

FEASIBILITY OF USING OSCILLATORY CATALYTIC OXIDATION PHENOMENON FOR SELECTIVE CARBON MONOXIDE SENSING

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Tin dioxide based sensors with different additives were constructed and tested in air environment containing carbon monoxide. Conductance oscillations were observed in samples containing palladium but not in those without. Oscillations occurred at temperatures ranging from 150°C to 320°C. Within this temperature region the range of CO concentrations at which oscillations appeared became higher as the test temperature increased. The lowest CO concentration at which oscillations were observed was 200 ppm and the highest 10000 ppm.

By comparing sensor responses obtained in synthetic and ambient air it was concluded that water vapour has a major influence on oscillations and increases the frequency. The ranges of CO concentrations in which oscillations occurred at different temperatures, however, remained roughly the same in both environments. It was also noticed that processing conditions had an influence on the oscillatory response characteristics of the sensors.

1. INTRODUCTION

Small amounts of CO together with oxygen have been found to cause conductance oscillations in tin dioxide based semiconductor gas sensors^{1,2,3}. These oscillations have been observed when sensors contain noble metal catalysts. The domain of appearance has been in the temperature range of 150°C to 300°C and in the CO concentration range of 500 to 8000 ppm.

It has also been noted that at any particular temperature the period and the amplitude of the oscillations depend on CO concentration. These observations have evoked the question as to whether this phenomenon could be put to use as the operation principle of a selective CO sensor.

In this study the applicability and reproducibility of SnO₂-based sensors is evaluated so as to establish the feasibility of using the oscillatory oxidation phenomenon as the basis of CO sensing. For this purpose sensors of different compositions were manufactured, some with addition of palladium and some without. The sensors were fabricated using thick film technology. The base material was SnO₂ to which Pd was added as the catalyst.

Oscillation characteristics of these sensors were investigated. Comparisons were made between sensors with the same composition but sintered at different temperatures. The ranges of CO concentration in which oscillations occurred at different sensor operating temperatures were determined. Measurements were carried out in synthetic and ambient air environments so as to evaluate the importance of the environment on the oscillation response of the sensors to CO.

The oscillations observed can be attributed to the oscillatory catalytic oxidation of CO. This aspect is discussed in terms of CO oxidation on supported noble metal catalyst.

2. EXPERIMENTAL PROCEDURE

The constituents of the sensing material were mixed with organic component to form a paste capable of being screen printed. One composition was similar to that used by S. Kanefusa et al² which was SnO₂ containing 1 wt% PdCl₂, 1 wt% Mg(NO₃)₂, 5 wt% ThO₂ and 2 wt%

SiO₂. Two other compositions were similar except that one of them was prepared without ThO₂ and the other without PdCl₂. The fourth composition contained only SnO₂ with 2 wt% SiO₂.

Sensors were fabricated using thick film technology⁴. The final sintering of the gas sensitive layer was carried out in a belt furnace at peak temperatures of 600°C and 850°C. The sintering time was 15 min.

The current responses of the sensors were measured at temperatures ranging from 150°C to 320°C. In the case where temperature control was accomplished by a platinum resistor printed on the reverse side of the substrate supporting the sensor, the sensors were placed in a glass chamber. A temperature-controlled oven with a CrNi-Ni thermocouple was used to calibrate the heating resistors. This oven was also used in some response measurements to ensure identical thermal conditions for the samples being compared.

The concentration of the gas was adjusted by mixing 1 vol% of CO in N₂ with synthetic air in a gas blender. Synthetic air was used to eliminate the influence of water vapour. The water content in the synthetic air used was around 10 ppm. In some experiments normal ambient air from the compressed air delivery system was used so as to evaluate the effect of water vapour.

In order to record responses and oscillations the sensors were connected, 4 to 7 at a time, with a 10 V DC voltage source and series resistors over which the voltages were recorded.

3. RESULTS

Oscillations occurred with sensors containing Pd at temperatures from 150°C to 320°C. Oscillatory behaviour varied widely with gas environment and temperature. Oscillations were found to be statistical in nature. Some variation around the mean value was observed in frequency and amplitude. The oscillatory behaviour seemed to be associated with the presence of Pd since oscillations were not observed when sensors did not contain Pd. Other additives did not greatly influence sensing characteristics. The oscillatory behaviour with and without ThO₂ were very similar.

