

5. Surface species and reactions on WO₃-based powders studied by DRIFTS and TPD

Introduction.....	148
5.1 DRIFTS studies	149
5.1.0 Experimental procedure.....	149
5.1.1 Pure WO ₃	149
5.1.2 Copper catalysed WO ₃	153
5.1.3 Vanadium catalysed WO ₃	155
5.1.4 Chromium catalysed WO ₃	157
5.1.5 Discussion.....	158
5.2 TPD studies.....	163
5.2.0 Experimental procedure.....	163
5.2.1 Pure WO ₃	164
5.2.2 Copper catalysed WO ₃	166
5.2.3 Vanadium catalysed WO ₃	168
5.2.4 Chromium catalysed WO ₃	170
5.2.5 Discussion.....	176
5.3 Conclusions.....	185
5.4 References.....	187

Introduction

The aim of this chapter is to explore the implementation of *real condition* characterisation techniques to WO₃-based nanopowders in order to study surface species and reactions involved in gas sensing. By *real condition*, we refer to a characterisation under controlled conditions of temperature and gas concentration on the sample, as similar to test conditions as possible. It is often argued that characterisation techniques, although being able to give valuable information, are not so useful in the field of gas sensors if they are not performed under *real* atmosphere and temperature conditions. These studies, which are standard in the field of catalysis, are not so common for gas sensors. This may occur because the correlation between surface interaction of the molecules and electrical response of the sensors is not well understood yet, so the interpretation is not so straightforward as in the field of catalysis. However, after many years of research, this is still a key point in the field of gas sensors at the moment: to obtain a deeper understanding of what occurs on the surface of the sensing material.

Before explaining the organisation of this chapter, the reader should take notice of the material included in this chapter. Unlike the chapters concerning structural characterisation and test of gas sensors, where the same set of samples is dealt with, only some selected samples were analysed here. There were several reasons for the choice of analysed materials, from suitability for the specific technique to their interest according to sensor results. Further explanations are provided at the beginning of each corresponding subsection.

The chapter has two main parts, corresponding to the results of DRIFTS and TPD techniques, and a final section for discussion. These first two sections are divided according to the different materials studied and both sections have an initial subsection where the experimental procedure followed for each technique is explained. As in the preceding chapters, only results and straightforward conclusions are provided here. Further and more elaborated conclusions are to be found in the final *Discussion* section, once all the experimental results have been presented.

5.1 DRIFTS studies

5.1.0 Experimental procedure

The interaction between ammonia gas and nanocrystalline WO₃ (pure and catalysed) was analysed by Diffuse Reflectance Infrared Fourier Transformed Spectroscopy (DRIFTS). Samples were firstly pretreated under a flow of 21% of O₂ in helium (called hereafter *oxygen atmosphere*) at 400°C for several hours. This process is necessary in order to clean the surface as much as possible and thus activate the material for adsorption. Due to the pre-treatment temperature, only 700°C-annealed powders were analysed by this technique.

After this pretreatment, samples were cooled down to room temperature and were stabilised under a flowing oxygen atmosphere for one hour, acquiring a spectrum. Then the flow was changed to 1000 ppm of NH₃ in 21% O₂ in helium (called hereafter *ammonia atmosphere*) for one hour and a spectrum was recorded. Finally, the sample was heated up to 400°C in oxygen atmosphere for one hour and cooled down to the next measurement temperature. Typically, measurement temperatures were room temperature, 100°C, 200°C, 300°C and 400°C.

Results are presented either as raw absorbance spectra (calculated using a mirror spectrum as a reference) or as a subtraction between two absorption spectra, which allows evaluating changes between different processes. Using this experimental procedure, two main features can be investigated. Firstly, dehydration-dehydroxylation of the material (desorption of adsorbed molecular water and OH groups, respectively) by comparing spectra in oxygen atmosphere at different temperatures (called hereafter *differential spectra*). Secondly, adsorption states of ammonia by comparing spectra in ammonia atmosphere to oxygen atmosphere at the same temperature (called hereafter *subtraction spectra*).

Hydrogen sulphide and nitrogen dioxide DRIFTS studies are not reported since they require some experimental conditions far from those used in gas sensing, basically high gas pressure and low adsorption temperature.

5.1.1 Pure WO₃

Fig. 1a and 1b present absorbance spectra in oxygen atmosphere at different temperatures in two different infrared regions. In these spectra it is interesting to pay attention to the evolution of those vibrations related to water and OH groups. Fig. 1a shows that the

5. Surface species and reactions on WO₃-based powders

intensity of the 1622 cm⁻¹ vibration decreases as temperature increases. Since this vibration was assigned to a bending mode of adsorbed water [1], it is easy to state that most of the adsorbed water disappears at temperatures over 250°C, according to the evolution of this vibration. On the other hand, the stretching vibration associated to OH groups at 1417 cm⁻¹ is present even at 400°C, what is showing that these OH groups are strongly attached to the surface of WO₃ and thus may play an important role in gas detection. Apart from this vibrations modes, vibrations corresponding to W=O terminal vibration modes (2063 and 1854 cm⁻¹), as well as a possible carbon contamination (1698 cm⁻¹) are also detected.

Fig. 1b displays the OH stretching region, presenting two main broad bands at 3420 and 3220 cm⁻¹ respectively. It is remarkable that the intensity of the 3420 cm⁻¹ decreases substantially when the temperature is over 100°C, confirming that this band represents the stretching vibration of weakly adsorbed water. On the other hand, the 3220 cm⁻¹ band is still present even at 400°C, confirming the existence of WOH groups on the surface of WO₃ nanocrystalline particles at high temperatures. The bands around 2923 cm⁻¹ are probably due to accidental carbon contamination. Comparing these results with those reported in chapter 3, it may be necessary to evacuate at low pressure to fully eliminate this carbon contamination.

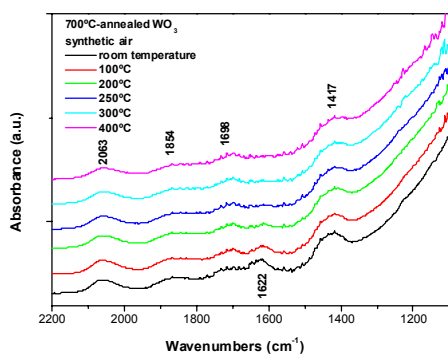


Fig. 1a: DRIFTS spectra of pure WO₃ in oxygen atmosphere (2200-1100 cm⁻¹).

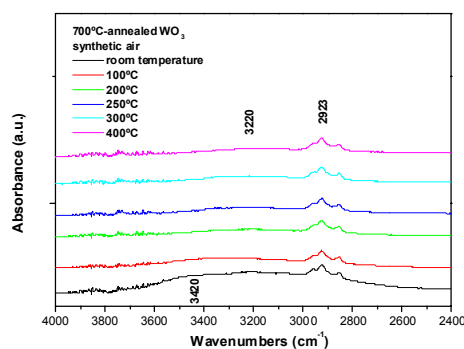


Fig. 1b: DRIFTS spectra of pure WO₃ in oxygen atmosphere (4000-2400 cm⁻¹).

These features can be better displayed if two absorbance spectra are subtracted in order to observe the increasing or decreasing intensity of these peaks with temperature (*differential spectra*). In Figures 2a and 2b differential spectra are displayed. Each spectrum was subtracted from the spectrum recorded at the next higher temperature. Therefore, negative bands correspond to those vibration modes disappearing when temperature increases. As it is displayed by Fig. 2a, the intensity of the vibration mode at 1622 cm⁻¹ is mainly reduced

5. Surface species and reactions on WO₃-based powders

when temperature is raised from room temperature to 100°C. At higher temperatures, this negative peak is displaced to 1610 cm⁻¹ until 300°C. This peak is probably due to a second type of more strongly adsorbed water. This change is mirrored by the vibration mode found at 3460 cm⁻¹ (Fig. 2b), although it is not possible to easily differentiate between two kinds of adsorbed water using this vibration mode. Vibrations corresponding to OH group (3220 cm⁻¹ and 1417 cm⁻¹) also decrease until 300°C, although it was previously shown that they are still present even at 400°C. The rest of vibrations only present minor changes with temperature, showing that they belong to stabilised groups.

Fig. 3 shows the DRIFTS spectra of pure WO₃ (700°C-annealed) under a flowing ammonia atmosphere at the indicated temperatures. All the spectra are referred to the sample at the experience temperature after the activation process in oxygen atmosphere (*subtraction spectra*), so positive bands are associated to the appearing species and negative bands belong to species disappearing in ammonia flow.

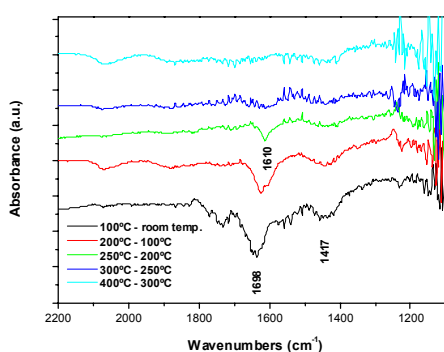


Fig. 2a: Differential DRIFTS spectra of pure WO₃ in oxygen atmosphere (2200-1100 cm⁻¹).

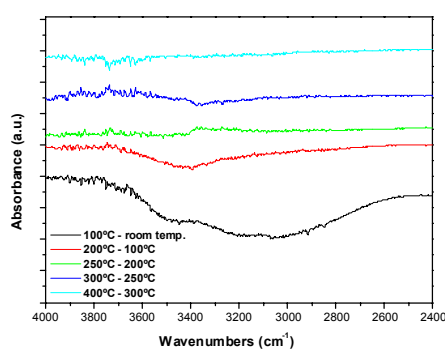


Fig. 2b: Differential DRIFTS spectra of pure WO₃ in oxygen atmosphere (4000-2400 cm⁻¹).

After adsorption of NH₃ at room temperature over pure WO₃ (Fig. 3), positive bands appear at 3393, 3318, 3167, 1601, 1270 and 1221 (coordinatively adsorbed ammonia on Lewis acid sites) and at 3253, 3203, 1467 and 1395 (NH₄⁺ ions adsorbed on Brønsted acid sites)*. It is interesting to notice that symmetric deformation of coordinated ammonia splits into a broad component around 1270 cm⁻¹ and in a sharper one at 1221 cm⁻¹. This suggests the presence of at least two different Lewis adsorption sites. Table 1 summarises the observed peaks and their corresponding species.

* See Appendix 2 for a brief description of acid and basic sites on metal oxides surfaces.

5. Surface species and reactions on WO₃-based powders

Increasing the adsorption temperature, the intensity of all these bands falls off, since the amount of adsorbed ammonia species that remains on the surface of the material is lower. At the same time, negative bands at 3500-3200 and 1636 cm⁻¹ also appear. The band between 3500 and 3200 cm⁻¹ is characteristic of surface hydroxyl groups, as mentioned above, and its disappearance is due to the replacement of part of the water on the WO₃ surface by ammonium adsorbed species. This agrees with the negative band at 1636 cm⁻¹, characteristic of $\delta(\text{HOH})$ of adsorbed water. Likewise, the intensity of these bands decreases when adsorption temperature increases.

Frequency (cm ⁻¹)	Vibration
3393	$\nu_{\text{as}} \text{NH}_3$
3318	$\nu_{\text{as}} \text{NH}_3$
3253	$\nu_{\text{s}} \text{NH}_3$
3203	νNH_4^+
3167	νNH_4^+
1601	$\delta_{\text{as}} \text{NH}_3$
1467	$\delta_{\text{as}} \text{NH}_4^+$
1395	δNH_4^+
1270	$\delta_{\text{s}} \text{NH}_3$
1221	$\delta_{\text{s}} \text{NH}_3$

Table 1: Identification of adsorbed ammonia species on pure WO₃ powder

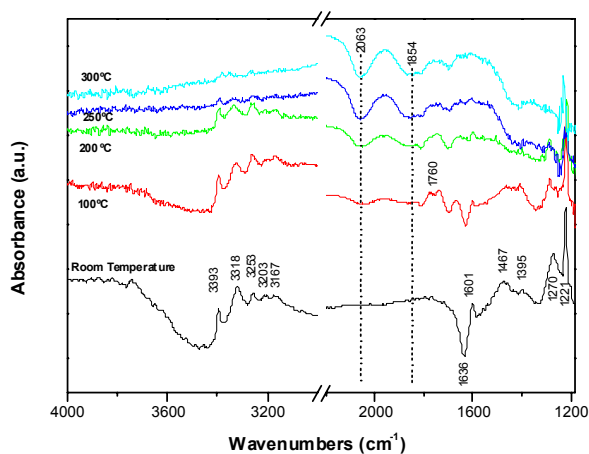


Fig. 3: Subtraction DRIFTS spectra (oxygen from ammonia atmosphere) of pure WO₃

New bands appear when adsorption temperature increases. Negative bands at 2063 and 1854 cm⁻¹ appear at 100°C and increase their intensity when the adsorption temperature increases. As mentioned in chapter 3, these vibrations come from surface terminal W=O and W-O bonds. They appear on the raw spectrum of WO₃ in oxygen atmosphere (Fig. 1a), so the introduction of ammonia makes these bands decrease their intensity. The observed decrease of intensity of the W=O bands could be due to the reaction of NH₃ molecules with surface WO₃ oxygen, which leads to reduction of tungsten atoms.

