed on anatase. Baraton reported a broad band at 2044 cm$^{-1}$ due to CO chemisorption on titania at room temperature [9]. Tanaka and White reported that two bands at 2185 and 2115 cm$^{-1}$ due to chemisorbed CO were formed on anatase at ambient temperatures, with evacuation resulting in loss of the 2185 cm$^{-1}$ band. They proposed that surface reduction of anatase occurred upon exposure to CO [11]. Busca et al. identified a band at 2100 cm$^{-1}$ as CO chemisorbed on Ti$_3^+$ [12], and is comparable to the present observation and our earlier study in an anaerobic environment [4].

Fig. 4b and c show that in the presence of CuO, there is a significant increase in the intensity of the chemisorbed CO band, indicating that Cu is promoting CO adsorption. Bands were observed at 2108 cm$^{-1}$ on CuO/TiO$_2$ and 2090 cm$^{-1}$ on ALC. Boccuzzi and Chiorino have reported a strong band at 2103 cm$^{-1}$ along with shoulders at 2017 and 2128 cm$^{-1}$ for CO on Cu/TiO$_2$ [13]. The frequency of the CO stretch is known to vary with the copper oxidation state as follows:
Cu\textsuperscript{0}, 2105–2130 cm\textsuperscript{-1}; Cu\textsuperscript{+}, 2115–2130 cm\textsuperscript{-1} and on Cu\textsuperscript{2+} leads to bands between 2140 to 2190 cm\textsuperscript{-1} at temperatures below 77 K [13–15]. Based on this literature, we assign the 2108 cm\textsuperscript{-1} band on TiO\textsubscript{2}/CuO and the 2090 cm\textsuperscript{-1} on ALC to CO adsorption on Cu\textsuperscript{0}. Inclusion of La\textsubscript{2}O\textsubscript{3} in the ALC sample appears to make the surface more electron-rich and leads to an 18 cm\textsuperscript{-1} red shift. The effect of La\textsubscript{2}O\textsubscript{3} on the reducibility of CuO has been noted previously in TPD studies by Jiang et al. [16]. It is also important to note that the CO is reducing the CuO to form Cu\textsuperscript{0} in an oxidizing environment at elevated temperatures. No CO chemisorption was noted on La\textsubscript{2}O\textsubscript{3} or La\textsubscript{2}O\textsubscript{3}/CuO samples under conditions comparable to the ALC sample. This also suggests that the bulk CuO present in the ALC sample is not contributing to the IR spectrum, presumably because of its low concentration level.

In the case of CH\textsubscript{4}, there was no evidence of chemisorption on any of the samples. Replacing the CH\textsubscript{4} in the gas stream by O\textsubscript{2}/N\textsubscript{2} led to the loss of IR bands due to CH\textsubscript{4}.

3.3. Reaction intermediates

The formation of intermediates as the gas molecules reacted on the sample surfaces was monitored via the IR spectra in the 1200–1800 cm\textsuperscript{-1} region at heater settings of 1073 K. As mentioned earlier, for both CO and CH\textsubscript{4} reactions on the samples, CO\textsubscript{2} was found to be a product. In order to distinguish the reaction intermediates formed on the sample surfaces during CO and CH\textsubscript{4} oxidation from species formed via adsorption of the product gas CO\textsubscript{2}, we examined the IR spectra upon CO\textsubscript{2} reaction with La\textsubscript{2}O\textsubscript{3} and ALC, also at high temperature. The corresponding infrared data are shown in Fig. 5. Strong bands were observed at 1447 and 1395 cm\textsuperscript{-1} on La\textsubscript{2}O\textsubscript{3} and weaker bands at 1515 and 1376 cm\textsuperscript{-1} on ALC. This frequency range is typical of the asymmetric stretching vibration (v\textsubscript{3}) of the carbonate ion [17]. Splitting of the v\textsubscript{3} band upon change in coordination of the carbonate ligand has been extensively studied [17]. A simple criterion for distinguishing between mono and bidentate carbonate is the extent of splitting of the v\textsubscript{3} band, ~100 and ~300 cm\textsuperscript{-1} for mono and bidentate, respectively. La\textsubscript{2}(CO\textsubscript{3})\textsubscript{8}H\textsubscript{2}O is reported to have strong infrared bands at 1460 and 1360 cm\textsuperscript{-1}, with a shoulder at 1330 cm\textsuperscript{-1} and assigned to a monodentate coordinated carbonate group [18]. Thus, considering that the splitting is of the order of 52 and 139 cm\textsuperscript{-1} on La\textsubscript{2}O\textsubscript{3} and ALC, respectively, these bands can be assigned to monodentate carbonate species coordinated to the La. It has also been reported that the value of the splitting within a fixed coordination geometry increases with the polarizing power of the coordinating cation [17,19]. The considerably larger splitting in the ALC sample is indicative of the fact that the environment of the La in the ALC sample is quite distinct from La\textsubscript{2}O\textsubscript{3}.

