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Titanium dioxide based high temperature carbon monoxide selective sensor

Nancy O. Savage[a], Sheikh A. Akbar[b], Prabir K. Dutta[a,*]

[a]Department of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, OH 43210, USA
[b]Department of Materials Science and Engineering, The Ohio State University, 2041 College Road, Columbus, OH 43210, USA

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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_2O 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_2O_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

* Corresponding author.

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catalyst than cobalt, manganese and iron oxides on titania [6]. In the present study, we compare the sensing behavior of anatase towards CO and CH_4 in an oxidizing environment more typical of practical applications, and find that the presence of CuO produces a CO sensor that discriminates against CH_4. 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/La_2O_3, anatase/La_2O_3/CuO and TiO_2/CuO were made by ball-milling commercial grade TiO_2 (anatase) with the desired weight percent of La_2O_3 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% O_2/N_2 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 Acquistion/Switch Unit (HP 34970A). Prior to starting sensing measurements, sensors were kept at 873 K and 5% O_2/N_2 for 2 h to allow for sample equilibration. Additional sensing measurements were made after the sample had been at 873 K and 5% O_2 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 N_2. A background measurement was made under a flow of 5% O_2/N_2, first at a 1073 K, and then at room temperature. The sample gas (either CO, CO_2 or CH_4) 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 La_2O_3 in KBr, La_2O_3/CuO in KBr and TiO_2/CuO to clarify some aspects of the AL and ALC spectra.

All the infrared data are reported in Kubelka Munk units: $KM = (1-r)^2/2r$, where r is the relative reflectance (r_s/r_0). The reference reflectance (r_0) is the single channel reflectance of a sample under a flow of 5% O_2/N_2 (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 CH_4. 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

TiO_2 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 TiO_2 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, La_2O_3 needed to be added to the anatase/

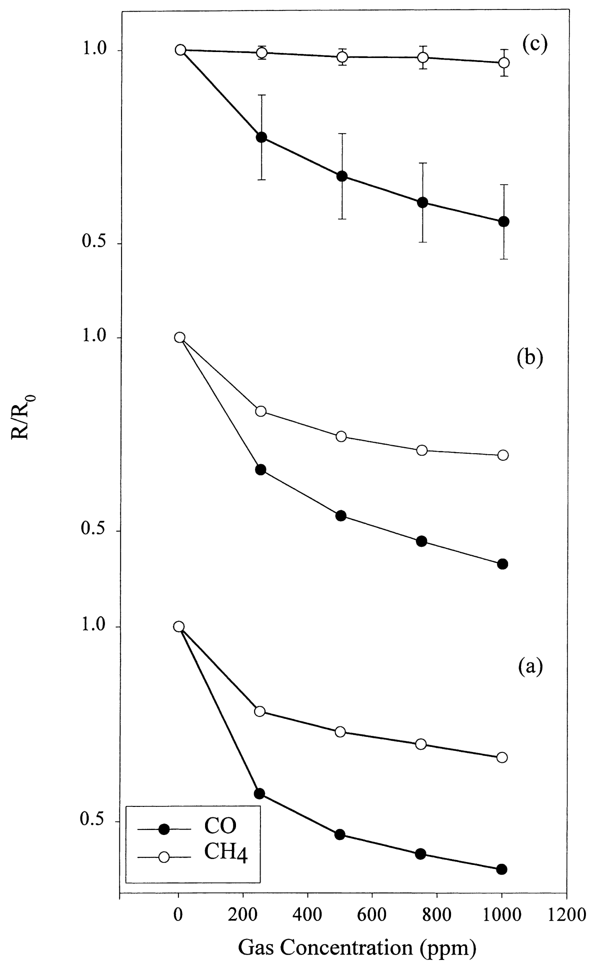

Fig. 1. Response of sensors to CO and CH_4 at 873 K in a background atmosphere of 5% O_2/N_2 balance (a) anatase; (b) anatase/La_2O_3; (c) anatase/La_2O_3/CuO.