For the sensor sintered at 600°C (Sample 1) at the test temperature of 150°C the oscillations occurred at the concentration of 200 ppm CO in synthetic air. The amplitude was 2.5 μA, or 33% of the maximum value of the oscillating current, and the period was ~3 min. For the sensor sintered at 850°C (Sample 2) oscillations occurred in the CO concentration range of 200–400 ppm. Only at a CO concentration of 400 ppm were the oscillations regular with a period of ~1 min and amplitude of 0.6 μA, or 75% of the maximum value of the oscillating current. At the temperature of 170°C the range where the oscillations occurred was 200–400 ppm of CO in synthetic air with Sample 1 and 400–800 ppm with Sample 2. The periods at 400 ppm of CO were ~3 min and 1 min in Samples 1 and 2, respectively, and amplitudes as indicated in Table I and II. The oscillation waveform of Sample 2 at a CO concentration of 800 ppm is shown in Figure 1, which also shows the cessation of oscillation when the CO concentration is increased.

Figure 2 shows the current values obtained at 200°C. The recordings were made at CO concentrations of 1500 and 2600 ppm. The oscillation frequency is lower for the sensor sintered at the lower temperature. The periods at 1500 ppm of CO were 25 s and 12 s, respectively, in sensors sintered at 600°C and 850°C. The corresponding amplitudes were 3.8 μA and 3 μA or 37% and 60% of the maximum value of the oscillating current. The oscillation patterns were different (Figure 2a).

The oscillations ceased at a CO concentration of ~2500 ppm for the sensor sintered at 600°C. At higher concentrations this sensor showed a steady current reading which increased as the CO concentration increased. The period of the oscillations of the sensor sintered at 850°C was 13 s at a CO concentration of 2600 ppm (Figure 2b). For this sensor the oscillations continued up to a CO concentration of 4500 ppm with the period and amplitude

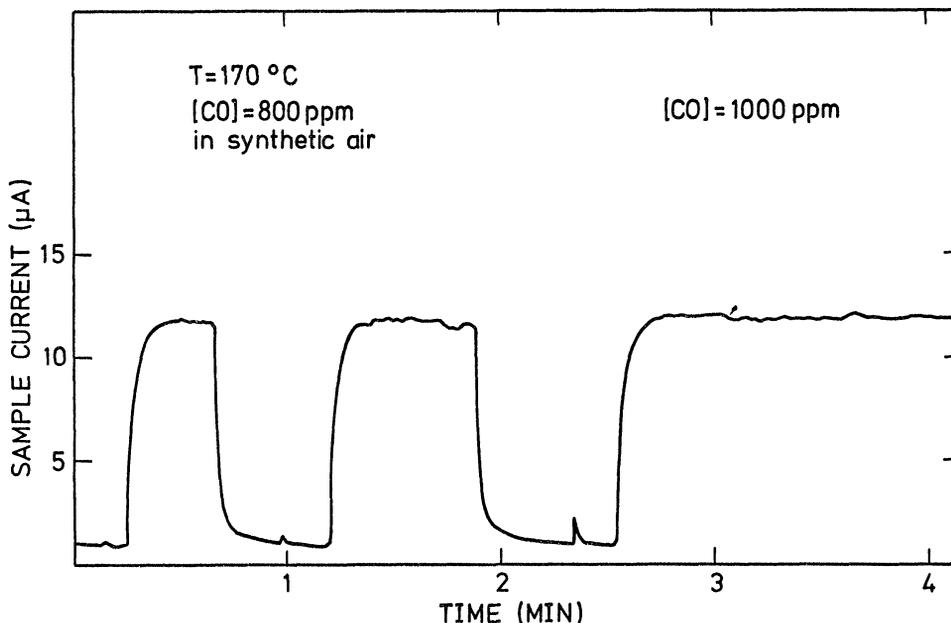


FIGURE 1 Oscillation waveform of sample 2 at 170°C in synthetic air. There is a cessation of the oscillation when CO concentration is increased from 800 to 1000 ppm.

increasing. This can be seen in Figure 3 which shows the dependence of the oscillation amplitude and period on CO concentration for Samples 1 and 2.