Simultaneously, positive bands at 1760 and 1800 cm⁻¹ appear at 100°C and their intensity slightly decreases when adsorption temperature increases. These bands could be ascribed to nitrosil species, due to the oxidation of gaseous or adsorbed ammonia species to NO. This would suggest that at least some NH₃ is converted into NO on the surface of pure WO₃.

5.1.2 Copper catalysed WO₃

In the case of WO₃:Cu nanocrystalline powder, only 700°C-annealed 0.2% and 2% copper-catalysed WO₃ were chosen for ammonia DRIFTS studies. These samples were chosen according to their annealing temperature (well over the pretreatment temperature) and to

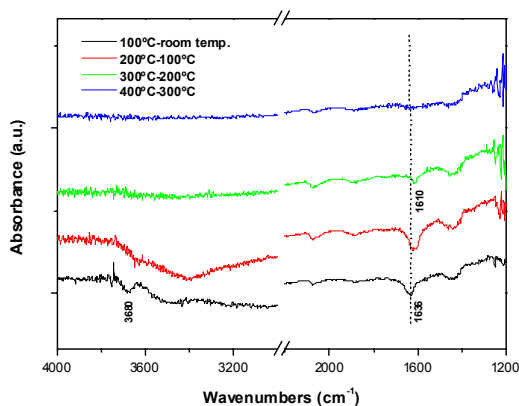


Fig. 4: Differential DRIFTS spectra of WO₃:Cu(0.2%) in oxygen atmosphere

the behaviour of gas sensors based on these materials. Pretreatment and measuring conditions were the same explained for pure WO₃. Briefly, samples were analysed in two different atmospheres: *oxygen atmosphere* (21%O₂ in He) and *ammonia atmosphere* (1000 ppm of NH₃, 21% O₂ and He). Absorbance spectra showed the same vibrations bands already described for pure WO₃, so only difference between spectra acquired under oxygen atmosphere at different temperatures (dehydration-dehydroxylation) and difference between spectra acquired under ammonia and oxygen atmosphere at the same temperature (ammonia adsorption) are displayed.

Fig. 4 displays the differential spectra in oxygen atmosphere. As already noted, these results provide information concerning the dehydration and dehydroxylation of the samples. It is shown that the situation is very similar to that of pure WO₃. The displacement of the 1630 cm⁻¹ to 1610 cm⁻¹ is showing again the presence of two kinds of adsorbed water. There is also a decrease in the presence of adsorbed OH groups, according to the 1417 cm⁻¹ vibration.

Nevertheless, there are two different features compared to the results of pure WO₃. A rather sharp band at 3680 cm⁻¹ appears when temperature is increased from room temperature to 100°C and 200°C. This band probably belongs to isolated WOH groups. The second difference is related to the intensity decrease at 2074 cm⁻¹, which is part of the broad band ascribed to the W=O bound at 2063 cm⁻¹. This may show a reduction of a certain type

5. Surface species and reactions on WO₃-based powders

of the W=O centres contributing to this band, probably by the desorption of chemisorbed oxygen.

After adsorption of NH₃ at room temperature over pure WO₃ (Fig. 5), positive bands are

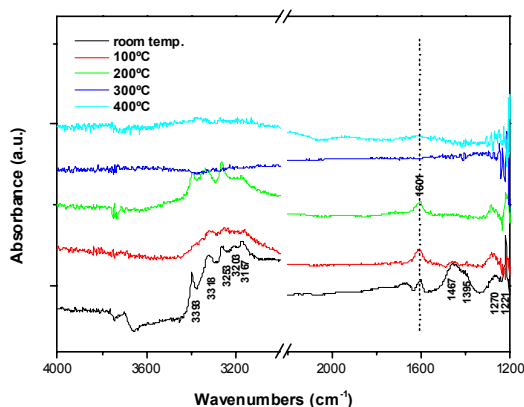


Fig. 5: Subtraction DRIFTS spectra (oxygen from ammonia atmosphere) of WO₃:Cu(0.2%)

virtually identical to those reported above for pure WO₃. Positive bands were again found at 3393, 3318, 3167, 1601, 1270 and 1221 (coordinatively adsorbed ammonia on Lewis acid sites) and at 3253, 3203, 1467 and 1395 (NH₄⁺ ions adsorbed on Brønsted acid sites). This suggests that ammonia adsorption was not affected by the addition of copper.

However, as ammonia adsorption temperature increases, some features come out. It is especially interesting to notice that neither decrease of the W=O vibration nor appearance of nitrosil vibration were found. This situation indicates that, although ammonia is adsorbed on the same sites, ammonia molecules are not reacting with oxygen centres of W=O vibrations. Besides, adsorption on Brønsted acid sites disappear when adsorption temperature is over room temperature, while coordinated ammonia on Lewis sites is still present at 200°C, as shown by the intensity of the 1601 cm⁻¹ vibration.

However, as ammonia adsorption

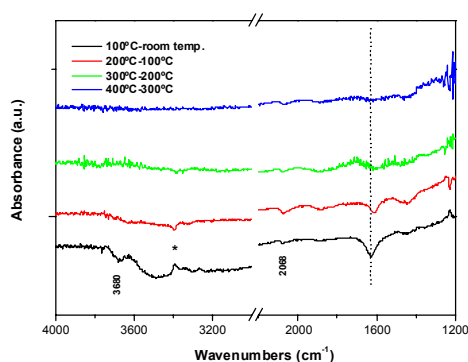


Fig. 6a: Differential DRIFTS spectra of WO₃:Cu(2%) in oxygen atmosphere

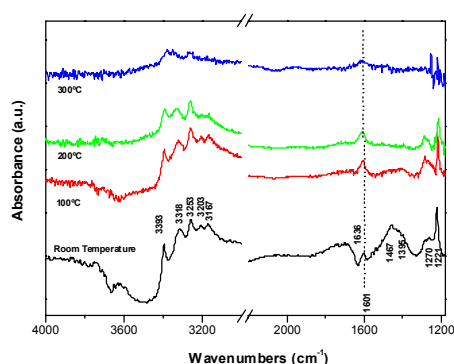


Fig. 6b: Subtraction DRIFTS spectra (oxygen from ammonia atmosphere) of WO₃:Cu(2%)

5. Surface species and reactions on WO₃-based powders

Fig. 6a and 6b present DRIFTS results for 700°C-annealed WO₃:Cu(2%). It is evident that dehydration-dehydroxylation and ammonia adsorption show a similar pattern to that presented by WO₃:Cu(0.2%). Therefore, compared to the situation described in the case of pure WO₃, it is again remarkable that neither decrease of the W=O vibration nor appearance of nitrosil vibration were found. On the other hand, adsorption sites of ammonia (Lewis and Brønsted acid sites) seem to be the same as in the case of pure WO₃, since vibration wavenumbers were almost identical in pure and copper catalysed samples.

5.1.3 Vanadium catalysed WO₃

In the case of WO₃:V nanocrystalline powder, only 700°C-annealed 0.2% and 2% vanadium catalysed WO₃ were chosen for ammonia DRIFTS studies. These samples were chosen according to their annealing temperature and to the behaviour of gas sensors based on these materials. Pretreatment and measuring conditions were the same explained for pure WO₃. Briefly, samples were analysed in two different atmospheres: *oxygen atmosphere* (21%O₂ in He) and *ammonia atmosphere* (1000 ppm of NH₃, 21% O₂ and He) at different temperatures. Absorbance spectra showed the same vibrations bands already described for pure WO₃, so only difference between spectra acquired under oxygen atmosphere at different temperatures (dehydration-dehydroxylation, *differential spectra*) and difference between spectra acquired under ammonia and oxygen atmosphere at the same temperature (ammonia adsorption, *subtraction spectra*) are presented.

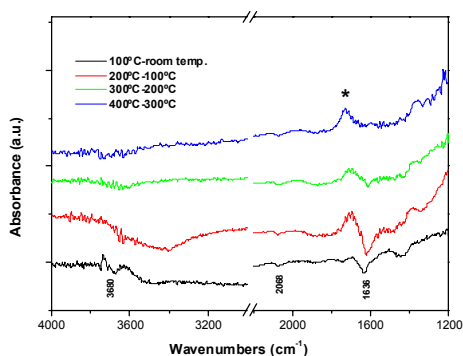


Fig. 7a: Differential DRIFTS spectra of WO₃:V(0.2%) in oxygen atmosphere

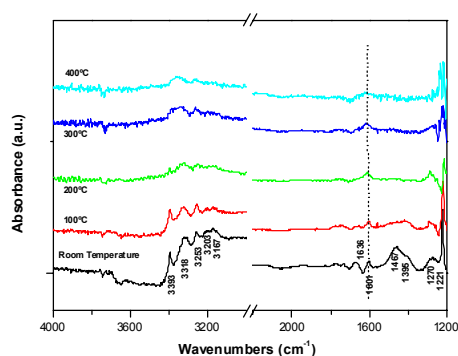


Fig. 7b: Subtraction DRIFTS spectra (oxygen from ammonia atmosphere) of WO₃:V(2%)

Fig. 7a and 7b show results for 700°C-annealed WO₃:V(0.2%). As for the previous samples, dehydration and dehydroxylation followed a similar pattern to that of pure WO₃,

5. Surface species and reactions on WO₃-based powders

so no further comments will be made about it. Concerning ammonia adsorption, it is again remarkable that no considerable decreases in terminal W=O or nitrosil species were found in ammonia atmosphere. Concerning adsorbed ammonia species, they were adsorbed on both Lewis and Brønsted sites in a similar proportion to that of pure WO₃. Therefore, it can be concluded that a 0.2% vanadium content did not affect ammonia adsorption sites but their reaction with oxygen on W=O centres.

Regarding 700°C-annealed WO₃:V(2%), similar results were found in the case of dehydration-dehydroxylation (Fig. 8). It must be pointed out, however, that most of the adsorbed water is already desorbed at 100°C (1636 cm⁻¹ vibration), whereas some dehydration was observed at higher temperatures for the rest of analysed samples.

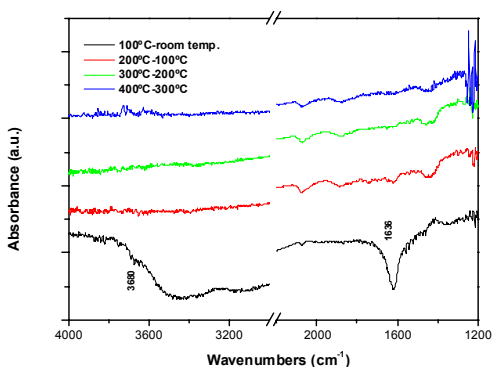


Fig. 8a: Differential DRIFTS spectra of WO₃:V(2%) in oxygen atmosphere

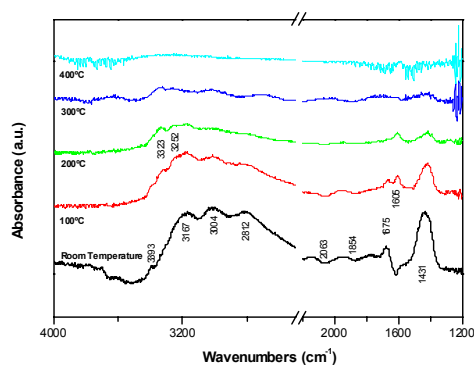


Fig. 8b: Subtraction DRIFTS spectra (oxygen from ammonia atmosphere) of WO₃:V(2%)

More interesting results are found for ammonia adsorption, since adsorbed ammonia species are quite different from those previously reported. At room temperature, there are positive bands corresponding to adsorbed ammonia on Lewis acid sites (3393, 3167, 3323 and 1605 cm⁻¹), but most intense bands correspond to NH₄⁺ ions adsorbed on Brønsted acid sites (3252, 3004, 2812, 1675 and 1431 cm⁻¹). The broad and more intense band at 1431 cm⁻¹ is probably hindering the 1467 and 1395 cm⁻¹ bands reported in previous samples. A slight decrease of W=O overtone band is found but it disappears as the adsorption temperature increases. Furthermore, NH₄⁺ ions are still present at 200°C (1431 cm⁻¹ vibration), what was not found in other samples. At this temperature, co-ordinated ammonia is also present (1610 cm⁻¹), revealing that both species may play a part in ammonia reactions at this temperature.