CuO [4]. The three samples that form the focus of the present investigation are anatase (A), anatase/La_2O_3 (AL) and anatase/La_2O_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_2O_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

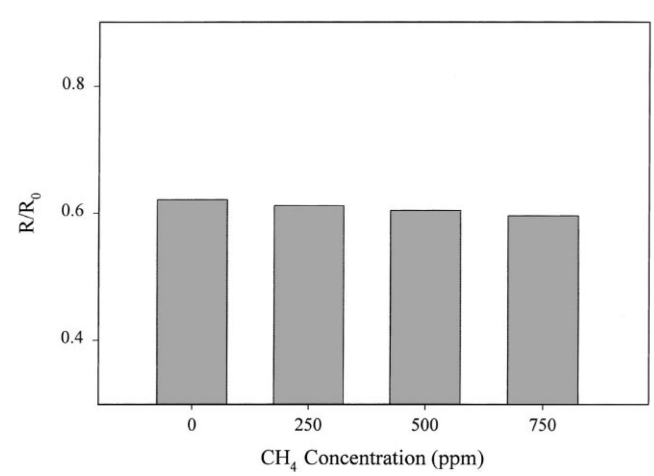

Fig. 2. Response of anatase/La_2O_3/CuO sensor to CH_4 in a background gas of 500 ppm CO/5% O_2/N_2 balance at 873 K.

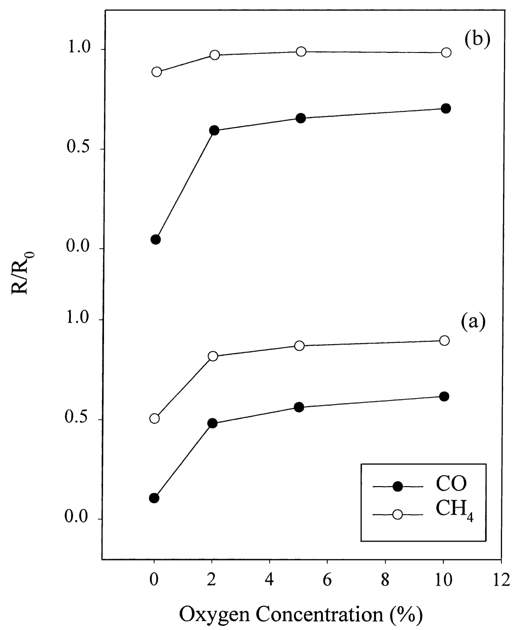

Fig. 3. Effect of oxygen concentration on the relative resistance change of TiO_2 sensors upon exposure to 750 ppm CO or 750 ppm CH_4 at 873 K (N_2 makes up the balance of the gas mixture) (a) anatase; (b) anatase/La_2O_3/CuO.

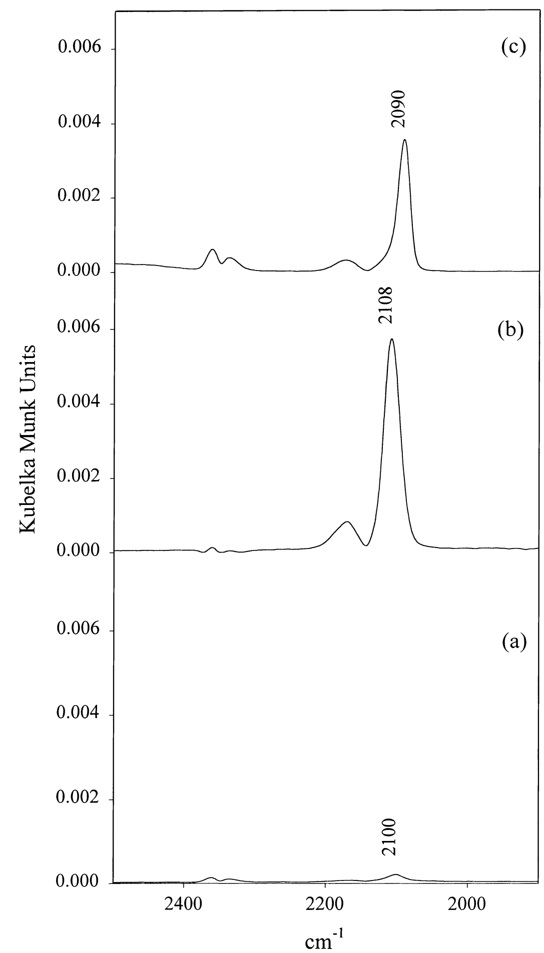

Fig. 4. Infrared data of (a) anatase, (b) TiO_2/CuO and (c) anatase/La_2O_3/CuO at room temperature after exposure to CO at a heater setting of 1073 K. Measurement made under a flow of 5% O_2/N_2 balance.