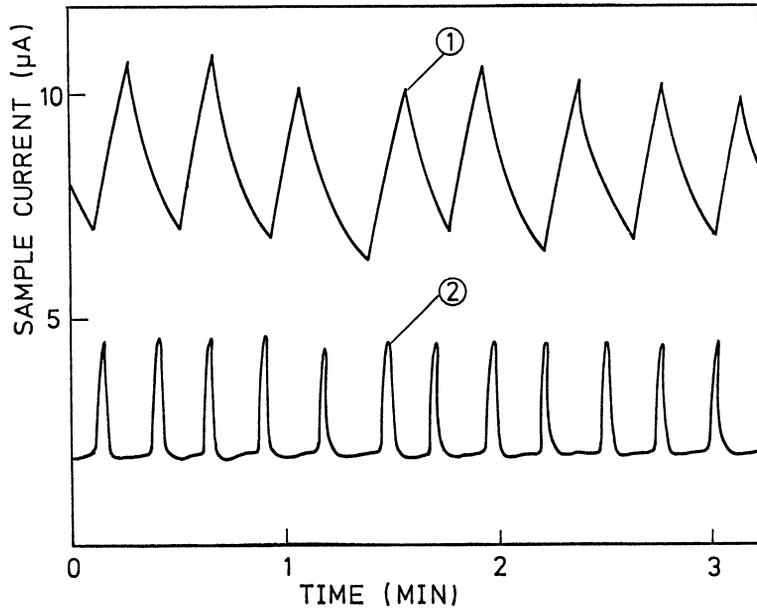
Generally it was noticed that the frequency of the oscillation was higher at higher test temperature (Table III and IV). Also the range of concentrations in which the oscillations appeared became higher with increasing test temperature as shown in Figure 4. For the sensor sintered at 600°C, for example, oscillations at the test temperatures of 300°C and 320°C occurred at the CO concentration of 10000 ppm or 1%, which was the highest concentration available with the experimental set-up. These oscillations were very quick, the shortest period being half a second.

The waveforms of the oscillation varied from a gentle gradient as seen in curve 1 in Figure 2a to a steep cut-off and onset. Even if the period was long the start-up and decline of the impulse could happen very quickly as is apparent from Figure 1. Between these two types a smooth oscillating waveform appeared, an example of which is shown in Figure 2b.

The oscillations recorded when compressed ambient air was the carrier gas had clearly higher frequencies than those with synthetic air as is apparent from Tables III and IV. The amplitudes of the oscillations remained essentially the same. The difference in frequency is believed to be caused by the influence of water vapour. The sensors without Pd addition showed a steady current reading the value of which in ambient air was about twice that in synthetic air.

The values of the test temperatures and the ranges of the concentration of CO in synthetic air in which oscillations appeared have been outlined in Figure 4 for two types of sensors with the same composition but different final sintering temperatures. It can be concluded that the oscillations tend to occur at lower concentration ranges for the sensor sintered at 600°C. At all temperatures and concentrations the oscillation period was longer for this sensor compared to that for the sensor sintered at 850°C as can be seen from Tables III and IV.

(a)



(b)