5.1.4 Chromium catalysed WO₃

In the case of WO₃:Cr nanocrystalline powder, only 700°C-annealed 0.2%, 2% and 5% copper catalysed WO₃ were chosen for ammonia DRIFTS studies. These samples were

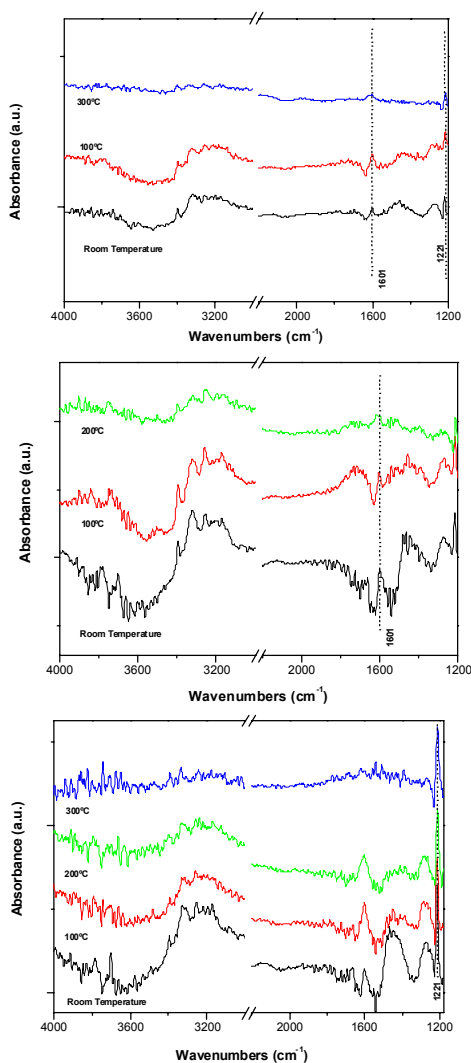


Fig. 9a, 9b and 9c: Subtraction DRIFTS spectra (oxygen from ammonia atmosphere) of WO₃:Cr(0.2%), WO₃:Cr(2%) and WO₃:Cr(5%), respectively

chosen according to their annealing temperatures and to the interest of gas sensors based on these materials. Pretreatment and measuring conditions were the same explained for pure WO₃. Briefly, samples were analysed in two different atmospheres: *oxygen atmosphere* (21%O₂ in He) and *ammonia atmosphere* (1000 ppm of NH₃, 21% O₂ and He). Absorbance spectra showed the same vibrations bands already described for pure WO₃, so only difference between spectra acquired under ammonia and oxygen atmosphere at the same temperature (ammonia adsorption) are displayed. Dehydration and dehydroxylation followed a similar pattern to that already presented, so these results are not showed for the sake of brevity.

Ammonia adsorptions on 0.2%, 2% and 5% chromium catalysed WO₃ (Fig. 9a-c) indicate that adsorption sites are roughly the same as those presented by pure WO₃; however, some differences can be highlighted. For instance, it is remarkable the presence of the 1221 cm⁻¹ vibration mode at high adsorption temperatures, especially in the case of 5% chromium catalysed WO₃, as it even broadens at 300°C. It is also interesting to point out that its counterpart vibration mode at 1270 cm⁻¹ do not follow this trend. In this sample, it also interesting to

5. Surface species and reactions on WO₃-based powders

notice that the 1601 cm⁻¹ vibration is stronger and broader than in the case of lower chromium content.

As in the case of the previous catalysed WO₃ powders analysed, the intensity of W=O vibration mode did not decrease with ammonia contact and no nitrosil bands were detected.

5.1.5 Discussion

Dehydration and dehydroxylation

As regards water and OH groups on the surface of WO₃ nanocrystalline powders, it is interesting to notice that the situation is very similar in all the analysed materials. Therefore, most of the comments hereafter can be applied to both pure and catalysed WO₃.

Firstly, water was present on the surface of the nanoparticles as revealed by the vibration mode at 1630 cm⁻¹. This vibration mode was assigned to the H₂O bending mode [1] and the

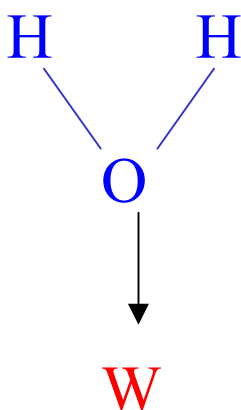


Fig. 10: Adsorbed water on a Lewis site through the oxygen atom

presence of water can be monitored by its intensity.

Interestingly, as temperature was raised, this vibration mode was displaced to 1610 cm⁻¹ until it disappears at 300°C. This fact suggest that two kinds of adsorbed water (strong and weakly bound) are present on the surface of WO₃. According to literature [1,2], the band at 1630 cm⁻¹ is attributed to a weakly held hydrogen bonded water layer similar to that found on oxides such as silica. On the other hand, the second more strongly adsorbed water has a band at a lower frequency, suggesting that it is adsorbed through the oxygen atom of the water via co-ordination with Lewis sites (Fig. 10). In support of this assignment, it is noted that a shift to lower frequency in the H₂O bending mode has been observed at 1609 cm⁻¹ for hydrate WO₃·1/3H₂O, and

this was assigned to water bounded through the oxygen atom of the water molecule. The existence of strongly adsorbed water that is resistant to removal is not unique to WO₃. Adsorbed water is also detected on TiO₂ anatase powder at 300°C. [4].

As to hydroxyl groups, two different kinds were also found. Most samples showed a decrease at 3680 cm⁻¹ when temperature raised from room temperature to 100°C. On oxides such as alumina, titania and silica, isolated surface hydroxyl groups produce sharp bands in

5. Surface species and reactions on WO₃-based powders

the 3750-3600 cm⁻¹ region [1,5], and so this vibration is assigned. Since this mode is only detected in room temperature-100°C differential spectrum, it must be concluded that few species of this kind are found on the surface of WO₃. On the other hand, it is reported that hydrogen-bonded hydroxyl groups give rise to broad bands between 3400 and 3000 cm⁻¹ [1,5]. Within this region, two vibrations at 3420 and 3220 cm⁻¹ were found, although only the second one is due to OH groups [1].

Interestingly, these modes are not so intense as the vibration mode at 1417 cm⁻¹, which has been attributed to a stretching vibration of OH groups [3,6]. By this mode it is possible to monitor the desorption of OH groups as temperature increases, probably as a condensation of adjacent surface WOH groups (Fig. 11). However, this vibration mode is even present at 400°C, what shows that these OH groups are strongly bonded to the surface.

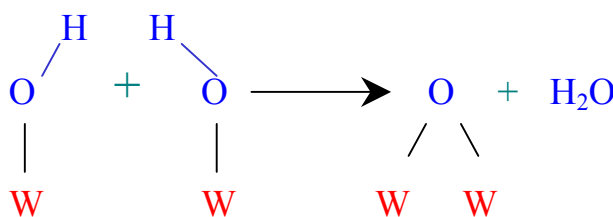


Fig. 11: Condensation of OH groups on the surface of WO₃ as temperature raises

Ammonia adsorption and reaction

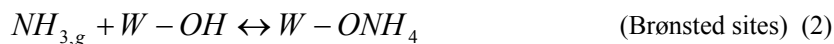
Broadly speaking, all the investigated materials offered two sites for the adsorption of ammonia at room temperature: Lewis and Brønsted sites. As Nakamoto notes [7], Lewis acid centres are coordinatively unsaturated metal cations at the surface. The formation of a coordination bond between NH₃ and the cation complex-forming agent leads to radical changes in the character of this molecule's vibration. Assuming that these vibrations were found to be very similar between differently catalysed WO₃ nanocrystalline powders, it must be concluded that NH₃ molecules are adsorbed onto unsaturated W cations, as already proposed by Ramis et al. [8]. These authors claim that, to preserve the charge neutrality of the pseudocubic faces, half of the exposed W atoms must be bonded to oxygen upright on the surface, forming the W=O terminal bonds (responsible for the 2063 and 1854 cm⁻¹ overtone vibrations). The other half of the exposed W atoms must be coordinatively

5. Surface species and reactions on WO₃-based powders

unsaturated, being thus the Lewis acid sites (See also Chapter 1, Fig 8). In our case, ammonia vibrations on Lewis sites were found at 3393, 3318, 3167, 1601, 1270 and 1221 cm⁻¹. Interestingly, symmetric deformation of co-ordinated ammonia splits into a broad component around 1270 cm⁻¹ and in a sharper one at 1221 cm⁻¹. This suggests the presence of at least two different Lewis adsorption sites, being the strength of the second one higher as evidenced by its presence even at high temperature. This second sites has been reported to be located on corners and edges of the different faces that form the grains [8]. As revealed by DRIFTS spectra, ammonia can be adsorbed on this site at temperatures up to 400°C, which highlights the importance of this site in sensing mechanisms.

On the other hand, Brønsted acid centres can be either hydroxyl groups with sufficiently mobile protons or coordinated water, which are actually present on the surface of WO₃. These centres are able to protonate ammonia molecules, yielding ammonium ions (NH₄⁺). It is interesting to notice that, as ammonia is introduced at room temperature, a decrease in 1636 cm⁻¹ vibrations was found. Assuming this vibration mode is due to adsorbed water, this implies that some ammonia is adsorbed onto this layer of water. This agrees with the fact that ammonia on Brønsted sites is easily desorbed. In our case, vibrations at 3253, 3203, 1467 and 1395 cm⁻¹ were always found but in the case of WO₃:V(2%), which presented bands at 3252, 3004, 2812, 1675 and 1431 cm⁻¹. These bands in vanadium catalysed WO₃ were stronger and broader, suggesting a great number of V-OH groups associated to vanadium centres, as stated in [9,10]. Moreover, these NH₄⁺ ions are present in WO₃:V(2%) at 300°C, what indicates that they must be taken into account in the possible reactions on vanadium catalysed WO₃.

To sum up, ammonia is adsorbed in two different sites involving tungsten oxide sites:



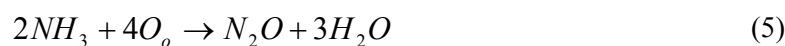
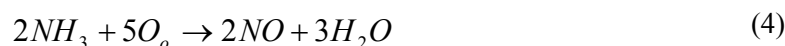
In these equations, NH_{3,g} refers to ammonia gas, whereas NH_{3,ads} refers to adsorbed ammonia. As previously explained, only ammonia adsorbed on Lewis sites is stable at temperatures over 100°C in copper and chromium catalysed WO₃, whereas ammonia on Brønsted acid sites occurs on vanadium catalysed WO₃ through V-OH groups.

Apart from the vibrations of adsorbed ammonia, it has been previously presented a fundamental difference between pure and catalysed WO₃. Pure WO₃ showed a decrease in

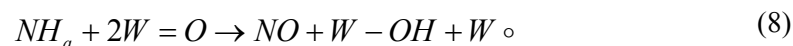
5. Surface species and reactions on WO₃-based powders

the intensity of the W=O overtone vibrations, as well as the formation of nitrosil species ascribed to NO. Vanadium-based catalysts show a similar pattern in the interaction between ammonia and V=O groups, as proved by Centeno et al. [11]. Since these two features were not found in any catalysed sample (even those with only 0.2% catalytic nominal content), it seems likely that they are connected.

As stated in Chapter 4, and according to literature [12,13], it is well known that NH₃ can react with oxygen species following several paths:



where O₀ refers to an oxygen species, either a lattice oxygen or an adsorbed one. However, these reactions only explain the process in general terms. More specifically, ammonia must be firstly adsorbed. Thereafter, it is generally accepted that ammonia is stripped to form NH_x species, which are the reactive elements. Unfortunately, there is still a great deal of disagreement concerning the reaction paths that NH_x species can take. Some of them have been extensively described in [9,10,13-16] and they can be applied to most of the transition metal oxides. Here are reported only those that include the reduction of W=O, as well as the formation of NO species as a possible path for the oxidation of ammonia on WO₃. Following [16,17], a possible path involving W=O sites reduction and NO formation might be:



5. Surface species and reactions on WO₃-based powders

In these equations, W^o refers to a reduced tungsten atom. These reactions are based on reported ammonia reactions with M=O centres (M representing a transition metal centre) and show that NH₃ loses hydrogen to form NH_x species and OH groups. Reduced tungsten centres appear due to a direct reaction of NH with W=O or from the condensation of two neighbour W-OH centres. Of course, as oxygen is present, the oxidation of these centres is possible and a balanced situation is reached:



It must be noticed that other reactions can occur at the same time to produce N₂ and N₂O and it is entirely possible that they are much more common than this NO route production. However, since their detection by DRIFTS was not possible, these routes are not considered here but discussed in the TPD section.

