57.1: Gas Sensing Properties of Catalytically Modified WO_3 with Copper and Vanadium for NH_3 Detection

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Abstract
Ammonia gas detection by pure and catalitically modified WO_3 based gas sensor was analysed. Sensor response of pure WO_3 to NH_3 was not only rather low but also presented an abnormal behaviour, probably due to the unselective oxidation of ammonia to NO_x. Copper and vanadium were introduced in different concentrations and the resulting material was annealed at different temperatures in order to improve the sensing properties for NH_3 detection. The introduction of copper and vanadium as catalytic additives improved the response to NH_3 and also eliminated the abnormal behaviour. Possible mechanisms of NH_3 reaction over these materials are discussed. Sensor responses to other gases like NO_2 or CO and interference of humidity on ammonia detection were also analysed so as to choose the best sensing element.

Keywords
WO_3, catalytic additives, NH_3, gas sensor

INTRODUCTION
Ammonia-gas detection is nowadays a very important target for different industrial processes, as it is used in many syntheses by chemical industries. Its control is also interesting for food freshness monitoring and human comfort in farming [1]. Besides, some pollutants such as NO_x are reduced by selective catalysts with NH_3, so an effective control of this gas is highly demanded in power plants and diesel exhausts in order to control the precise rate of NH_3 injection [2,3].

Current NH_3 measurement techniques, such as chromatography or infrared absorption, are often too expensive or not so fast to be used in a real time control systems. It is also very difficult to adapt these techniques to in-situ measurements. On the other hand, gas sensors based on metal oxides have been investigated for many years and present these advantages. Regarding NH_3 gas detection, some materials have been proposed, such as SnO_2[4], TiO_2[5], Nb_2O_5[6] or MoO_3 [7]. However, WO_3 has been recently reported as one of the most promising materials for this purpose and some works concerning its response to ammonia-gas [8], interference from NO_x [1] or influence of some other oxides introduced as additives [9] have been reported. In this paper we present gas sensor devices based on pure and catalytically modified nanocrystalline WO_3 powder, which was obtained by a sol-gel process from tungstic acid. It has been shown that this route is able to obtain pure WO_3 with a fine control over the crystalline properties and gas sensor devices based on this material have a high sensor response to NO_2 and a low response to CO and CH_4 [10]. We have now studied the response of this material to NH_3 and how it can be improved by the introduction of copper and vanadium as catalytic additives. Catalytic additives are often used in gas sensors based on metal oxides in order to improve not only the sensitivity but also the selectivity, response time and the power consumption, as they can reduce the optimum operating temperature of the gas sensor device. In our case, Cu and V were chosen as they have been successfully used in catalysis involving NH_3 [11,12]. These additives were introduced at different concentrations and the resulting material was annealed at different temperatures so as to achieve the optimal material for NH_3 detection. Although the target gas was ammonia, gas sensor response was also evaluated in NO_2, CO and humid synthetic air atmospheres in order to test the gas sensing properties of the obtained materials.

EXPERIMENTAL
Pure WO_3 nanocrystalline powders were obtained following a sol-gel route using tungstic acid (*Fluka*) as a precursor. Tungstic acid was dissolved in a mixture of methanol and water and then this solution was heated at 80°C for 24h under stirring in atmospheric air. Afterwards, it was heated at 110°C until drying. In the case of copper and vanadium catalytically modified WO_3, copper acetate or ammonium metavanadate (*Fluka*) were added respectively to the initial solution in 0.2% and 2% Cu/W and V/W percentages. The resulting material was annealed in a furnace under a flow of synthetic air at 400°C and 700°C for five hours. Using X-ray diffraction and Raman spectroscopy, nanocrystalline WO_3 was identified in all samples. However, no phase of copper or vanadium was found, probably due to their low concentration. Copper modified WO_3 in 0.2% will be named as WO_3:Cu(0.2%) and so on for the rest of materials.

The obtained powders were mixed with an organic vehicle to obtain a paste. Gas sensor devices were obtained by

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screen-printing of this paste over alumina substrates, which had already printed platinum electrodes on the front side and a platinum heater on the backside to control the operating temperature. These gas sensor devices were placed in a stainless steel test chamber where a controlled atmosphere was provided by means of mass flow controllers connected to a computer. The same computer, using acquisition boards, acquired the response of the sensors to different concentrations of NH_3, NO_2 and CO in synthetic dry and humid air. Gas sensor response was calculated as the resistance ratio R_{AIR}/R_{GAS} for reducing gases (NH_3 and CO) and R_{GAS}/R_{AIR} for NO_2 (oxidising gas). The operating temperature of the sensor devices was varied between 200°C and 350°C.