Fig. 6 shows the data for CO reaction on A, La\textsubscript{2}O\textsubscript{3}, AL and ALC surfaces. The frequencies of the IR bands are distinct from those shown in Fig. 5 formed via CO\textsubscript{2} reaction, indicating that we are not observing bands related to the mere readesorption of the reaction product CO\textsubscript{2}. The intensity axis (y-axis) in Fig. 6 has been kept the same in all cases to provide a quantitative picture of the extent of reaction. On the anatase surface, as well as on TiO\textsubscript{2}/CuO (data not shown), no bands were observed at heater settings of 1073 K. Literature reports indicate that reaction products of CO on metal oxide surfaces are only observed at low temperatures. Bands at 1420 and 1600 cm\textsuperscript{-1} assigned to bicarbonate species have been reported on exposure of anatase to CO [11]. Bands around 1370, 1680 cm\textsuperscript{-1} assigned to carbonate like species have been reported upon exposure of anatase to CO at room temperature, but these species disappear at ~373 K indicating weak binding to the surface [9]. Harrison and Guest have reported the formation of bidentate, monodentate and carboxylate species upon exposure of SnO\textsubscript{2} to CO, and beyond 400 K, the monodentate carbonates became the dominant species [20]. Harrison and Willet have examined the infrared spectra after exposure of CO to SnO\textsubscript{2}, pre-treated at various temperatures. These experiments were done at 329 K and evidence was found for mono, bidentate and carboxylate species [21]. Supported CuO has been reported to exhibit infrared absorptions for bidentate and monodentate carbonates in the presence of either CO or CO\textsubscript{2}, but at considerably lower temperatures [22]. The sensing data on anatase (Fig. 1a) confirm the reactivity of the surface towards CO, and the absence of IR bands indicate that the concentration of the intermediate oxidation products of CO on the anatase surface at the elevated measurement temperatures is too small to be detected.
Upon addition of La$_2$O$_3$ to anatase, several bands were observed upon CO exposure for both AL and ALC samples, even at the heater settings of 1073 K. In order to verify that the IR signal was not arising from reactions on bulk La$_2$O$_3$ in the AL and ALC samples, pure La$_2$O$_3$ was also examined. In the case of CO reaction on La$_2$O$_3$, peaks were observed at 1540, 1474, 1375 and 1347 cm$^{-1}$ (Fig. 6b). The intensity of these peaks were at least an order of magnitude lower than the AL and ALC samples, demonstrating that the contribution of the free La$_2$O$_3$ to the spectroscopic signal in AL and ALC sample is negligible. The two sets of bands at 1540, 1347 cm$^{-1}$ and 1474, 1375 cm$^{-1}$ on La$_2$O$_3$ are assigned to bidentate and monodentate carbonates, respectively. Rosynek and Magnuson assign monodentate carbonates at 1500 and 1390 cm$^{-1}$, with bidentate carbonates at 1565 and 1310 cm$^{-1}$ on La$_2$O$_3$ [23]. Tsyganenko et al. have reported carbonate bands formed via CO oxidation on La$_2$O$_3$ at 1559 and 1317 cm$^{-1}$ along with weaker bands at 1465, 1393 and 1330 cm$^{-1}$, which appear to be similar to the data shown in Fig. 6b [24].