As regards ammonia reaction on catalysed WO₃, DRIFTS data are apparently indicating that this route is prevented from occurring. From these spectra it can only be stated that ammonia adsorption sites on copper and chromium catalysed WO₃ are nearly the same as in pure WO₃. This suggests that their role is mainly focused on offering a new reaction path for ammonia. Concerning vanadium, it not only avoids this reaction, but also offers a new adsorption site on V-OH groups. Nevertheless, DRIFTS data actually provide limited further information about the role played by these catalytic additives, so more conclusions will be drawn at TPD section.

5.2 TPD studies

5.2.0 Experimental procedure

The interaction between ammonia/hydrogen sulphide and pure nanocrystalline WO₃ was studied by means of Temperature Programmed Desorption. Essentially, WO₃ powder was pressed into discs and then crushed into granules, which were pre-treated in synthetic air (50 ml/min) at 650°C for 1 hour in a glass reactor connected to a flow apparatus. Afterwards, temperature was decreased to the adsorption temperature (which varied between room temperature and 200°C, depending on the specific experiment). A flow of 800 ppm of NH₃ in air or 390 ppm of H₂S in air (100 ml/min) passed then through the reactor for 3 hours. Then the flow was changed to He (10 ml/min) and the granules were quenched to room temperature. Finally, temperature was risen from room temperature to 650°C at a rate of 5°C/min in the same He stream. The desorbed species (NH₃, N₂, N₂O, NO and H₂O for ammonia adsorptions; H₂S, SO₂ and H₂O for hydrogen sulphide adsorptions) were analysed by a gas chromatography-mass spectrometer during TPD runs. Only the sample annealed at 700°C was selected, due to the high pretreatment temperature. TPD has not been applied to nitrogen dioxide since it requires concentrations over 2 orders of magnitude higher than common concentrations in gas sensing.

Vertical axes of these figures represent the area of the GC-MS peaks of the desorbed species at different temperatures of the heating ramp. This magnitude represents the desorption rate of each gas and so it can not be compared between different gases. The horizontal axis shows the temperature. According to the interpretation of TPD spectra, each desorption peak of ammonia or hydrogen sulphide will belong to a differently adsorbed species. As regards combustion products of these gases with oxygen, it is not so straightforward to decide if, after their production, they are produced, adsorbed and later desorbed or are just desorbed as soon as they are produced. For instance, it is highly probable that N₂ is desorbed as soon as it is produced and that H₂O is easily adsorbed, according to the properties of these gases and the experimental conditions. However, neither in the case of these gases, nor for the rest, it is possible to determine their past behaviour with absolute certainty. Therefore, it will not be considered whether these species belong to different kinds of adsorbed species.

5. Surface species and reactions on WO₃-based powders

5.2.1 Pure WO₃

Ammonia investigation

Fig. 12 (adsorption at room temperature and 200°C) shows that NH₃ presents two broad desorption peaks that overlap after the room temperature adsorption. These peaks are centred on 150°C and 330°C, respectively. As explained above, they must belong to two different species of adsorbed NH₃.

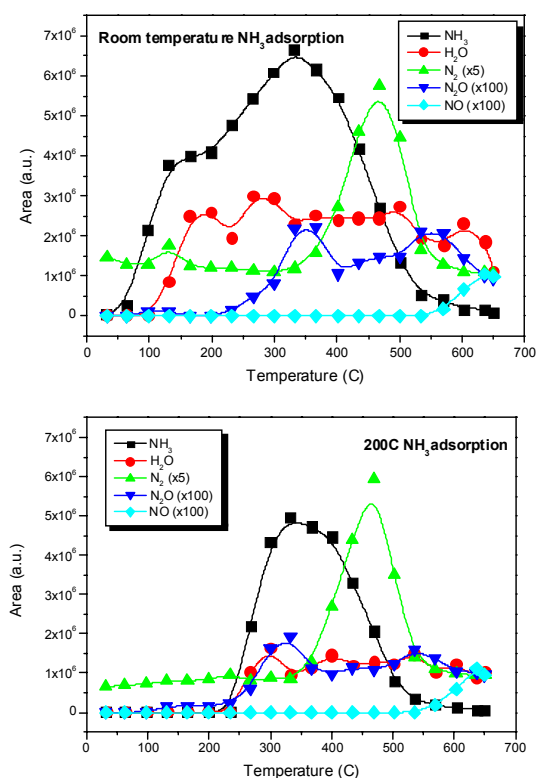


Fig. 12: Ammonia-TPD spectra of pure WO₃ at room temperature and 200°C

Hydrogen sulphide investigation

Fig. 13 displays the desorption of H₂S (adsorbed gas), SO₂ and H₂O (both products of the oxidation of H₂S with oxygen) at different adsorption temperatures. In the case of H₂S, two desorption peaks are found at room temperature adsorption. The first one is around 80°C, whereas the second one is centred around 270-300°C. These two peaks indicate the presence of two different species of H₂S adsorbed on the surface of WO₃. When adsorption temperature was risen to 100°C and 200°C, only the second peak was found. Besides, as

different species of adsorbed NH₃.

Water presents a complex desorption spectrum, with several peaks in the range analysed. On the other hand, nitrogen presents a single main peak centred at 470°C and N₂O presents three main desorption peaks at 350°C, 475°C and 550°C, respectively. Finally, NO is detected from 570°C on.

Concerning the adsorption at 200°C, NH₃ desorption spectrum just presents the broad peak at 330°C, although its intensity is lower. Water roughly presents the same spectra from 200°C, although its intensity is also lower. By contrast, N₂O and N₂ present a very similar desorption spectrum.

5. Surface species and reactions on WO₃-based powders

Fig. 13 illustrates, not only the intensity of this second peak decreases with adsorption temperature, but also the temperature of maximum intensity slightly increases. The first feature (intensity reduction) just confirms the lower surface coverage that is obtained when

adsorption temperature increases, whereas the second one indicates that the activation energy of desorption of the second peak species increases with adsorption temperature.

This figure also illustrates the desorption behaviour of SO₂. Two peaks are found in this case too: the first one around 270-285°C, and the second one around 395-480°C. The intensity of the first one increases with adsorption temperature, indicating an increase in the oxidation rate of preadsorbed H₂S with adsorption temperature as expected.

Finally, desorption behaviour of water is also presented in Fig. 13. It is evident from this figure that the amount of desorbed water decreases as adsorption temperature is reduced. It is interesting to notice that SO₂ presented an opposite trend, suggesting that SO₂ is adsorbed at the surface much stronger than water, since both are the product of the combustion reaction between H₂S (or intermediate species) and oxygen species.

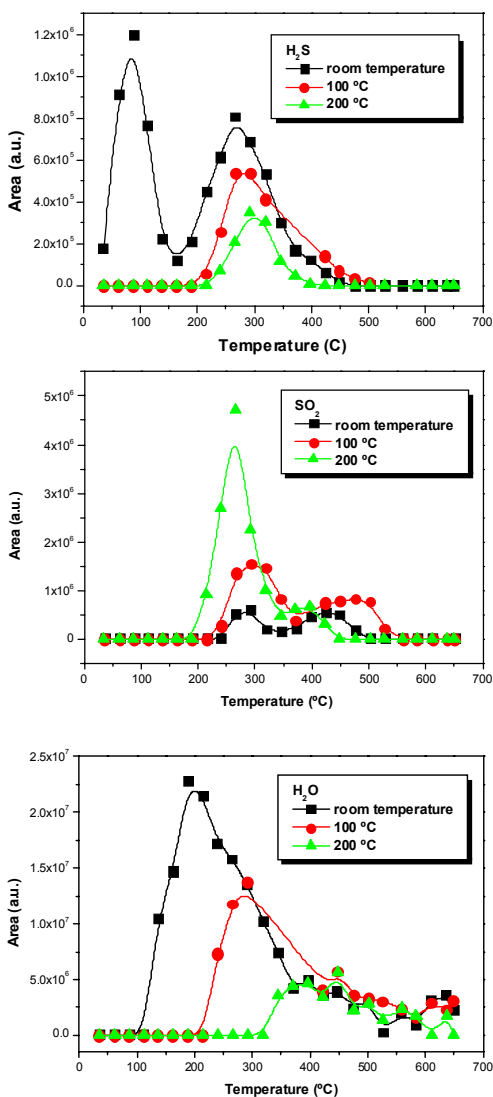


Fig. 13: Hydrogen sulphide-TPD spectra of pure WO₃ at room temperature and 200°C

5. Surface species and reactions on WO₃-based powders

5.2.2 Copper catalysed WO₃

Ammonia investigation

Fig. 14 displays the desorption of ammonia and its combustion products (N₂O, NO, N₂ and H₂O) after the adsorption of ammonia at room temperature. Corresponding results for pure WO₃ are also shown for comparison.

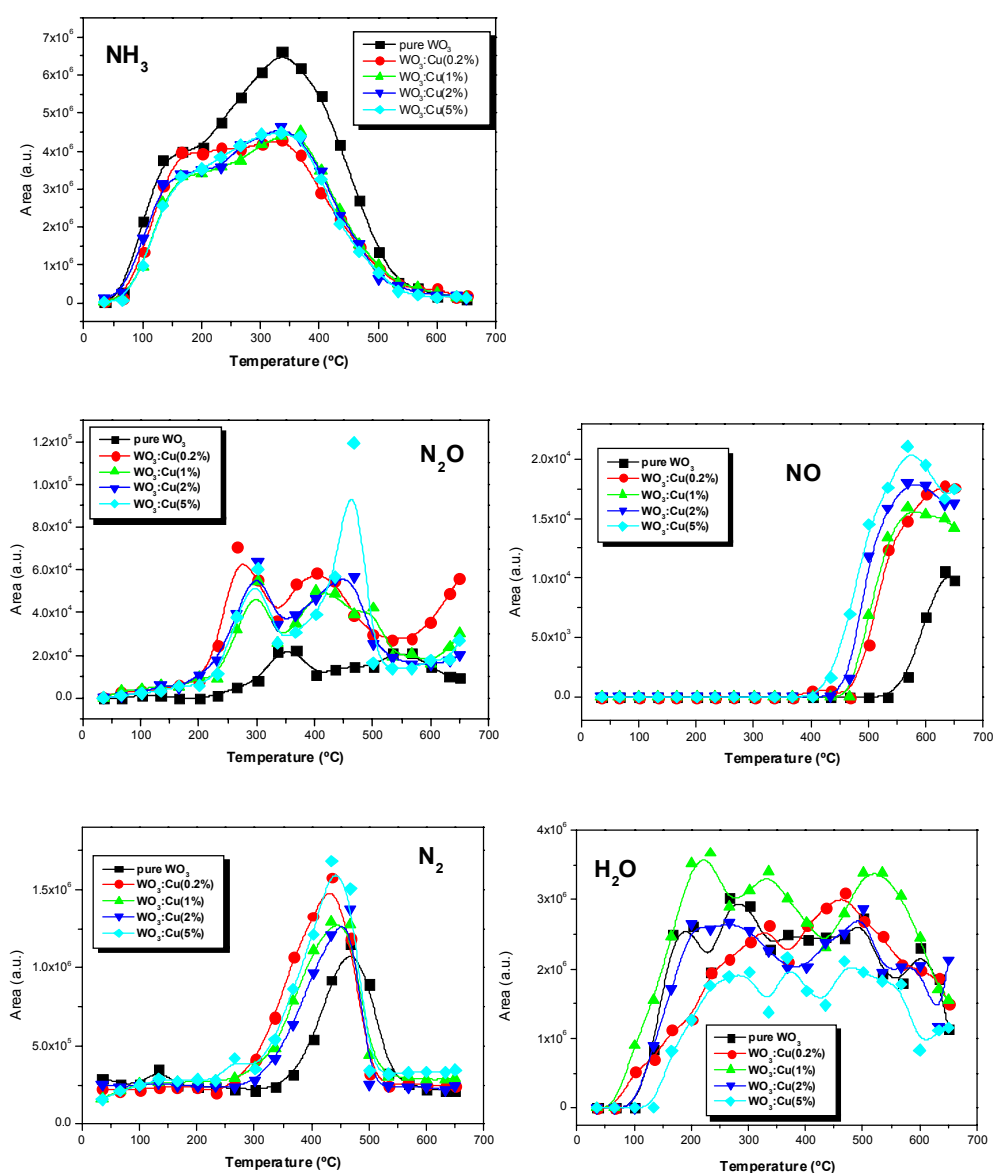


Fig. 14: Ammonia-TPD spectra of copper catalysed WO₃ at room temperature

5. Surface species and reactions on WO₃-based powders

First of all, this figure illustrates that NH₃ desorption from copper-catalysed WO₃ presents two broad peaks, which are similar to those presented by pure WO₃. However, for copper catalysed samples, the intensity of the second peak is distinctly lower than in the case of pure WO₃.