RESULTS

Fig. 1 shows the variation of the sensor resistance under a pulse of NH_3 (500 ppm) in air for different operating temperatures of the gas sensor device based on pure WO_3 annealed at 700°C. Sensor response was rather low (less than 5 for the whole range of temperatures studied). Moreover, this response presented an abnormal behaviour for temperatures over 300°C: an abrupt decrease of resistance followed by a slow increase when NH_3 was introduced and a reverse behaviour when NH_3 was removed. For lower temperatures, overshooting problems were found on the resistance value when NH_3 was removed, as the resistance was higher than before NH_3 introduction. Besides, recovery times were too long for the range of temperatures studied. A very similar sensor response was found in sensors based on pure WO_3 annealed at 400°C, so pure WO_3 was considered to be not suitable enough for NH_3 detection due to its low sensor

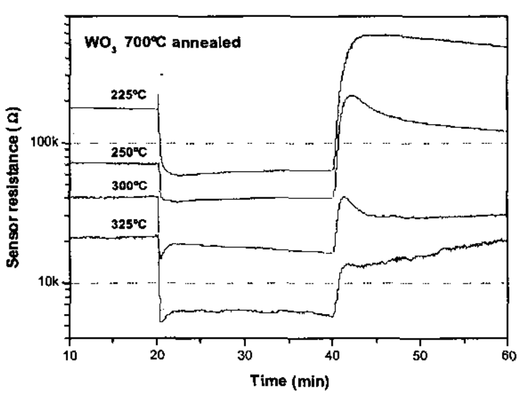

Figure 1. Variation of the pure WO_3 sensor resistance under a pulse of NH_3 (500 ppm) in air

response and long recovery time.

Sensor response was slightly improved with the introduction of 0.2% of catalytic additive, as it can be seen in Fig. 2, which shows some of the responses of the sensor devices based on 0.2% modified WO_3. However, some of the abnormal behaviours described before were still found in these sensors. At low temperatures, very long recovery times and overshooting were found when NH_3 was removed. On the other hand, abrupt decrease of resistance followed by a slow increase of resistance when NH_3 was introduced, and a reverse behaviour when NH_3 was removed, was found for higher temperatures, as it was reported before for pure WO_3. Although this abnormal behaviour was slightly reduced with the introduction of catalytic additives at 0.2%, it was considered that sensor response was not satisfactory yet.

Fig. 3 shows some of the responses of the sensor devices

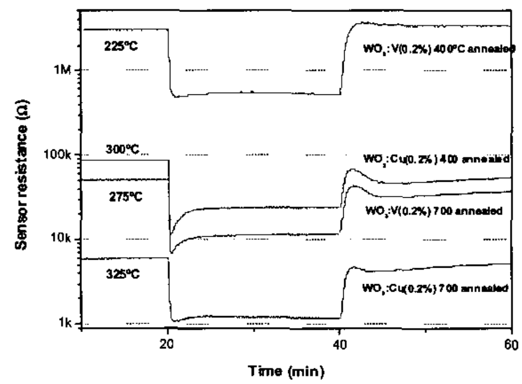

Figure 2. Variation of the 0.2% catalysed WO_3 sensor resistance under a pulse of NH_3 (500 ppm)

based on copper and vanadium modified WO_3 in a 2% atomic percentage, annealed at 400°C and 700°C. In this case, sensor response was not only improved, but also no abnormal behaviour was found for Cu modified sensors operated at low temperatures and for V modified sensors in the whole range of temperatures studied. Response and recovery times were very satisfactory and no overshooting was found. Fig. 4 shows the sensor response to 500ppm of NH_3 in air as a function of the working temperature. It can be seen that sensors based on Cu showed a maximum of sensor response in the temperature range studied at 200°C. Their sensor response decreased to a minimum on the range between 250°C and 300°C and increased again for higher temperatures. Gas sensors based on V showed smaller sensor response, with a maximum sensor response of 14 for 700°C annealed WO_3:V(2%).Their behaviour with operating temperature was different from that showed by Cu modified gas sensors. While 700°C annealed WO_3:V(2%) improved its sensor response when operating temperature decreased, 400°C annealed WO_3:V(2%) presented a maximum at 275°C. Fig. 5 shows the resistance variation of some of these sensors to different 30 minutes pulses of NH_3

(from 20 to 500 ppm in air). Sensors showed a good dynamic response, with response and recovery times lower than one minute. Their response is compared to the one of a sensor based on pure WO_3, which presented the already reported unsatisfactory response.