For reaction of CO on the AL sample (Fig. 6c), intense bands at 1503 and 1356 cm$^{-1}$ are assigned to monodentate carbonates. For the ALC sample, there is a strong and broad absorption band centered at 1449 cm$^{-1}$ and cannot readily be assigned to either monodentate or bidentate carbonates. We assign these bands to polydentate carbonates. Complicated polydentate bridged structures in which all three oxygens are bound to metal ions usually show smaller $\Delta v_3$ splitting [17]. Bocuzzi et al. have proposed that CO on Cu/ZnO can be held by bonding to both the Cu and Zn sites, with the bonding to Zn via a $\pi$-bond [25]. We are proposing that in ALC sample, the carbonate is bonded to the La at the Ti/Cu interface.

Fig. 7 shows the infrared data for CH$_4$ reaction on A, La$_2$O$_3$, AL and ALC samples monitored at heater settings of 1073 K. No products were noted on anatase, as with the CO experiments. However, on La$_2$O$_3$, strong bands are observed with CH$_4$, at 1492 and 1352 cm$^{-1}$ (Fig. 7b), indicative of monodentate carbonates. Strong bands were also observed on the AL sample at 1492, 1463, 1435 and 1382 cm$^{-1}$ (Fig. 7c), and appear to be a combination of spectra of CO$_2$ and the CH$_4$ reaction on La$_2$O$_3$ (combination of Figs. 5a and 7b). Thus, free La$_2$O$_3$ may be contributing to the infrared spectra. The difference between the CH$_4$ and CO oxidation on La$_2$O$_3$ may arise from the fact that CH$_4$ oxidation leads to formation of H$_2$O. La$_2$O$_3$ has been reported to form La(OH)$_3$ in the presence of water and such hydrated lanthanum can be readily carbonated, even under ambient conditions [26]. Moreover, thermal analysis of the hydroxycarbonate species have shown that CO$_2$ desorption occurs beyond 900 K [26]. We find evidence of a band at 3499 cm$^{-1}$ due to OH stretching on the La$_2$O$_3$ samples, strongly suggesting that hydroxycarbonates are indeed forming on the sample.

Finally, Fig. 7d shows that in the case of CH$_4$ oxidation on the ALC sample, there is no appearance of any intermediate carbonates. Clearly, the inclusion of CuO appears to be inhibiting the formation of carbonates on the sample surface.

4. Discussion

The two interesting aspects of this study are the discovery that ALC is a high temperature CO sensor relatively insensitive to CH$_4$ and that ALC exhibits reasonable rapid recovery upon turning the CO off in the gas stream, as compared to the A and AL samples. We focus in this discussion on the role of lanthanum and copper in reducing the sensitivity of ALC towards CH$_4$, though, keeping the response to CO at reasonable levels. Understanding the origin of the lack of sensing response of ALC towards...
CH$_4$, even at temperatures as high as 873 K, as compared to the A and AL samples, is of importance, since it will provide the framework for development of high temperature selective sensors.