On the other hand, the spectra of N₂O desorption is clearly different in the case of copper catalysed samples, since it presents two marked peaks around 275°C (actually 250°C for the 0.2% copper catalysed sample) and 400-450°C, respectively. The first peak does not have a counterpart in pure WO₃ at that temperature. On the other hand, the second peak may correspond to one already found in pure WO₃, since they are present at similar temperatures. Besides, the intensity of the N₂O desorption as a whole is far higher than that exhibited by pure WO₃. Interestingly, 5% copper catalysed WO₃ presents a marked increase in the intensity of the second peak.

Regarding N₂ and NO, copper catalysed WO₃ present quite similar features to pure WO₃, but for the intensity. N₂ presents a single peak around 470°C as in the case of pure WO₃. Interestingly, the position of this peak matches that of the second N₂O peak. The intensity of this N₂ peak is clearly higher in the case of copper catalysed WO₃ than in the case of pure WO₃. As for NO, its desorption appears at lower temperatures when copper is present, being its intensity also higher.

Finally, water keeps on presenting a rather complex desorption spectra, with multiple peaks that apparently show little correlation. Besides, intensity varied highly with copper concentration, unlike previous results. This may well imply that these results concerning water might be misleading.

5. Surface species and reactions on WO₃-based powders

5.2.3 Vanadium catalysed WO₃

Ammonia investigation

Fig. 15 displays the desorption of ammonia and its combustion products (N₂O, NO, N₂ and H₂O) after the adsorption of ammonia at room temperature. Corresponding results for pure WO₃ are also shown for comparison.

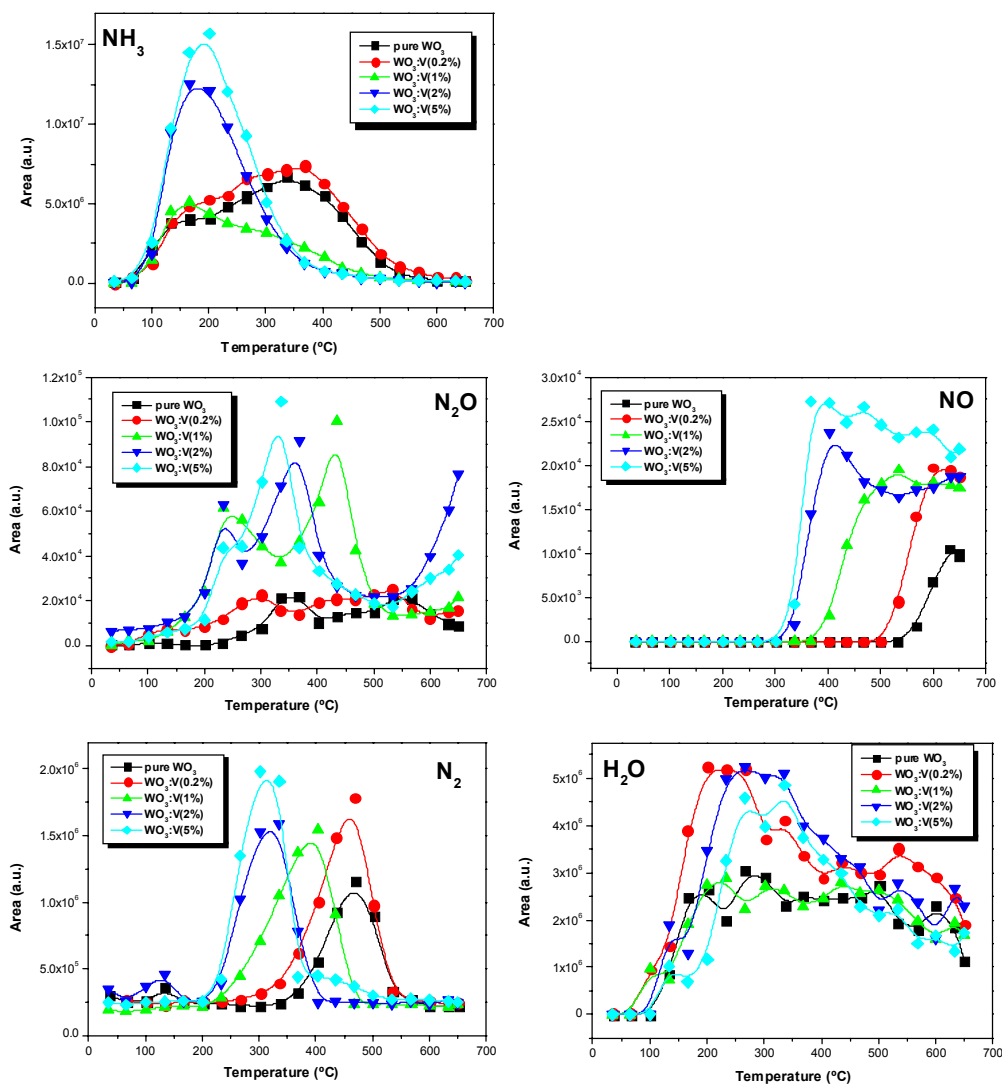


Fig. 15: Ammonia-TPD spectra of vanadium catalysed WO₃ at room temperature

5. Surface species and reactions on WO₃-based powders

Data on Fig. 15 suggest a clear correlation between the amount of catalytic additive and the evolution of the desorption spectra in certain cases. Therefore, comments about these data will be made emphasising the evolution with vanadium content.

Firstly, from Fig. 15 it is obvious that vanadium introduction changes NH₃ desorption. While WO₃:V(0.2%) presents a similar spectra to that of pure WO₃, WO₃:V(1%) clearly shows a decrease in the intensity of the second desorption peak at 330°C. As nominal vanadium content increases to 2% and 5%, this peak disappears and the first peak at 150°C augments its intensity. This rise is clearly correlated with the increase of vanadium content.

N₂O desorption is also being affected by vanadium content. As revealed by Fig. 15, vanadium contents over 1% not only enlarge N₂O desorption, but also displace desorption peaks to lower temperatures. Actually, the first N₂O desorption peak is centred on 230°C and is very similar in the 1-5% vanadium content range. On the other hand, the maximum of this peak decreases from 430°C (1% vanadium catalysed WO₃) to 340°C (5% vanadium catalysed WO₃).

Interestingly, N₂ and NO are also desorbed at lower temperatures as more vanadium is added. As regards N₂, its desorption spectra presents a single peak that is displaced from 470°C (0.2% vanadium catalysed WO₃) to 320°C (5% vanadium catalysed WO₃). On the other hand, NO presents a more complex desorption spectra, since multiple peaks seem to be present in vanadium catalysed WO₃. Essentially, NO is always presenting a steep rise in its desorption at temperatures between 600°C and 370°C, depending on the vanadium content.

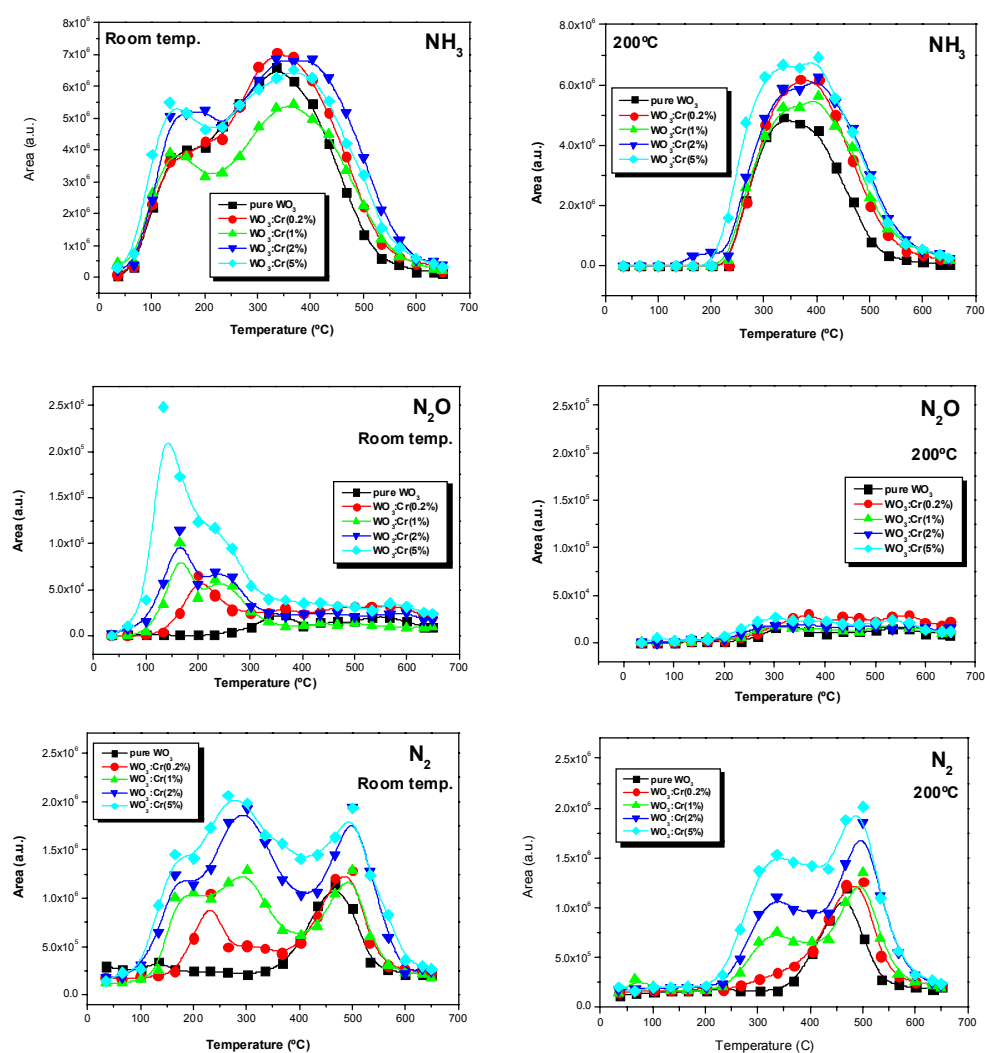
Finally, water presents again a rather complex desorption spectra. In this case, vanadium seems to increase the amount of desorbed water compared to pure WO₃ (but for 1% vanadium catalysed WO₃). The interpretation of the data is again complicated by the number of peaks and their low correlation with vanadium content.

5. Surface species and reactions on WO₃-based powders

5.2.4 Chromium catalysed WO₃

Ammonia investigation

Fig. 16 displays the desorption of ammonia and its combustion products (N₂O, NO, N₂ and H₂O) after the adsorption of ammonia at room temperature. Adsorption at 200°C was also studied due to the interesting results presented by sensors based on WO₃:Cr for ammonia detection. Corresponding results for pure WO₃ are also shown for comparison. It must be observed that, in order to help comparisons, data corresponding to the same gas have been displayed within the same axis range for both adsorption temperatures.