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^0, 2105–2130 cm^{-1}; Cu^+, 2115–2130 cm^{-1} and on Cu^{2+} leads to bands between 2140 to 2190 cm^{-1} at temperatures below 77 K [13–15]. Based on this literature, we assign the 2108 cm^{-1} band on TiO_2/CuO and the 2090 cm^{-1} on ALC to CO adsorption on Cu^0. Inclusion of La_2O_3 in the ALC sample appears to make the surface more electron-rich and leads to an 18 cm^{-1} red shift. The effect of La_2O_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^0 in an oxidizing environment at elevated temperatures. No CO chemisorption was noted on La_2O_3 or La_2O_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_4, there was no evidence of chemisorption on any of the samples. Replacing the CH_4 in the gas stream by O_2/N_2 led to the loss of IR bands due to CH_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^{-1} region at heater settings of 1073 K. As mentioned earlier, for both CO and CH_4 reactions on the samples, CO_2 was found to be a product. In order to distinguish the reaction intermediates formed on the sample surfaces during CO and CH_4 oxidation from species formed via adsorption of the product gas CO_2, we examined the IR spectra upon CO_2 reaction with La_2O_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^{-1} on La_2O_3 and weaker bands at 1515 and 1376 cm^{-1} on ALC. This frequency range is typical of the asymmetric stretching vibration (v_3) of the carbonate ion [17]. Splitting of the v_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_3 band, $\sim$100 and $\sim$300 cm^{-1} for mono and bidentate, respectively. $La_2(CO)_3{\cdot}8H_2O$ is reported to have strong infrared bands at 1460 and 1360 cm^{-1}, with a shoulder at 1330 cm^{-1} and assigned to a monodentate coordinated carbonate group [18]. Thus, considering that the splitting is of the order of 52 and 139 cm^{-1} on La_2O_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_2O_3.

Fig. 6 shows the data for CO reaction on A, La_2O_3, AL and ALC surfaces. The frequencies of the IR bands are distinct from those shown in Fig. 5 formed via CO_2 reaction, indicating that we are not observing bands related to the mere readsorption of the reaction product CO_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_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^{-1} assigned to bicarbonate species have been reported on exposure of anatase to CO [11]. Bands around 1370, 1680 cm^{-1} assigned to carbonylate like species have been reported upon exposure of anatase to CO at room temperature, but these species disappear at $\sim$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_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_2, pre-treated at various temperatures. These experiments were done at 329 K and evidence was found for mono, bidentate and carbonylate species [21]. Supported CuO has been reported to exhibit infrared absorptions for bidentate and monodentate carbonates in the presence of either CO or CO_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.

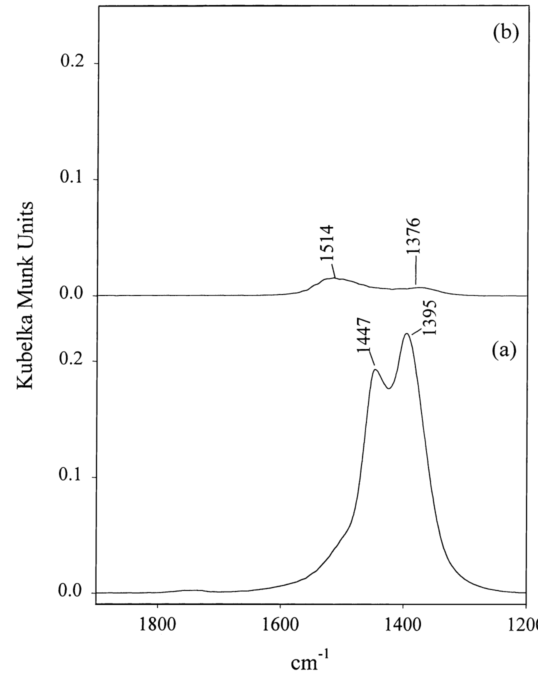

Fig. 5. Infrared data for the CO_2 reaction at a heater setting of 1073 K on (a) La_2O_3; (b) anatase/La_2O_3/CuO.