4.1. Nature of ALC: role of La$_2$O$_3$

In an earlier study, we have reported electron microscopic studies on the ALC sample [4]. Though, La$_2$O$_3$ could be observed as discrete particles, no evidence of any La$_2$O$_3$ on the anatase was found. However, since the phase transformation of anatase to rutile is being inhibited upon the addition of La$_2$O$_3$, lanthanum must be interacting with the TiO$_2$. Two possibilities can be suggested based on the literature: interstitial substitution of La into the TiO$_2$ lattice [8] or formation of a thin coating of LaO$_x$ on the TiO$_2$ surface [27]. Since a LaO$_x$ layer was not detected by TEM [4], the layer, if present, is very thin and subsurface deep. Several observations from the infrared spectroscopic data presented in this paper strongly suggest that lanthanum oxide (LaO$_x$) is present on the TiO$_2$ surface, though, it does not preclude the fact that La may also be penetrating into the TiO$_2$. First, we note that the intermediate carbonate species are observed on AL and ALC samples, but not on A, and the frequencies are different from that on La$_2$O$_3$ crystallites, suggesting a different form of La on the anatase surface. Second, CO chemisorption on Ti$^{3+}$ sites occur in A but not on AL samples, indicating that the surface redox properties of A has been modified in the AL samples. Third, the frequency of the CO stretch is different for CO adsorption on TiO$_2$/CuO with and without La$_2$O$_3$, again suggesting that the presence of La is altering the electronic properties of the ALC surface. These observations can be explained if a layer of LaO$_x$ is present on the titania surface. The presence of a LaO$_x$ surface phase on titania has been previously noted by Nair et al. [27]. They suggest that La$^{3+}$ wets the surface of the titania particles. Similar surface LaO$_x$ phases have been proposed on alumina [28]. LaO$_x$ species decorating the surface of Ni crystallites has also been proposed as the active catalyst in CO$_2$ reforming of CH$_4$ to synthesis gas. The role of LaO$_x$ was thought to involve storage of CO$_2$ in the form of La$_2$O$_2$CO$_3$ and releasing it to appropriate Ni-based reaction sites [29].

We propose that the presence of lanthanum oxide on the anatase surface is providing the sites for adsorption of the reaction intermediates during CO and CH$_4$ oxidation. On the anatase surface at high temperatures, there would be no way to detect these species. The stability of lanthanum carbonates at high temperatures [24] is making it possible to observe the extent of reaction on TiO$_2$. Previous studies have noted the formation of carbonates upon CO oxidation on Cu/Al$_2$O$_3$ support, with the Al$_2$O$_3$ playing a similar role to that of LaO$_x$ on the AL and ALC samples [14,22]. However, the carbonates were not used for the type of diagnostic study that we have presented in this paper.

4.2. Sensing mechanism

Since we are trying to correlate the resistance change during sensing with the infrared data, it is important to highlight the relationship between these measurements. In order for resistance changes to occur, oxidation of CO/CH$_4$ must involve reaction with O$^-$ (ads) on the titania surface, desorption of the oxidation products from titania and the release of electrons into the bulk solid. Thus, if carbonate species remain on the anatase surface, then resistance change is not going to be manifested. We do not observe any carbonate species on the anatase surface in the A sample, indicating that at the temperatures at which infrared measurements are being made, most of the carbonates have desorbed. However, in the AL and ALC samples, we do observe intermediate carbonate species that we assign as

![Fig. 7. Infrared data for the CH$_4$ reaction at a heater setting of 1073 K on (a) anatase; (b) La$_2$O$_3$; (c) anatase/La$_2$O$_3$; (d) anatase/La$_2$O$_3$/CuO.](image)
originating from the LaOx on the anatase surface. We propose that these lanthanum carbonates are not influencing the resistance of the sample, as they are formed by release of oxidation products from the anatase surface and immediate interaction with the LaOx because of the intimate contact of LaOx with the anatase.

Of primary interest is the difference in sensing behavior of ALC towards CO and CH4. We discuss the CO results first. Studies indicate two forms of copper on supported catalysts. For CuO/Al2O3, a Cu2+ surface phase as well as discrete CuO particles were found to be present on Al2O3 [30]. Jiang et al. also report that highly dispersed CuO is present on La2O3–CuO/Al2O3 catalysts [16]. Larsson et al. have found that CuO/TiO2 consist of well dispersed CuO species as well as CuO crystallites [6]. The dispersed CuO species have high catalytic activity for combustion and similar results have also been reported for Cu–Ce oxide catalysts [6]. We have reported that transmission electron microscopy of ALC indicated the presence of nanometer-sized CuO crystallites decorating the surface of anatase [4]. No evidence was found for a distinct CuO coating on the titania by electron microscopy indicating that such a layer, if present, must be very thin with the copper well dispersed.