5. Surface species and reactions on WO₃-based powders

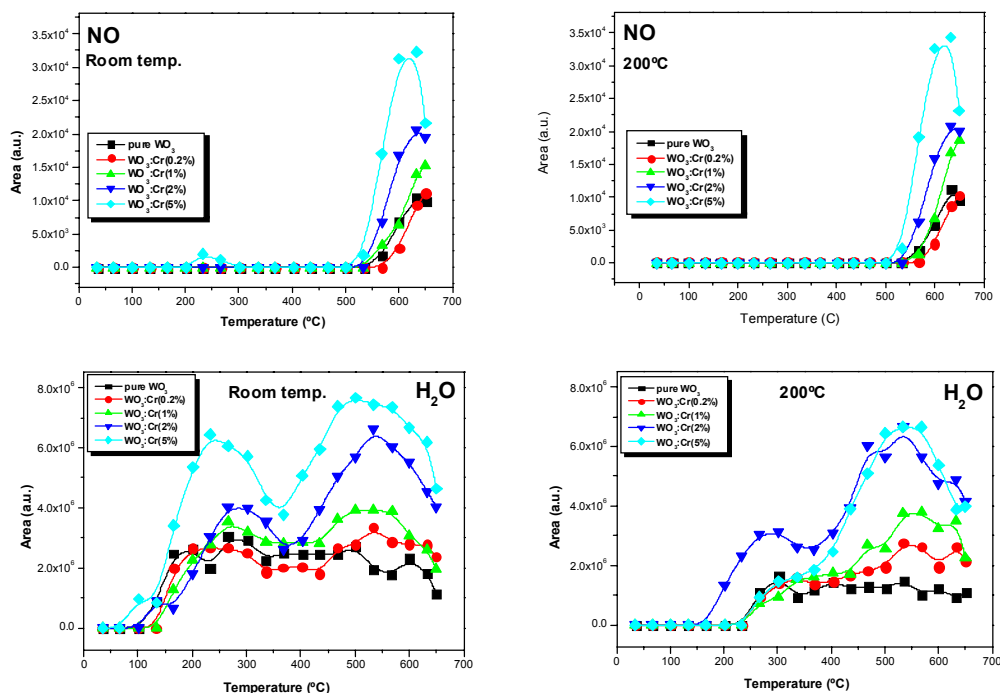


Fig. 16: Ammonia-TPD spectra of chromium catalysed WO₃ at room temperature and 200°C

As in the previous case of vanadium catalysed WO₃, data on Fig. 16 indicate some degree of correlation between the amount of catalytic additive and the evolution of the desorption spectra in certain cases. Therefore, comments about these data will be made emphasising the evolution with chromium content.

Fig. 16 reveals that chromium addition does not alter significantly the shape of NH₃ desorption peaks. As regards room temperature adsorption, only after 2% or 5% chromium introduction is the intensity of the first desorption peak raised, whereas the second peak remains rather stable. Interestingly, after the 200°C adsorption, the quantity of NH₃ desorbed from chromium catalysed WO₃ is clearly greater than in the case of pure WO₃. Nevertheless, the position of the peaks is unaltered.

N₂O desorption data indicate a significant correlation with chromium content after room temperature NH₃ adsorption. WO₃:Cr(0.2%) presents a peak centred on 200°C and it seems this peak is displaced at lower temperatures (130°C for 5% chromium catalysed WO₃). However, since a shoulder is also present around 200°C, it is not clear whether the peak is

5. Surface species and reactions on WO₃-based powders

really displaced to lower temperatures or it just remains as a shoulder and a new peak is actually present. In any case, it is evident that chromium addition intensify the desorption of N₂O. By contrast, the amount of N₂O desorbed after the 200°C NH₃-adsorption is significantly lower, with values more similar to those of pure WO₃ than in the previously described case, although still slightly higher.

Desorption of N₂ from chromium catalysed WO₃ presents a striking feature, not reported for the rest of materials reported in this work: multiple desorption peaks appear. Fig. 16 reveals that single peak present in pure WO₃ increases its intensity as chromium content rises. Besides, new peaks appear at lower temperatures. In particular, a new peak appears in WO₃:Cr(0.2%) at 225°C, shifting to lower temperatures until 150°C for WO₃:Cr(5%). Actually, this peak becomes a shoulder in that sample since a new peak centred on 275°C is also present. It must be pointed out that the intensity of these peaks is well correlated with the nominal chromium content. As regards 200°C NH₃-adsorption, a similar situation is found. Not only increases the intensity of the high-temperature peak, but also a new peak appears around 330°C. Their intensity is again correlated with nominal chromium content.

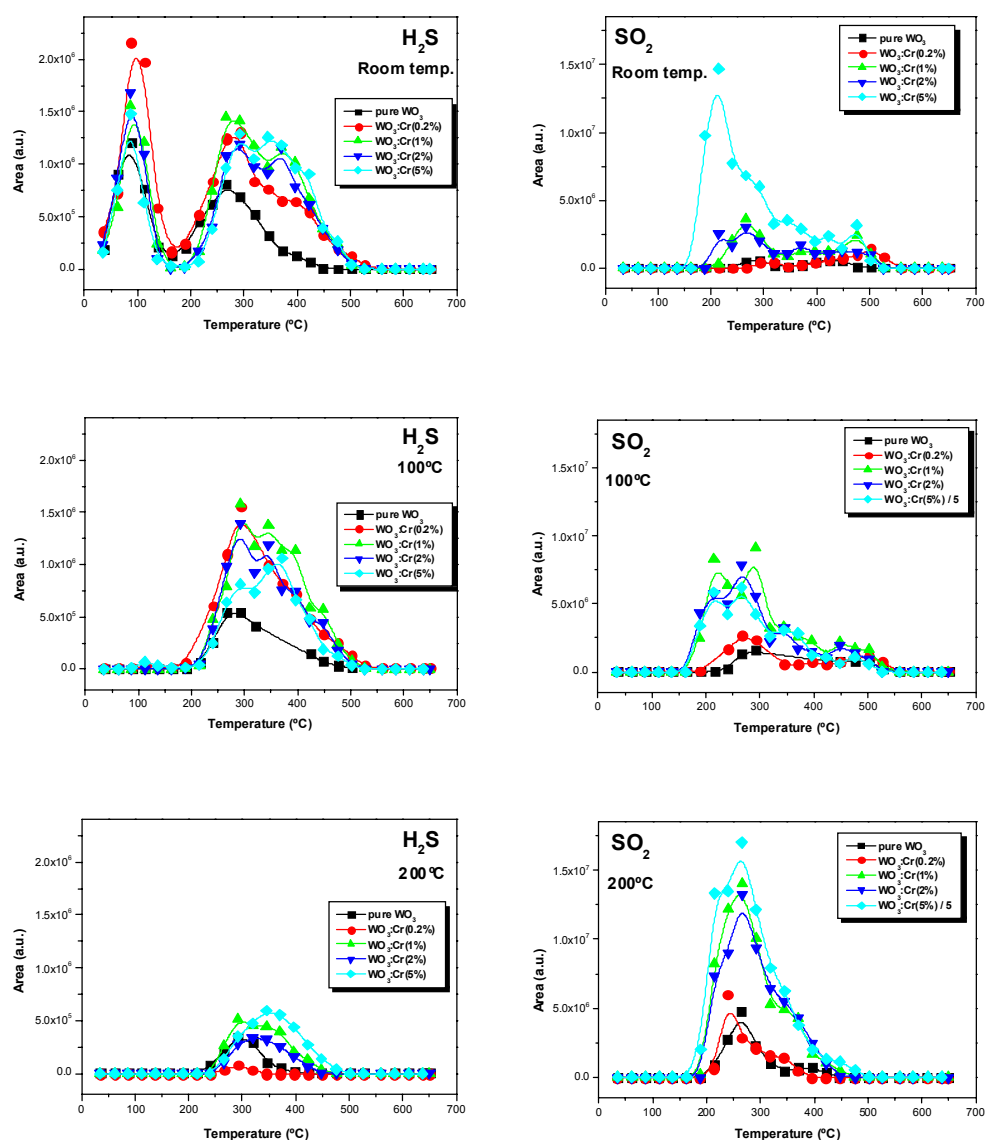
As to NO desorption, it shows a similar pattern to that of pure WO₃. This gas is detected from 550°C on and a complete peak is not detected. The intensity is correlated with the nominal chromium content; that is to say, intensity raises as chromium content is higher. It is remarkable that there is a great deal of similarity between both desorptions (room temperature and 200°C NH₃-adsorptions).

Finally, water presents again a rather complex desorption spectra. Data suggest the presence of two main peaks centred on 250°C and 550°C, especially in 2% and 5% chromium catalysed WO₃. Besides, as chromium content is higher, intensity raises, what illustrates some correlation with chromium content.

5. Surface species and reactions on WO₃-based powders

Hydrogen sulphide investigation

Fig. 17 displays the desorption of hydrogen sulphide and its combustion products (SO₂ and H₂O) after the adsorption of hydrogen sulphide at room temperature, 100°C and 200°C. Corresponding results for pure WO₃ are also shown for comparison. It must be observed that, in order to help comparisons, data corresponding to the same gas have been displayed within the same axis range.



5. Surface species and reactions on WO₃-based powders

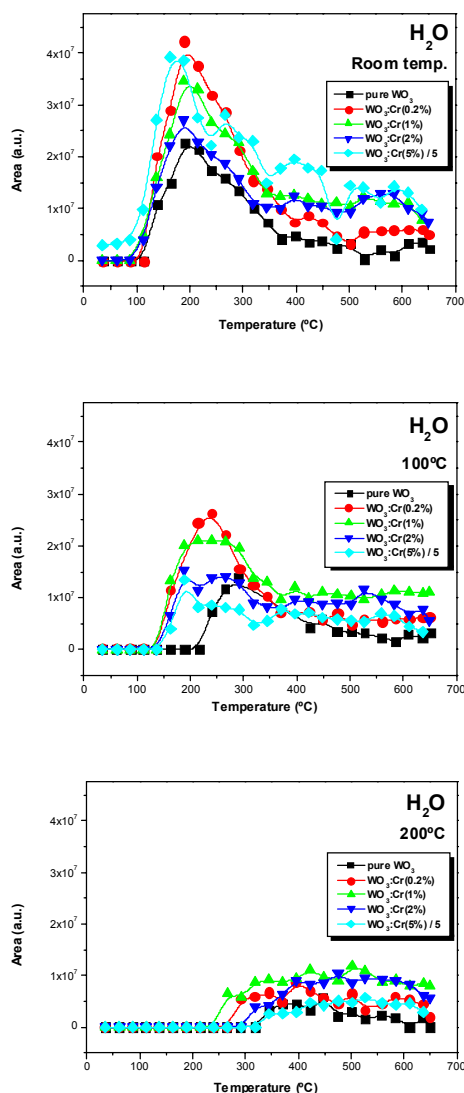


Fig. 17: Hydrogen sulphide-TPD spectra of chromium catalysed WO₃ at room temperature, 100°C and 200°C.

the presence of chromium has an evident effect on H₂S adsorption, although the outcome of different concentrations between 1% and 5% is not so straightforward.

As regards SO₂ desorption, it is evident from Fig. 17 that chromium addition promotes the conversion of H₂S into SO₂ and thus the latter is desorbed in higher quantities when chromium is present, especially over 1% nominal content. With the exception of WO₃:Cr(5%), the amount of SO₂ desorbed increased as the adsorption temperature was risen, as in the case of pure WO₃. By contrast, desorption spectra was much more complex,

Fig. 17 reveals an interesting effect of chromium addition to WO₃ in H₂S desorption spectra. After the H₂S adsorption at room temperature, chromium catalysed WO₃ spectra are not only showing the two peaks reported for pure WO₃, but a new one. This new peak appears at a higher temperature (around 350°C-400°C) and its intensity seems to be slightly correlated with chromium nominal content. Concerning the other two peaks, it is remarkable that chromium catalysed samples actually show higher intensity, although there was little correlation between chromium content and the intensity of these peaks.

Concerning adsorptions at higher temperatures, both high temperature peaks are still present at 100°C and, at 200°C, finally become a single broad peak. Apart from the reduction of intensity, it is not evident whether more significant information can be obtained from this data, since the effect of different concentrations of chromium is rather ambiguous. To sum up, the

5. Surface species and reactions on WO₃-based powders

presenting at least four peaks after 100°C and room temperature adsorption. Moreover, desorption at these temperatures begins at lower temperatures than in the case of pure WO₃, which is consistent with a higher catalytic activity. Finally, desorption of SO₂ after the 200°C adsorption shows a similar pattern to that of pure WO₃, although the intensity is higher, especially for chromium nominal concentrations over 1%. To sum up, these data clearly indicates the higher catalytic activity of chromium catalysed WO₃. Besides, some correlation between nominal chromium content and intensity of SO₂ desorption is apparently happening. Broadly speaking, more water is desorbed when chromium is present, although correlation with exact nominal chromium content is rather ambiguous.

Finally, desorption behaviour of water is also displayed in Fig. 17. As already stated, water desorption is always appearing rather complex and with little correlation with the desorption of the rest of gases or catalyst concentration; this applies for its desorption after H₂S adsorption on chromium catalysed WO₃.

5. Surface species and reactions on WO₃-based powders

5.2.5 Discussion

Ammonia TPD

The TPD data of ammonia desorption from pure WO₃ revealed that this gas is adsorbed in two different sites at room temperature. When adsorption temperature raises to 200°C, only the second desorption peak at high temperature is found. As DRIFT experiments revealed, ammonia can be adsorbed on two different acid sites (Lewis and Brønsted). Moreover, ammonia adsorbed on Brønsted acid sites disappeared as adsorption temperature was over 100°C, so this may lead to think that the first desorption peak in TPD belongs to desorbed NH₄⁺ ions and the second one would come from chemisorbed ammonia on Lewis acid sites.