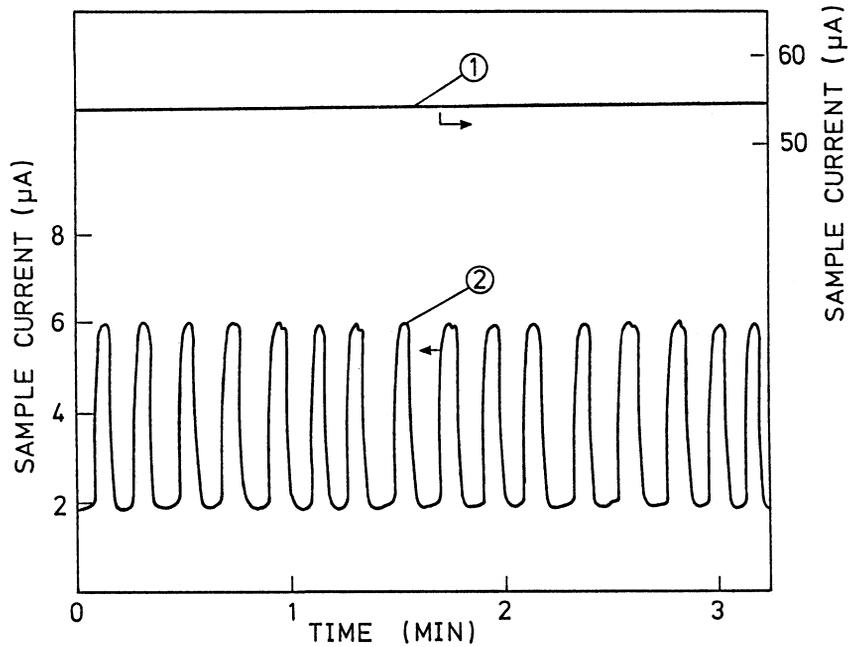


FIGURE 2 Current recordings at 200°C of samples sintered at 600°C (1) and 850°C (2). Carbon monoxide concentration in synthetic air was (a) 1500 ppm and (b) 2600 ppm.

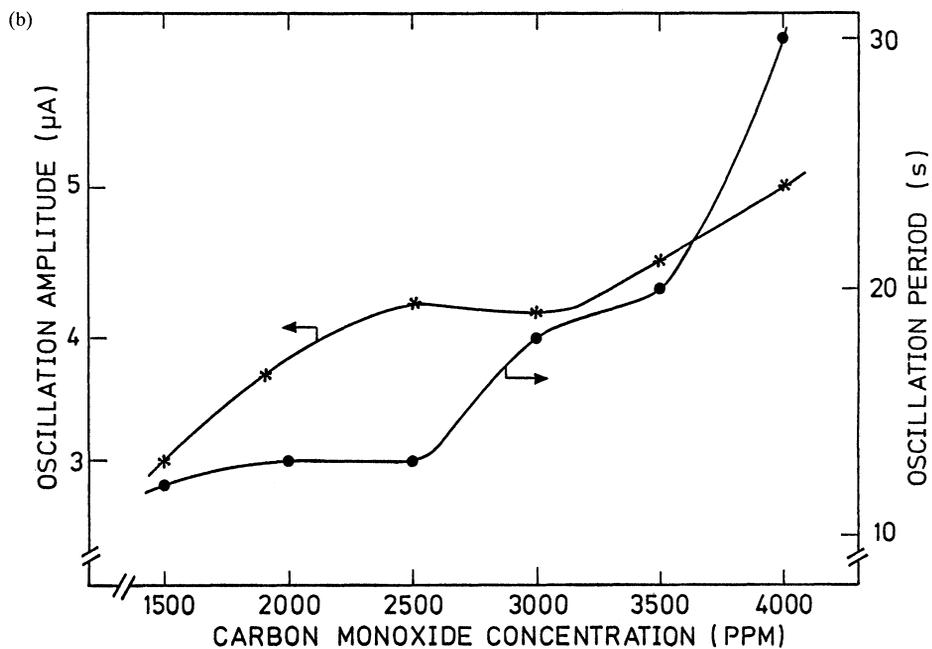
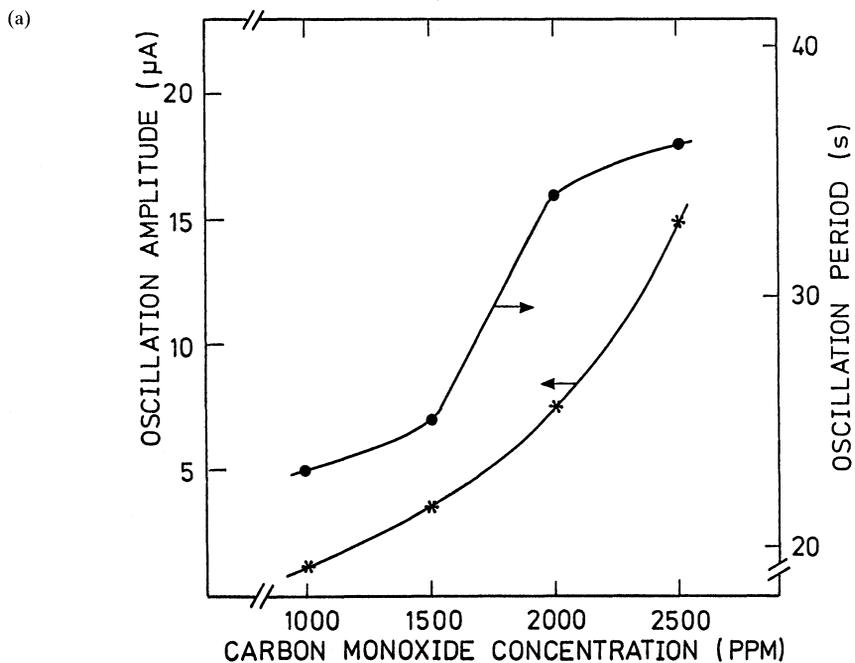