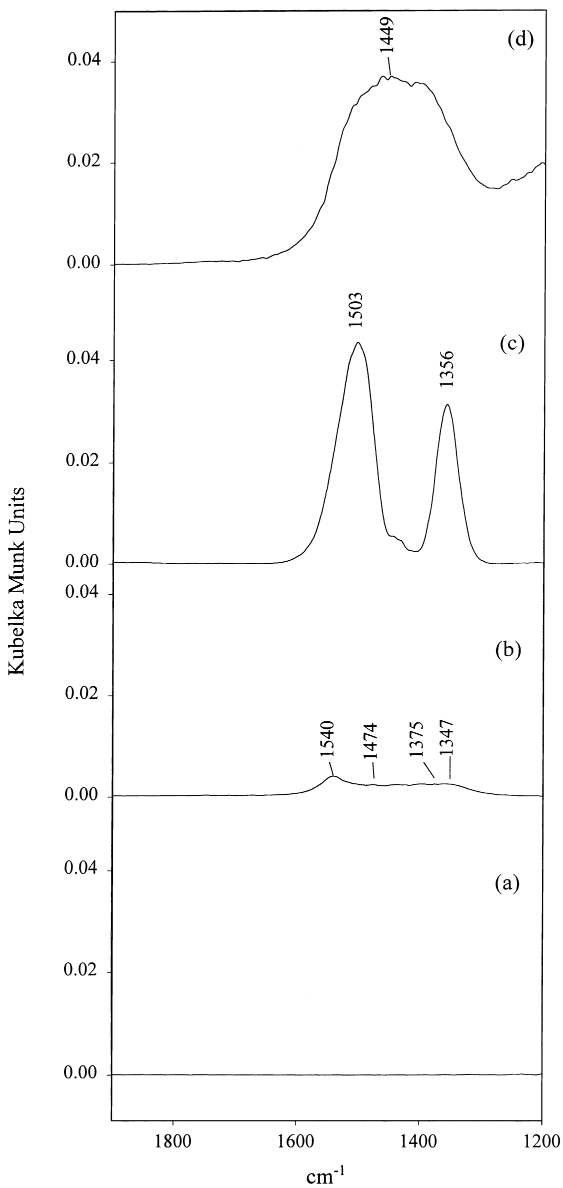

Fig. 6. Infrared data for the CO reaction at a heater setting of 1073 K on (a) anatase; (b) La_2O_3; (c) anatase/La_2O_3; (d) anatase/La_2O_3/CuO.

Upon addition of La_2O_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_2O_3 in the AL and ALC samples, pure La_2O_3 was also examined. In the case of CO reaction on La_2O_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_2O_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_2O_3 are assigned to bidentate and monodentate carbonates, respectively. Rosynek and Magnuson assign mondentate carbonates at 1500 and 1390 cm^{-1}, with bidentate carbonates at 1565 and 1310 cm^{-1} on La_2O_3 [23]. Tsyganenko et al. have reported carbonate bands formed via CO oxidation on La_2O_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 $\Delta\nu_3$ 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 π-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_2O_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_2O_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_2O_3 (combination of Figs. 5a and 7b). Thus, free La_2O_3 may be contributing to the infrared spectra. The difference between the CH_4 and CO oxidation on La_2O_3 may arise from the fact that CH_4 oxidation leads to formation of H_2O. La_2O_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_2O_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

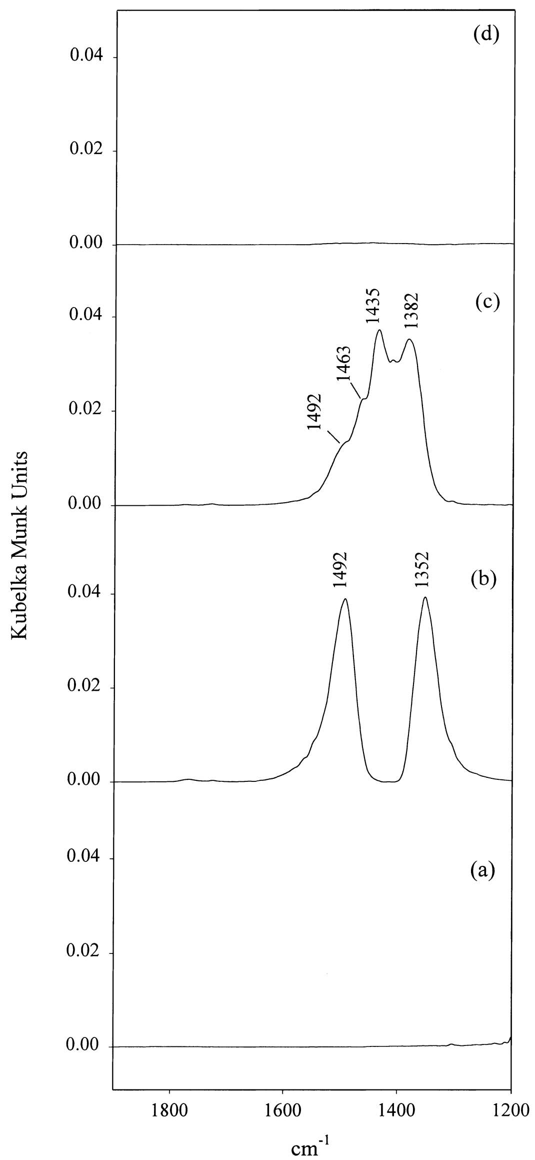

Fig. 7. Infrared data for the CH_4 reaction at a heater setting of 1073 K on (a) anatase; (b) La_2O_3; (c) anatase/La_2O_3; (d) anatase/La_2O_3/CuO.