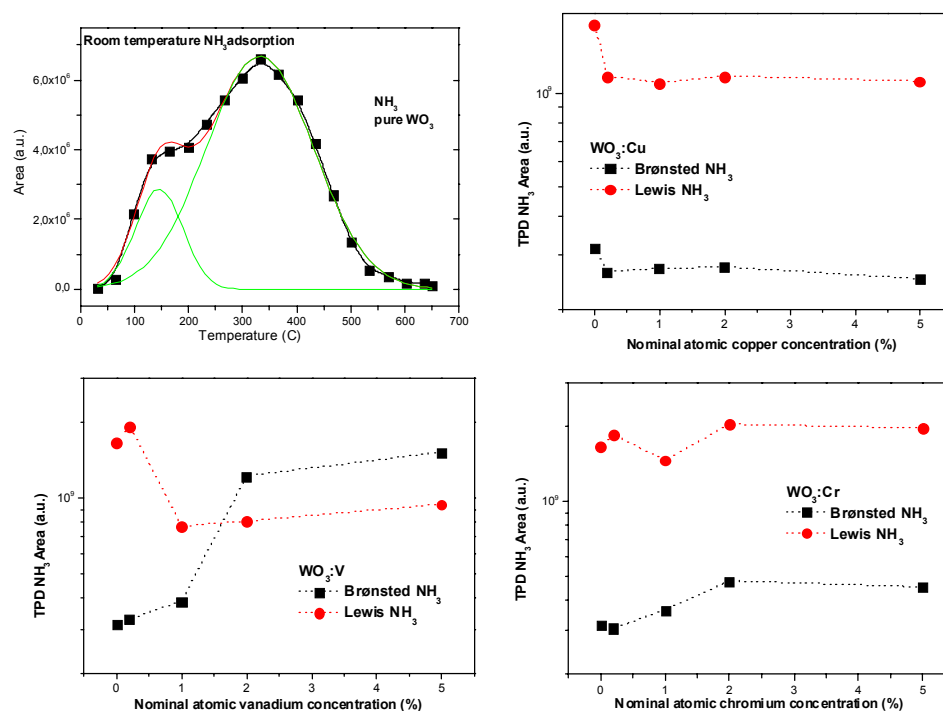


Fig. 18: (upper left) Fit instance of NH₃ TPD peaks; (upper right) NH₃ peak area from WO₃:Cu; (bottom left) NH₃ peak area from WO₃:V; (bottom right) NH₃ peak area from WO₃:Cr

This interpretation is further supported after analysing the evolution of peak area with additive concentration. Fig. 18 displays the area of the two ammonia peaks obtained from the deconvolution of the TPD peak. From this figure, it is evident that ammonia-TPD of WO₃:V shows a high rise of the labelled Brønsted peak as vanadium concentration increases. Taking into account the DRIFTS data, which showed the strong Brønsted acidity

5. Surface species and reactions on WO₃-based powders

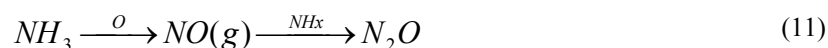
of these samples, the first desorption of ammonia is probably coming from NH₄⁺ ions on Brønsted acid sites. On the other hand, ammonia desorption from copper and chromium catalysed WO₃ shows a similar pattern to that of pure WO₃, confirming the previously reported DRIFTS results. This would clarify that this first desorption peak must come from ammonia adsorbed on Brønsted acid sites.

Nevertheless, this interpretation is rather tentative since current literature does not clearly show the source of these ammonia peaks. In fact, some TPD experiments where NH₃ was adsorbed at room temperature on metal oxides are showing a single desorption peak [18-20], whereas some other papers show a double peak [21,22], although its nature is sometimes attributed to ammonia on two different Lewis acid sites. Actually, DRIFTS data revealed that ammonia is adsorbed on two different Lewis sites in our WO₃ since the symmetric deformation of coordinated ammonia splits in a broad component around 1270 cm⁻¹ and in a sharper one at 1221 cm⁻¹. Moreover, only the sharper vibration appeared at high temperature. It is also necessary to point out that the second ammonia desorption peak is rather broad, what suggests that there may be several different Lewis acid sites with small differences in their desorption energy. However, TPD data of vanadium-catalysed seem to support our assignment.

TPD data also indicate that ammonia is oxidised by chemisorbed oxygen to form N₂, N₂O, H₂O and NO following the reactions (3)-(5) described above. However, it must be assumed that these reactions are only describing the whole process, since it is accepted that, as ammonia is adsorbed, NH_x (x=2,1,0) species are formed by H-abstraction (ammonia molecule is 'stripped'). Although there is not a fully agreement on the chemical reactions of ammonia on metal oxides, it has been suggested that N₂ and water are formed upon recombination of two adjacent NH_x species followed by decomposition of the intermediate surface species [13,18,22]. Therefore, the N₂-reaction is enhanced as the density of NH_x-sites increases, since two of these species must recombine and their mobility on the surface of metal oxides is reduced [13]. On the other hand, NO is reported to come from the reaction of a NH_x species with lattice oxygen. This situation may become common when the number of active sites is low and so NH_x species can not recombine. Finally, the source of nitrous oxide is less clear and two paths have been proposed: the recombination of two NH_x species with lattice oxygen or the reaction of previously formed NO with a NH_x species. Surprisingly, this second path is reported to be more likely since the formation of N₂ from NH_x species has thermodynamic preference over the formation of N₂O [13].

5. Surface species and reactions on WO₃-based powders

If these reaction paths are correct, and considering that N₂ must be desorbed as soon as it is produced, TPD data suggest that NO species are produced and that they are recombined with NH_x species to produce N₂O. This is clearly revealed by the fact that water is desorbed before N₂, indicating that the NO-forming reaction is produced before following the path:



Besides, some of the NO is not reacting and is actually strongly bonded to the surface of WO₃. On the other hand, N₂ formation should come from the recombination of two NH_x species. Nevertheless, our TPD data cannot rule out the possible direct formation of N₂O and water from NH_x species.

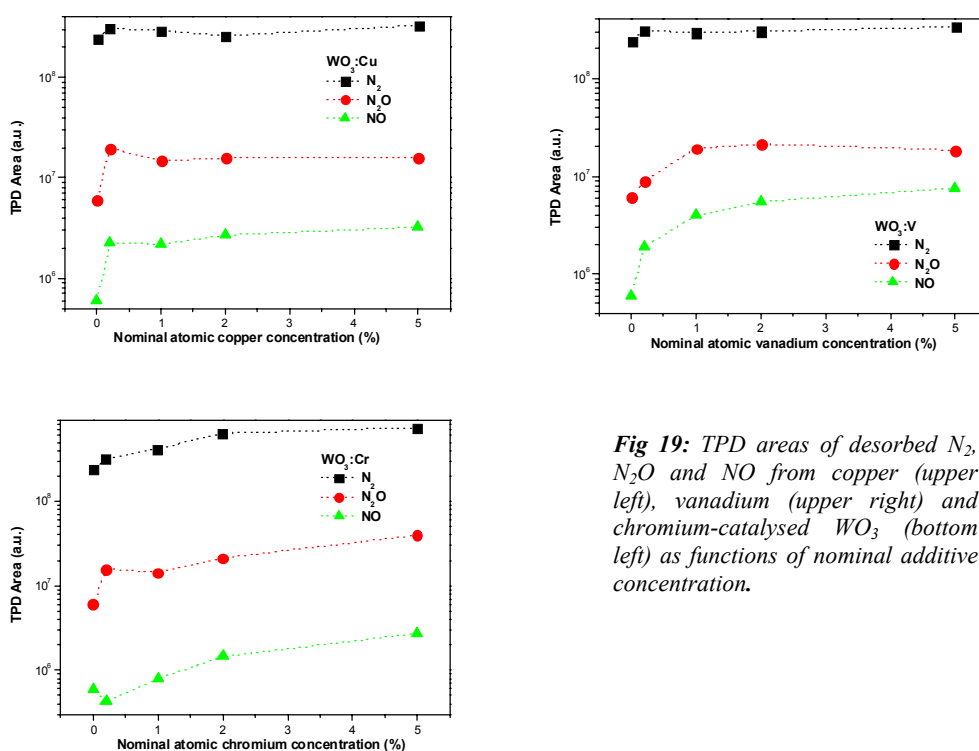


Fig 19: TPD areas of desorbed N₂, N₂O and NO from copper (upper left), vanadium (upper right) and chromium-catalysed WO₃ (bottom left) as functions of nominal additive concentration.

The influence of additives on these reactions can be further clarified if the area of the previously presented TPD peaks is evaluated and compared. From Fig. 19, it is clear that the desorption of N₂, N₂O and NO is higher when additives are present. Moreover, the amount of desorbed species is in some cases raising as the additive concentration increases.

5. Surface species and reactions on WO₃-based powders

This feature is two-fold: as the amount of desorbed NH₃ was similar in pure and catalysed samples, from Fig. 19 it must be concluded that the amount of ammonia adsorbed is clearly higher when additives are present, since all N-containing species must come from preadsorbed ammonia. Besides, catalysed-WO₃ promotes the catalytic oxidation of ammonia. This is a key point that it is worthy mentioning again: additives not only catalyse the reaction but also enhance the adsorption of the target molecule.

Fig. 20 displays some features of the nitrogen desorption from catalysed samples. It is evident that copper addition slightly increases the amount of N₂ produced (Fig. 19) and displaces the desorption peak a little bit to lower temperatures, compared to pure WO₃. This suggests that copper addition has little impact on ammonia oxidation into nitrogen. On the other hand, vanadium catalysed samples show a clear displacement to lower temperatures of the single N₂ desorption peak, but the amount of nitrogen desorbed is virtually the same as from pure WO₃. This indicates that vanadium is probably enhancing the 'stripping' of the ammonia molecule so their recombination into N₂ with a lower activation energy. However, the mechanism would be mainly the same as there is a single peak again. Finally, chromium addition leads not only to enhance N₂ desorption at the same temperature of pure WO₃, but also make new peaks appear at remarkable lower temperatures. Therefore, chromium enhances the formation of NH_x species adsorbed on WO₃-sites and additionally

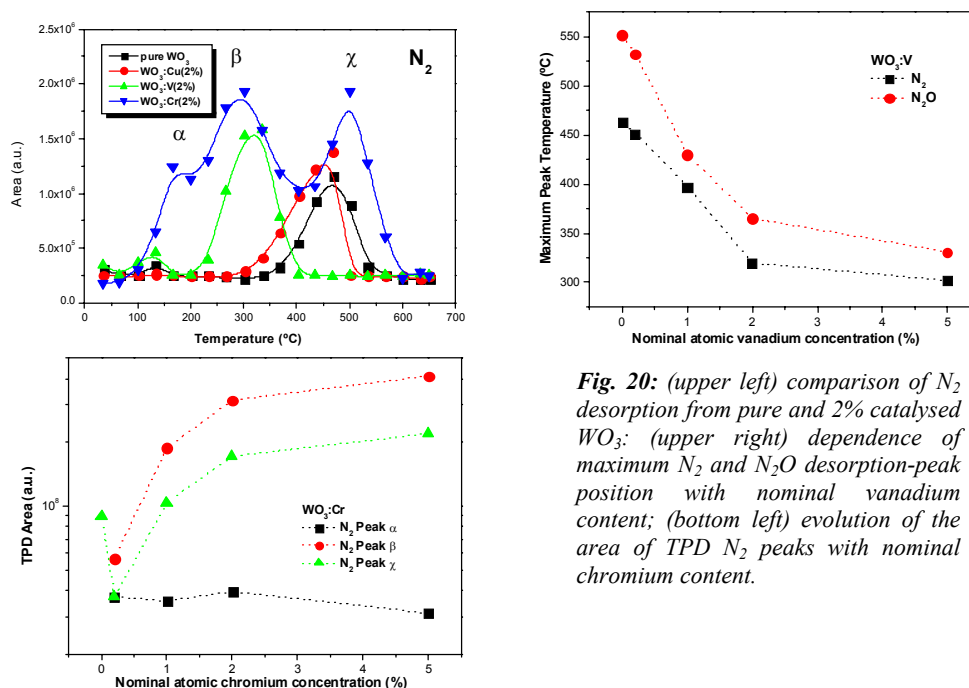


Fig. 20: (upper left) comparison of N₂ desorption from pure and 2% catalysed WO₃; (upper right) dependence of maximum N₂ and N₂O desorption-peak position with nominal vanadium content; (bottom left) evolution of the area of TPD N₂ peaks with nominal chromium content.

5. Surface species and reactions on WO₃-based powders

provides new sites for the recombination of these groups, probably on chromium centres. Evidently, this is the sort of mechanism that seems better for gas sensing since nitrogen would not interfere on sensor response.