FIGURE 3 The dependence of oscillation amplitude and oscillation period on CO concentration in synthetic air. Test temperature was 200°C and sensors were sintered at (a) 600°C and (b) 850°C.

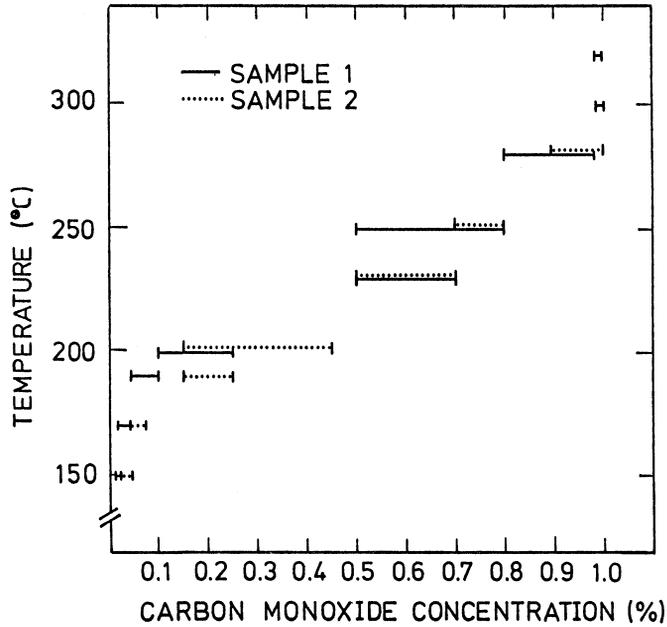


FIGURE 4 Ranges of CO concentrations in which oscillations occurred at different temperatures in synthetic air.

TABLE I
Oscillation amplitudes of Sample 1 at different temperatures and CO concentrations in synthetic air. The amplitude value (AV) and the maximum value (MV) of the oscillating current in μA are given.

Conc. of CO ppm	Test Temperature °C																	
	150		170		190		200		230		250		280		300		320	
	AV	MV	AV	MV	AV	MV	AV	MV	AV	MV	AV	MV	AV	MV	AV	MV	AV	MV
200	2.5	7.5	0.7	3.2														
400			5.6	12.3	15.1	17.1												
700					0.6	3.2												
1000							1.2	5.2										
1500							3.8	10.4										
2000							7.5	17.5										
2500							15	28										
3000																		
3500																		
4000																		
4500																		
5000									57	65	48	60						
6000									82	91	66	80						
7000									114	127	96	116						
8000											157	195	6.5	65				
9000													198	280				
10000													290	375	150	390	70	260

TABLE II

Oscillation amplitudes of Sample 2 at different temperatures and CO concentrations in synthetic air. The amplitude value (AV) and the maximum value (MV) of the oscillating current in μA are given.

Conc. of CO ppm	Test Temperature °C																	
	150		170		190		200		230		250		280		300		320	
	AV	MV	AV	MV	AV	MV	AV	MV	AV	MV	AV	MV	AV	MV	AV	MV	AV	MV
200	0.22	0.5																
400	0.6	0.8	4.5	7.5														
700			7.5	10.5														
1000																		
1500					2	2.65	3	5										
2000					2.9	3.65	3.7	5.6										
2500					3.8	4.65	4.25	6										
3000							4.2	5.7										
3500							4.4	5.8										
4000							5	5.8										
4500							5.1	6										
5000									5.2	8								
6000									7.5	10.2								
7000									9.8	13.6	10.2	15						
8000											12	16						
9000													16	31				
10000													39	56				

TABLE III

Periods of the oscillations in seconds in Sample 1 at different test temperatures and CO concentrations. Synthetic air (S) and ambient air (A) environments are indicated.