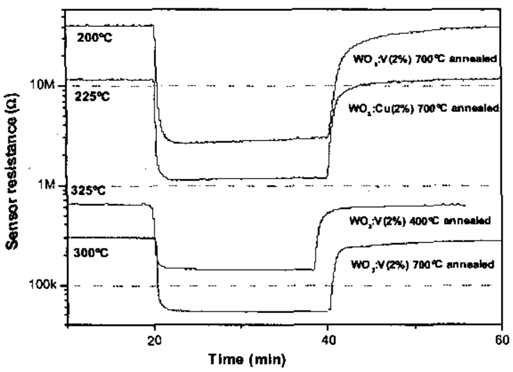

Figure 3. Variation of the 2% catalysed WO_3 sensor resistance under a pulse of NH_3 (500 ppm)

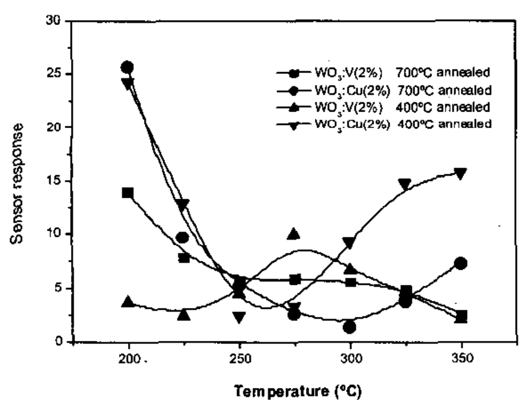

Figure 4. Variation of the 2% catalysed WO_3 sensor response to 500ppm NH3 with temperature

Taking into account these characteristics, gas sensors based on WO_3:Cu(2%) (annealed at 400°C and 700°C) operated at 200°C were chosen as the best sensing elements for NH_3 detection. These sensors were further studied under different concentrations of NO_2, CO and humidity in order to test their sensor response to these gases. For a comparison, sensors based on WO_3:V(2%) were also studied at an operating temperature of 200°C (700° annealed) and 300°C (400°C and 700°C annealed) as they showed a good response to NH_3 at these temperatures too. Fig. 6 shows a comparison of the sensor response of these gas sensors devices to 100ppm of NH_3, 1ppm of NO_2 and 100ppm of CO. It can be seen that sensor based on WO_3:Cu(2%) annealed at 400°C annealed presented a sensor response over 2 for 1ppm of NO_2 and 100ppm of CO, while gas sensor based on WO_3:Cu(2%) annealed at 700°C presented a lower sensor response to NO_2 and CO (1.4 for 1 ppm of NO_2 and 1.6 for 100 ppm of CO in air). On the other hand, gas sensors based on WO_3:V(2%) operated at 300°C presented a very low sensor response to NO_2 and CO, although their response to NH_3 was lower than that of sensors based on WO_3:Cu(2%) (between 3 and 4). To sum up, WO_3:Cu(2%) annealed at 700°C and operated at 200°C and WO_3:V(2%) annealed at 700°C and operated at 300°C showed the best properties for detection of NH_3 combined with low response to NO_2 and CO.

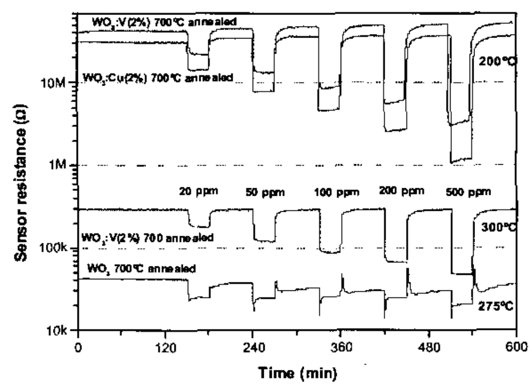

Figure 5. Variation of the sensor resistance of different sensors under pulses of NH_3 (20-500ppm)

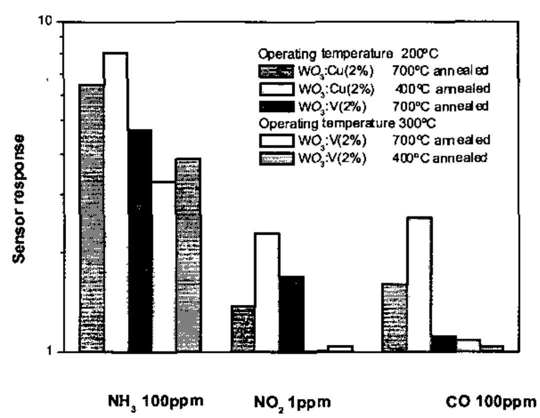

Figure 6. Sensor response of 2% catalysed WO_3 to 500ppm NH3, 1ppm NO_2 and 100ppm CO