The role of these two types of copper on oxidation reactions has been discussed in the literature. Cu(II)–SnO2 system has been investigated for catalytic oxidation of CO and the role of Cu2+ has been proposed to be a scavenger of electrons following reaction of CO with surface oxygen (O2−) and desorption of CO2. In this case, only surface Cu2+ was proposed to be active, and formation of CuO was predicted to kill catalytic activity [31]. Park and Ledford have examined the catalytic activity of CuO/Al2O3 towards CO and CH4 oxidation. They noted that CO oxidation is promoted on distinct CuO crystallites, but poor on the highly dispersed Cu2+ surface phase on Al2O3 [30]. Two pathways that have been proposed for CO oxidation on Cu/TiO2 and Cu/ZnO include direct oxidation of CO adsorbed on metallic particles by gas phase oxygen or reaction of the adsorbed CO at the metal/metal oxide interface with surface lattice oxygens to form carbonate-like species that are desorbed as CO2 [13]. The latter pathway can be written as follows:

\[
\text{CuO} \cdot \text{O}_2 \rightarrow \text{CO} \Rightarrow \text{CuO} \cdot \text{CO}_2 \rightarrow \text{Cu} + \text{CO}_2 + \text{O}_2
\]

The copper valence in the catalytic reaction was proposed to cycle between Cu(II) and Cu(0) [32]. A redox cycle mechanism involving CuO and Cu2O has also been proposed for CO oxidation on CuO [33].

With this background on CO reactions on Cu, we discuss two interrelated issues. First, why does the ALC sensor, even though it adsorbs more CO, have a lower sensitivity (smaller \(R/R_0\)) than the A and AL sensor (Fig. 1). Second, why is the sensitivity of the ALC sensor reduced in the O2 environment as compared to anaerobic environment (Fig. 3) [4]. Based on the IR studies, it is clear that the addition of CuO to the AL sample improves the adsorption of CO via reduction of the CuO surface, thereby providing sites for CO adsorption. The resistance change that is measured upon CO sensing indicates that adsorbed oxygen species on TiO2 (O2−, O−, O2−) are involved in the CO oxidation. A possible reaction model would involve adsorption of CO on the reduced CuO on anatase and migration of CO to the Cu–TiO2 interface, where the oxidation occurs [4]. In an anaerobic environment, the oxygen species on the anatase are the main source for CO oxidation. Since the adsorption of CO on the ALC sensor is larger, the ALC sensor should have higher sensitivity than A or AL, since more oxygen on the titania surface is reacting.

The other issue of importance is the insensitivity of ALC towards CH4 sensing. We have seen no evidence for any chemisorption of CH4 to the surface. This is probably not surprising, considering that the H’s do not provide a convenient atom for chemisorption and the C is saturated. The infrared data provide clues regarding the insensitivity of ALC towards CH4. In the case of AL sample, monodentate carbonate species are evident for both CO and CH4 oxidation, however, in the presence of CuO, the carbonate bands have disappeared in the case of CH4 reaction. The lowered reactivity of CH4 directly on the anatase surface in ALC is also evident from the data shown in Fig. 2, which shows the relative resistance changes as a function of O2 in the gas stream. There is increased sensitivity towards CO when decreased amounts of oxygen are present, indicating enhanced reaction on the anatase surface. In the case of methane oxidation, the same cannot be said. While on A, the oxygen dependence is apparent, the sensitivity of methane on ALC is relatively independent of oxygen, indicating lower reactivity with the anatase surface even under low oxygen concentrations.