Conc. of CO ppm	Test Temperature °C																	
	150		170		190		200		230		250		280		300		320	
	S	A	S	A	S	A	S	A	S	A	S	A	S	A	S	A	S	A
200	168	14.4	53	2.9														
400			176	15	17			1.6										
700				28	28			2.7										
1000					41			23	4.4									
1500								25	6.1									
2000								34	20									
2500								36										
3000																		
3500																		
4000																		
5000									34	15								
6000									26	15								
7000									25	12	3.5							
8000										14	7.5	7						
9000												9						
10000												8	2.5		1	0.5		

TABLE IV
 Periods of the oscillations in seconds in Sample 2 at different test temperatures and CO concentrations. Synthetic air (S) and ambient air (A) environments are indicated.

Conc. of CO ppm	Test Temperature °C																	
	150		170		190		200		230		250		280		300		320	
	S	A	S	A	S	A	S	A	S	A	S	A	S	A	S	A	S	A
200																		
400	60	11	60	5														
700			50															
1000									1									
1500					21		12	1.1										
2000					26		13	1.3										
2500					30		13	1.6										
3000							18											
3500							20											
4000							30											
5000									38									
6000									18									
7000									14		9	0.5						
8000											11	0.8						
9000																	8	
10000																	8	

The oscillatory responses to CO in air were different for sensors from different fabrication batches with different sintering temperature even if the compositions were the same. Within the same batch the results of both frequency and amplitude measurements between two sensors appeared to be similar with an accuracy of about 10%.

The reproducibility of the repeated experiments on successive days was generally within 25%.

4. DISCUSSION

The catalytic oxidation of CO on supported noble metal catalyst is characterized by dual dependence of reaction rate on CO concentration. This rate has a maximum value at a certain CO concentration, perhaps some percent of CO in O₂. When CO concentration increases over that concentration the reaction order with respect to CO changes from positive to negative.

Oscillations can occur when the ratio of CO and oxygen concentrations is in the vicinity of that critical value.

According to E. McCarthy et al⁵ the rate R_o of catalytic oxidation of CO on supported Pt catalyst can be described as follows:

$$R_o = \frac{1}{1/k_1(\text{CO}) + (\text{CO})/k_2}$$

where (CO) is the CO concentration,

k₁ is the rate constant for the reaction CO + O_(a) → CO₂,

k₂ is the rate constant for the adsorption of oxygen and

O_(a) denotes the active chemisorbed form of oxygen on Pt.

This expression shows the maximum as a function of CO concentration. It also includes two distinct rate constants that dominate at different CO concentrations so that the rate

determining step of the overall reaction depends on CO concentration. Of the rate constants k_1 can be sensitive to crystallite size of the catalyst metal.

The rate of CO oxidation on supported Pt catalyst at different temperatures as a function of CO concentration was determined by E. McCarthy et al⁵. Their rate curves had maxima in the temperature range of 200°C–250°C approximately. This is comparable to the range in which oscillations were observed in this study, namely about 150°C–300°C.

It has also been observed that the maximum value of the CO oxidation rate is obtained at a higher CO concentration when the substrate temperature becomes higher^{5,6,7}. A similar effect was found in this study — the CO concentration ranges in which the oscillations occurred were higher at higher temperatures as shown in Figure 4.

In the oscillatory oxidation reaction of CO the adsorption and desorption steps can be critical. For example in the theory described above the dissociative adsorption of oxygen on noble metal catalyst is required to start the reaction. These adsorption and desorption steps can be influenced by other species adsorbed on the surface. In ambient air there is water vapour always present. The influence of water vapour can be the reason why the oscillations were quicker with CO in ambient air than with CO in synthetic air. Water vapour is known to increase the rate of CO oxidation on a solid catalyst. Water vapour also greatly enhances the sensitivity of semiconductor gas sensors to CO⁸.