Finally, the influence of humidity on the sensor response to 100 ppm of NH_3 was studied. Fig. 7 shows the results for

WO_3:Cu(2%) and WO_3:V(2%) based gas sensors, operated at 200°C and 300°C respectively. Gas sensors based on WO_3:Cu(2%) operated at 200°C presented a lower variation with humidity (9% for 700°C annealed and 5% for 400°C annealed), whereas gas sensors based on WO_3:V(2%) were much more influenced by humidity and their sensor response decreased when humidity increased. As a result, gas sensors based on copper modified WO_3 present better properties for the detection of NH_3 under a changing humid atmosphere. In particular, WO_3:Cu(2%) annealed at 700°C presented a lower sensor response to CO and NO_2 than that annealed at 400°C, so it is considered the best tested gas sensor for the detection of NH_3. The response of this sensor to different concentrations of NH_3 (20-200 ppm) at different humidity is presented in fig. 8.

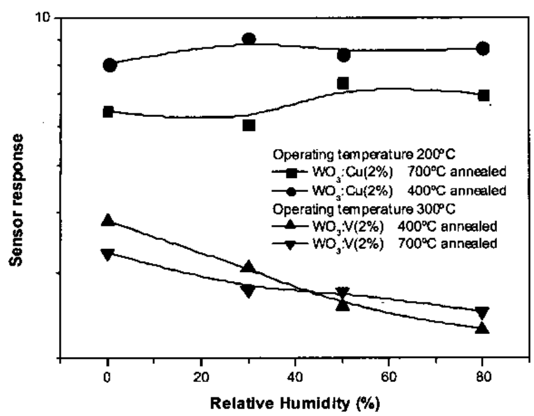

Figure 7. Variation of 2% catalysed WO_3 sensor response to 100ppm NH3 with relative humidity

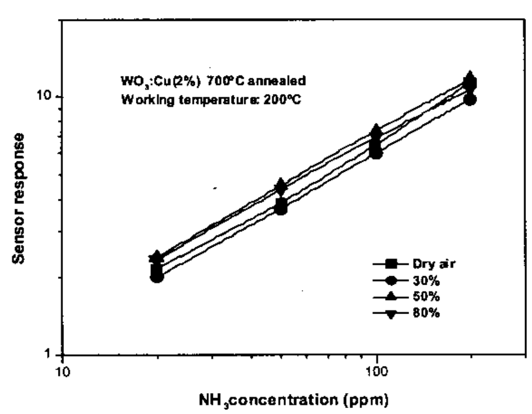

Figure 8. Variation of the WO_3:Cu(2%) sensor response to NH3 with humidity

DISCUSSION

Oxidation of NH_3 over the surface of metal oxides have more than one possible route, so several competitive processes take place at the same time. At least, three main reactions for NH_3 oxidation have been proposed in the field of gas sensors and catalysis [13,14]:

$$2NH_3 + 3O^- \rightarrow N_2 + 3H_2O + 3e^- \qquad (1)$$

$$2NH_3 + 5O^- \rightarrow 2NO + 3H_2O + 5e^- \qquad (2)$$

$$2NH_3 + 4O^- \rightarrow N_2O + 3H_2O + 4e^- \qquad (3)$$

where O^- represents a negatively chemisorbed oxygen species and e^- free electrons. It should be also taken into account that other oxygen chemisorbed species or lattice oxygen could participate in NH_3 oxidation.

The abnormal behaviour showed by pure WO_3 in NH_3 detection has been already described for TiO_2 and In_2O_3 based gas sensors [13]. It was attributed to the predominance of reaction (2) over the other ones, as sensor response of metal oxides gas sensors to N_2O is very low [15]. On the other hand, NO could be the responsible of the abnormal behaviour described. Although WO_3 has shown a rather low sensor response to NO in an inert atmosphere [16], it is very well known that NO is easily transformed into NO_2 in the presence of oxygen, so it is often called NO_x. WO_3 is very sensitive to this gas, which makes the resistance increase. Therefore, when NH_3 is introduced, sensor resistance decreases as oxygen is consumed and more free electrons are available for electrical conduction. However, as NO_x is produced, the resistance would increase as NO_x^- is adsorbed on the surface, where it traps electrons. This would explain why at higher temperatures there is an abrupt decrease of the resistance, followed by a slow increase when NH_3 is introduced, as reaction (2) is specially promoted at high temperatures [17]. On the other hand, when NH_3 is removed, oxygen is quickly adsorbed on the surface, which makes sensor resistance increase. However, NO_x^- is hard to desorb [13], especially at low temperatures. This would explain overshooting problems on the resistance after NH_3 removal, as it has a higher value than before NH_3 contact and a very slow recovery. To sum up, sensor response of pure WO_3 to NH_3 is not completely satisfactory probably due to the interference of NO_x, so selective catalytic oxidation of NH_3 is needed in order to improve sensor response.