We propose that the inhibition of CH4 reaction on the anatase in ALC is related to the catalytic activity of the CuO. Optimal CH4 oxidation has been reported for isolated Cu2+ species on Al2O3 [30]. Studies where bulk CuO was dispersed in a matrix have shown a decrease in methane oxidation activity compared to samples of similar concentrations made with wet impregnation techniques [34]. The sensing temperatures of 873 K is near the reported values of 50% oxidation (\(T_50\)) for methane by CuO based catalysts [35], and the presence of La2O3 is known to lower the \(T_50\) and \(T_{90}\) of CuO, suggesting that oxidation of CH4 must be occurring on AL. Though, it has been reported that in an anaerobic environment on Cu/TiO2 catalysts, metal Ti\(^{n+}\) (n < 4) or metal Ti\(^{n+}\)–O\(^{m-}\) sites can activate CH4 as well as promote the decomposition of intermediate oxidation products, the presence of oxygen may minimize the importance of this pathway [36]. La2O3 is also known to promote the activity of CuO/γ-Al2O3 towards CO and CH4 oxidation by...
increasing the oxygen recovery rate on the CuO [16]. This would also promote oxidation on the CuO without involving titania, and is the most likely pathway for methane oxidation. So, both CO and CH₄ are getting oxidized on the copper species, but methane appears to have minimal interaction with the anatase surface, suggesting that the type of copper species being formed on the ALC sample is an excellent catalyst towards CH₄ oxidation.

A second hypothesis for why the ALC samples show no resistance change upon exposure to CH₄ could arise from the fact that the products and intermediates of the CH₄ oxidation, such as water, can adsorb onto the surface of the sensor and trap electrons. When water is adsorbed in molecular form it can have donor properties [37]

\[ \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ (\text{ads}) + \text{e}^- , \]

however, if water is adsorbed dissociatively as hydroxyl groups, it will behave as an acceptor [37]

\[ \text{H}_2\text{O} + \text{O}_0 \rightarrow 2\text{OH} (\text{ads}) \]

\[ \text{OH} (\text{ads}) + 2\text{e}^- \rightarrow 2\text{OH}^- (\text{ads}) \]

At lower temperature, there would be mostly molecular adsorption, and as the temperature increases, the water would adsorb more in the form of a hydroxyl group. Giber et al. noted that for H₂O sensing between 853 and 923 K, the resistance ratio \((R/R_0)\) decreases, whereas there is an increase in \(R/R_0\) between 923 and 1053 K, consistent with the explanation that at higher temperatures, the OH from H₂O (product of H₂ oxidation) is trapping electrons [37]. We have noted the creation of OH groups on the sample surface during methane oxidation. Even though such an electron trapping mechanism could play a role, the lack of any carbonate products on the ALC surface indicates that the modification of the chemical reactivity of CH₄ is more important.

4.3. Response times

The increased response time for the ALC versus the AL sample can be explained based on the ease of oxygen readsoption and the role of the reduced Cu. We have assigned the IR spectrum of the intermediates formed upon CO oxidation on the ALC surface as due to polydentate carbonates partly held by the Cu. Upon turning off the CO, these Cu species can get oxidized by O₂, releasing the carbonate as CO₂ and freeing up the surface sites for oxygen readsoption. In the case of AL samples, the carbonates are bound to the surface and not influenced by redox chemistry and will be replaced by O₂ at slower rates.

5. Conclusion

An anatase based semiconducting oxide sensor was discovered to be selective for CO sensing with almost complete discrimination against CH₄ at operating temperatures of 873 K. In order to maintain the anatase phase, La₂O₃ was added which inhibited the anatase to rutile transformation. The lanthanum oxide layer that formed on the anatase also served as an excellent probe for monitoring the extent of CO and CH₄ oxidation on the anatase by trapping the reaction products as carbonates, which could be readily detected by high temperature diffuse reflectance infrared spectroscopy. The key player in achieving selectivity towards CO versus CH₄ was CuO, which efficiently catalyzed CH₄ oxidation, thus, minimizing the reaction of CH₄ on the anatase surface.

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