A typical feature of sensors manufactured in this study was the variation of the oscillatory response to CO in frequency and amplitude and in some cases also in CO concentration where the oscillations appeared between different batches. This could be attributed to different particle and surface structures of the Pd catalyst. The difference in the oscillation frequency, for instance, was very clear between sensors sintered at different peak temperatures which were 600°C and 850°C.

How the oscillatory oxidation of CO by heterogeneous catalysis on sensor surface manifests itself as the oscillation of conductivity of the SnO₂ base material has not yet been unambiguously explained. In the present study of current oscillations the sharp decline of the current pulse and the quick onset of the current increase appear to be salient features. They mean quick decrease and increase in sensor conductance.

It has been suggested that the conductance oscillations could be due to the variation of temperature caused by the catalytic reaction. In the context of the oscillatory catalytic oxidation reaction of CO the thermal nature of the conductance variation must be excluded because this oxidation reaction has been pointed out to be isothermal under relevant conditions^{5,9}.

The rapid changes observed in the conductance cannot be explained by any slow process like electron transfer between surface species at particle boundaries and the material. Such transfers can change the conductivity by changing the heights of the energy barriers caused by surface charges at boundary surfaces between particles. But these charge transfer processes are much too slow at the test temperatures used in this study.

The barrier energies and consequently the conductance could, however, be changed even quickly by changes in the donor concentration of the SnO₂ material. The donor concentration could in turn be affected by changes in the stoichiometry due to oxidation or reduction reactions. Yet the quick oxidation of the SnO₂ surface by oxygen adsorbed directly from the atmosphere is not expected to happen, because this type of oxidation of the surface of SnO₂ has been found to be a slow process¹⁰.

One explanation for the quick decrease of the conductance could be the fast oxidation of the surface caused by dissociated active oxygen. This form of oxygen could be formed in a spill-over reaction over Pd (or any other noble metal) catalyst. After this step the oxidation of CO would start rapidly and result in the formation of CO₂ residing adsorbed at the surface. The reacting CO would partly reduce the SnO₂ surface. After the initial stage the rate of the CO oxidation reaction would decrease, as seen in Figure 1. When the saturation condition of surface CO₂ is reached quick desorption of CO₂ would happen giving way to a fast reoxidation step.

That the dissociated form of oxygen plays a role in the oscillation process has been demonstrated by quickly dropping the temperature of SnO₂ gas sensors from 380°C to 125°C¹¹. These sensors did not contain any noble metal catalyst. After the drop in temperature current oscillations appeared at 125°C and decayed away slowly. This thermal treatment is believed to leave dissociated oxygen ions (O⁻) formed on the surface at 380°C even at 125°C. This dissociated form of oxygen slowly vanishes which manifests itself as the slow decay of the oscillation.

Gases other than CO which show oscillatory behaviour include hydrogen and ammonia. According to Kanefusa et al² these oscillations occur around temperatures of 90°C (H₂) and 370°C (NH₃) which are outside the range of oscillations due to CO. As the sensor compositions were also different in both these cases there should be no interference by these gases when CO is being sensed using this technique.

6. CONCLUSIONS

Conductance oscillations in the presence of CO were observed in sensors containing Pd at temperatures between 150°C and 320°C. The range of CO concentration in which conductance oscillations occurred increased with increasing test temperature. At the lowest the concentration range was around 200 ppm CO and at the highest from 8000 to 10000 ppm. By controlling the sensor operating temperature different ranges of CO concentration could be utilized for detection.

The presence of water vapour seems to make oscillations rapid and clear. Even if it changes the frequency of oscillations the concentration ranges of the occurrence of oscillations seem to remain roughly the same.

Due to the statistical nature of the oscillations the surface and particle structure of the catalytic additive is probably critical. This means strict control of processing conditions is essential. On the other hand it allows the control of the sensing properties like the concentration range and oscillation frequency.

CO sensors utilizing the conductance oscillation phenomenon might find use, for example, in threshold value indicators or alarm systems. Better understanding of the phenomenon and control of fabrication and operation conditions could lead to feasible use of this type of sensor for more exact measurements. The specificity of the phenomenon seems to indicate that it is possible to obtain good selectivity under appropriate conditions.

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