Fig. 2 and 3 showed that the addition of copper and vanadium improved the sensor response. The role of catalytic additives has been extensively studied in the field of gas sensors based on metal oxides in order to improve sensor response, selectivity and operating temperature [18,19]. Although copper and vanadium have been scarcely studied in gas sensors applications [20,21], they are extensively used in the field of catalysis, especially when selective catalytic reduction/oxidation (SCR, SCO) of NH_3 and NO is involved [22]. These metals form stable oxides that are reduced by NH_3 and reoxidised by O_2 when NH_3 is removed, closing a redox-type catalytic cycle. In the case of gas sensors, the oxidised metal produces a strong electron-depleted space-charge layer inside the metal oxide (WO_3 in our case). This implies important changes on the conductivity of the material and therefore on the sensor response of the gas sensor device, which is improved by the addition of these catalytics.

Nevertheless, our target was not only to improve sensor response but also eliminate interference from NO_x, which avoided a suitable detection of NH_3 with pure WO_3. It has been shown that this is achieved by using a 2% atomic percentage of copper or vanadium, probably due to the selective oxidation of ammonia gas. Two major routes can be proposed for this selective oxidation of NH_3 to N_2. Firstly, NH_3 could be catalytically oxidised to N_2 over copper and vanadium catalytic centres, as these metals have been already described as responsible for this SCO of NH_3 [2,12]. The other one is the in situ or internal selective catalytic reduction, which is a two-step mechanism and involves the oxidation of NH_3 to NO_x, which would happen mostly over WO_3 centres. The second step of this route would be the interaction of these molecules with NH_3 over copper or vanadium centres, the so-called selective catalytic reduction of NO with NH_3. Spectroscopic measurements are needed to decide which of the two routes is happening in our case. However, gas sensors based on WO_3:Cu(2%) and WO_3:V(2%) annealed at 700°C presented a minimum (copper based) or a plateau (vanadium based) of sensor response to NH_3 between 250°C and 300°C. This is probably due to the effect of some non selective oxidation of NH_3 to N_2 but to NO_2 over WO_3 centers. Therefore, probably both mechanisms are present at the same time.

Gas sensors catalysed with 2% also showed a rather low sensor response to NO_2, especially if it is compared to that presented by gas sensor devices based on pure WO_3. This is probably due to the fact that both copper and vanadium can not be further oxidised by NO_2 in air, so sensor response to this gas is reduced. Concerning sensor response to CO, considered as an interfering gas for NH_3 detection, it was shown that sensor response was higher in the case of WO_3:Cu(2%) annealed at 400°C, so gas sensor device based on WO_3:Cu(2%) annealed at 700°C was chosen as the best sensing element for NH_3 detection with low response to NO_2 and CO. Besides, interference of humidity was considered to be very low, especially if compared to the case of vanadium modified WO_3 based gas sensors. This is probably due to the different adsorption sites provided by these additives to NH_3. Vanadium offers Brønsted acid centre [22] for the adsorption of NH_3 molecules and these centres are hydroxyl groups, coordinated water or H_3O^+ ions. On the other hand, copper offers Lewis acid centre [22], which are coordinatively unsaturated metal cations at the surface. Therefore, it is reasonable to consider that the presence of humidity has more effects over sensor response of gas sensors based on vanadium modified WO_3 than over copper modified WO_3.

CONCLUSIONS

Gas sensors based on pure WO_3 exhibited a rather low and complex sensor response to NH_3, probably due to the interference of NO_x. This sensor response was improved by the introduction of copper and vanadium as catalytic additives, especially when the concentration was 2% atomic. Moreover, no abnormal behaviour was found, probably due to the selective catalytic oxidation of NH_3 to N_2 over copper and vanadium centres. Gas sensors based on copper modified WO_3 presented the best sensor response to NH_3, with low interference of humidity, while gas sensors based on vanadium modified WO_3 had a sensor response to NH_3 highly dependent on humidity. Regarding sensor response to other gases like NO_2 or CO, WO_3:Cu(2%) annealed at 700°C operated at 200°C presented a low response to this gases, which makes it suitable for ammonia gas detection with low interference from humidity and low response to other gases like NO_2 and CO.

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