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_2O_3

In an earlier study, we have reported electron microscopic studies on the ALC sample [4]. Though, La_2O_3 could be observed as discrete particles, no evidence of any La_2O_3 on the anatase was found. However, since the phase transformation of anatase to rutile is being inhibited upon the addition of La_2O_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_2O_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_2O_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 $La_2O_2CO_3$ 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_2O_3 support, with the Al_2O_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^{n-}(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 originating from the LaO_x 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 LaO_x because of the intimate contact of LaO_x with the anatase.

Of primary interest is the difference in sensing behavior of ALC towards CO and CH_4. We discuss the CO results first. Studies indicate two forms of copper on supported catalysts. For CuO/Al_2O_3, a Cu^{2+} surface phase as well as discrete CuO particles were found to be present on Al_2O_3 [30]. Jiang et al. also report that highly dispersed CuO is present on La_2O_3–CuO/γ-Al_2O_3 catalysts [16]. Larsson et al. have found that CuO/TiO_2 consist of well dispersed CuO_x species as well as CuO crystallites [6]. The dispersed CuO_x 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_x 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)–SnO_2 system has been investigated for catalytic oxidation of CO and the role of Cu^{2+} has been proposed to be a scavenger of electrons following reaction of CO with surface oxygen (O^{2-}) and desorption of CO_2. In this case, only surface Cu^{2+} 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/Al_2O_3 towards CO and CH_4 oxidation. They noted that CO oxidation is promoted on distinct CuO crystallites, but poor on the highly dispersed Cu^{2+} surface phase on Al_2O_3 [30]. Two pathways that have been proposed for CO oxidation on Cu/TiO_2 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 CO_2 [13]. The latter pathway can be written as follows:

$$\mathrm{CuO\cdot O_2(O_{ads}) + CO \Rightarrow CuO\cdot OCO_2(O_{ads})}$$
$$\mathrm{\Rightarrow Cu + CO_2 + O_2(O_{ads})}$$

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 Cu_2O 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 O_2 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 TiO_2 (O_2^-, O^-, O^{2-}) 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–TiO_2 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. In the presence of O_2, direct oxidation of CO on the copper species can occur, without involvement of TiO_2, which would lead to decreased sensitivity, as compared to A and AL, where reaction has to occur on the anatase surface.

The other issue of importance is the insensitivity of ALC towards CH_4 sensing. We have seen no evidence for any chemisorption of CH_4 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 CH_4. In the case of AL sample, monodentate carbonate species are evident for both CO and CH_4 oxidation, however, in the presence of CuO, the carbonate bands have disappeared in the case of CH_4 reaction. The lowered reactivity of CH_4 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 O_2 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 CH_4 reaction on the anatase in ALC is related to the catalytic activity of the CuO. Optimal CH_4 oxidation has been reported for isolated Cu^{2+} species on Al_2O_3 [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 La_2O_3 is known to lower the T_{50} and T_{99} of CuO, suggesting that oxidation of CH_4 must be occurring on ALC. Though, it has been reported that in an anaerobic environment on Cu/TiO_2 catalysts, metal Ti^{n+} ($n < 4$) or metal Ti^{n+}–O^{m-} sites can activate CH_4 as well as promote the decomposition of intermediate oxidation products, the presence of oxygen may minimize the importance of this pathway [36]. La_2O_3 is also known to promote the activity of CuO/γ-Al_2O_3 towards CO and CH_4 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 CH_4 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 CH_4 oxidation.

A second hypothesis for why the ALC samples show no resistance change upon exposure to CH_4 could arise from the fact that the products and intermediates of the CH_4 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]

$$H_2O \rightarrow H_2O^*(\mathrm{ads}) + e^-,$$

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

$$H_2O + O_0 \rightarrow 2OH_{(\mathrm{ads})}$$

$$OH_{(\mathrm{ads})} + 2e^- \rightarrow 2OH^-_{(\mathrm{ads})}$$

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 H_2 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 H_2O (product of H_2 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 CH_4 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 readsorption 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 O_2, releasing the carbonate as CO_2 and freeing up the surface sites for oxygen readsorption. In the case of AL samples, the carbonates are bound to the surface and not influenced by redox chemistry and will be replaced by O_2 at slower rates.

5. Conclusion

An anatase based semiconducting oxide sensor was discovered to be selective for CO sensing with almost complete discrimination against CH_4 at operating temperatures of 873 K. In order to maintain the anatase phase, La_2O_3 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 CH_4 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 CH_4 was CuO, which efficiently catalyzed CH_4 oxidation, thus, minimizing the reaction of CH_4 on the anatase surface.

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