As to nitrous oxide desorption (Fig. 21), a rather different dependence on catalytic additive is observed. Copper addition enhances the production of N₂O and displaces the two desorption peaks to lower temperatures. This is clear evidence that copper addition catalyse

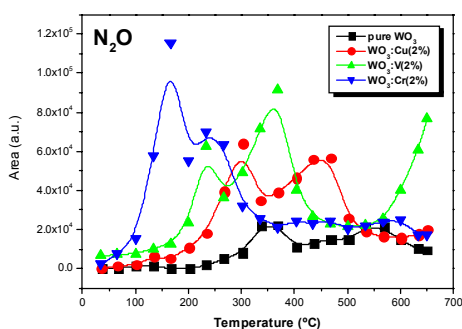


Fig. 21: Ammonia-TPD spectra of pure and 2% copper, vanadium and chromium-catalysed WO₃ at room temperature (only N₂O desorption).

this conversion of ammonia into nitrous oxide. A similar situation is exhibited by vanadium catalysed WO₃, although it presents a more evident evolution with vanadium nominal content (see Fig. 20). On the other hand, WO₃:Cr is again presenting additional desorption peaks at lower temperatures. This is indicating that chromium addition is providing new reaction sites and, assuming that N₂O is produced as a reaction of NO with NH_x species, additional oxygen species that

react with NH_x species to produce the intermediate nitrogen monoxide.

Lastly, NO desorption is very similar in all analysed materials but for the vanadium catalysed ones, where this gas is desorbed at lower temperatures as vanadium content increases. The interpretation of this dependence is not clear, although one tentative proposal might be that as vanadium content increases, more oxygen species are available for the reaction with NH_x groups to form NO at lower temperatures.

To recap:

- TPD ammonia-desorption data indicate that ammonia is adsorbed on Brønsted acid sites (low temperature peak) and Lewis acid sites (high temperature peak) on pure WO₃.
- Nitrogen is desorbed at high temperatures in pure WO₃, probably because the ammonia molecule suffer H-abstraction to form enough NH_x species (x=2,1,0) that can recombine to form N₂.

5. Surface species and reactions on WO₃-based powders

- Nitrous oxide is formed at lower temperatures, probably due to the reaction of previously formed NO groups with NH_x species. Therefore, NO formation on the surface of WO₃ is the first step in the catalytic reaction of ammonia.
- Nitrogen monoxide is desorbed at high temperatures, probably due to the fact that no more NH_x species are available and it can not be adsorbed any more.
- Introduction of catalytic additives is clearly enhancing the adsorption of ammonia, according to the higher quantities of ammonia, nitrogen, nitrous oxide and nitrogen monoxide desorbed from catalysed WO₃.
- Only vanadium is affecting the ammonia desorption, limiting its adsorption to Brønsted acid sites.
- Nitrogen and nitrous oxide desorption reveals that copper and vanadium increase the number of NH_x species (reacting on WO₃ sites) and that chromium is also able to provide new sites for the NH_x recombination at lower activation energies.

Hydrogen sulphide TPD

TPD data of H₂S adsorption on pure WO₃ revealed that this gas is adsorbed on two different sites at room temperature. When adsorption temperature raises, only the desorption peak at high temperature is found. Similar findings have been reported in [24,25]. These works deal with the adsorption of hydrogen sulphide on different metal oxides and assign these two adsorption peaks to nondissociative (low temperature peak) and dissociative (high temperature peak) adsorption of H₂S. These assignments are supported by infrared investigations [26,27].

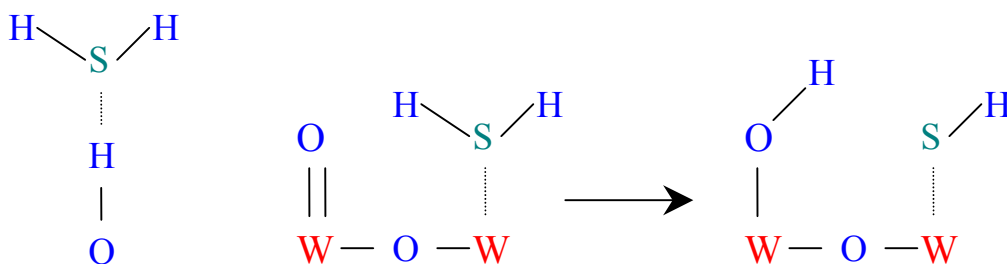


Fig. 22: Non-dissociative (left) and dissociative (right) adsorption of hydrogen sulphide on tungsten oxide.

The associative desorption of H₂S is understood as an adsorption where the molecule is not split but remains adsorbed as H₂S. Reference [26] also suggests that this adsorption could

5. Surface species and reactions on WO₃-based powders

occur on OH groups (Brønsted acid sites) on Al₂O₃. Since these acid sites are commonly present on the surface of WO₃, as already mentioned on DRIFTS section, it may be that this adsorption take place on OH groups (Fig. 22) since water must be completely desorbed after the pretreatment.

Nevertheless, TPD data indicate that this species is not present at temperatures over 100°C and thus it is not so interesting for the understanding of sensing mechanisms on gas sensors. On the other hand, dissociative adsorption of H₂S on WO₃ is found at 100°C and 200°C. This dissociative adsorption means that the H₂S molecule lead to the formation of a HS (sulfhydryl) and OH (hydroxyl) groups with the aid of superficial oxygen species. Since HS groups are supposed to stabilise on unsaturated cation sites [27] and considering the distribution of surface W atoms on the surface of tungsten oxide (as already noted in the DRIFTS *Discussion* section), one tentative proposal of adsorption may be that displayed in Fig. 22. As a matter of fact, this is the same route that ammonia molecules follow to form NH_x species.

These HS groups are the only stable species over 100°C, what means that they are participating in the reactions of combustion on the surface. As revealed by TPD data, the products of the combustion are SO₂ and H₂O, so a possible reaction path might be:



It should be noted that the reaction above is just representing the combustion of SH groups in one just one single step that may contain actually some other reactions. For instance, it is assumed that sulphur can be found after breaking SH groups by further H-abstraction [28]. Moreover, it has been even proposed in many works that sulphur can replace oxygen atoms and so lead to sulphurise the surface of some metal oxides. In particular, this is the sensing mechanism proposed for the hydrogen sulphide sensors based on SnO₂-CuO [29,30]. These works state that CuS is formed and, as the conductivity of CuS is higher than that of CuO, the resistance of the sensing layer decreases. Regarding specifically the detection of hydrogen sulphide by WO₃, as stated in Chapter 4, a paper in the early 1990s [31] hypothesised a similar sensing mechanism. Since WS₂ has a higher conductivity, exchange of oxygen by sulphur may be responsible for the increase of conductivity when the atmosphere was changed from synthetic air to H₂S. However, Frühberger et al. [32] have more recently experimentally concluded that oxygen vacancies are produced on the surface

5. Surface species and reactions on WO₃-based powders

of WO₃ by the consumption of oxygen species and that sulphurisation would need atmospheric pressures of H₂S. Moreover, it was stated that hydrogen sulphide was firstly decomposed in SH groups and that it was the reaction of these groups with oxygen species the responsible for the conductivity variation and so for sensor response. To sum up, hydrogen sulphide is adsorbed on the surface of WO₃ as HS groups at temperatures over 100°C and this species react further with oxygen centres to form SO₂ and H₂O.

Finally, it is necessary to point out that, although hydrogen sulphide is converted into SH, it is H₂S what it is later desorbed. This process occurs through a recombination of SH groups, which has been already described in [28]. Accepting that only SO₂ or H₂O can be finally obtained in catalytic reaction, a possible path could for SH recombination might be:

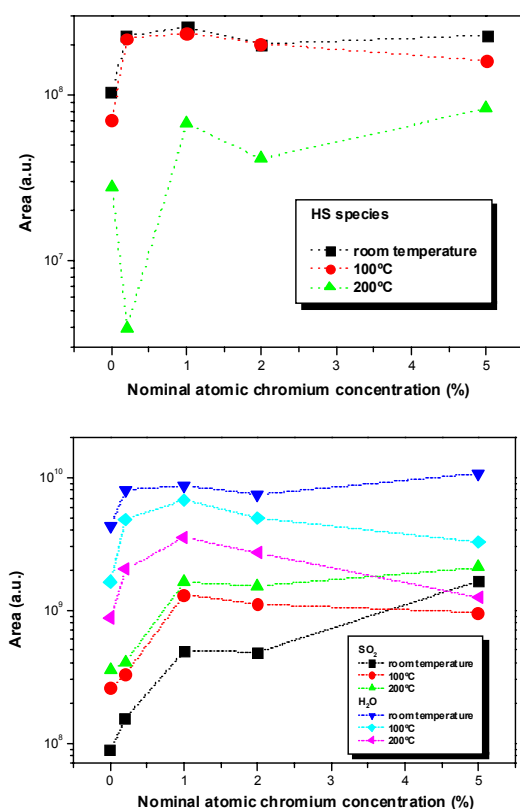
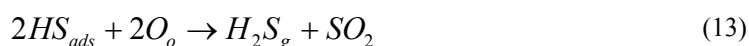


Fig. 23: Variation of the amount of desorbed products of hydrogen sulphide-TPD experiments with nominal chromium content.

As regards SO₂ desorption from pure WO₃, its quantity is maximum after the 200°C-adsorption. This fact is twofold: it shows that catalytic combustion is enhanced as adsorption temperature increases and that most of the SO₂ produced is not easily desorbed at that temperature. By contrast, the amount of H₂O decreases as adsorption temperature raises. This indicates that water is not so strongly adsorbed as SO₂. The desorption of SO₂ is a feature that must be taken into account when dealing with gas sensors, since it is necessary that catalytic combustion products do desorb so as to reoxidise the surface by oxygen gas and thus recover the initial level of sensor conductivity.

5. Surface species and reactions on WO₃-based powders

Concerning the influence of chromium addition, TPD data revealed that a new adsorption site appears for HS species when chromium is present after the room temperature adsorption. This second peak was found at a higher desorption temperature than the first dissociative, what implies that this second HS species is more strongly adsorbed. Moreover, the quantity of dissociative adsorption on the first site also increases. This would suggest that not only unsaturated chromium atoms are present, but also that the addition of chromium increases the number of sites on tungsten centres. As adsorption temperature raised, these two peaks overlapped and finally became a single broad one.

Accordingly, the amount of SO₂ desorbed is also higher when chromium is present. Multiple peaks were found after room temperature-adsorption, what points to consider that more oxygen species are available for the reaction with SH species than in the case of pure WO₃. As adsorption temperature increases, the number of peaks is reduced but their intensity is still higher in chromium catalysed samples. Finally, it is interesting to notice that there was little correlation between the amount of gases desorbed and the concentration of chromium on WO₃. Fig. 23 display the amount of H₂S (only the dissociative peak), SO₂ and H₂O desorbed from the analysed samples. This was calculated from the area under TPD peaks. Generally speaking, 1%-2%-5% samples showed similar results, what may indicate that there is a sort of *saturation* of the catalytic activity as the concentration of chromium is over 1%.

To sum up:

- Hydrogen sulphide is both undissociatively and dissociatively adsorbed on pure and chromium catalysed WO₃, although only HS species are found over 100°C.
- Chromium introduction provides a new adsorption site for SH species, apparently contributing to the dissociation of hydrogen sulphide
- Combustion products of hydrogen sulphide with oxygen on pure and chromium catalysed WO₃ are SO₂ and H₂O.
- Chromium addition leads to enhance the catalytic combustion of hydrogen sulphide, although there is not a straightforward correlation between nominal chromium content and catalytic activity.

5.3 Conclusions

These are the general conclusions drawn from the DRIFTS and TPD investigation on pure and catalysed WO₃ nanocrystalline powders. Unless it is clearly pointed out, it must be understood that these conclusions are applicable to all the analysed samples.

- Two different kinds of water are adsorbed on the surface of the powders at room temperature, according to DRIFTS results. One species is desorbed as temperature is risen over room temperature, while the other one is not desorbed until the temperature is over 200°C in synthetic dry air.
- Two different kinds of hydroxyl groups are also adsorbed on the surface of the powders at room temperature, according to DRIFTS results. In this case, one species decreases as temperature is above room temperature, whereas the other one is stable up to 400°C. Therefore, the latter may play an important role in surface reactions on WO₃.
- Ammonia adsorption revealed that two different acid sites are present on the surface of WO₃ following DRIFTS measurements: Lewis and Brønsted acid sites. This fact is confirmed by TPD of ammonia, since it presents two peaks that are attributed to ammonia on these different sites.
- Ammonia on Brønsted acid sites (OH groups) is desorbed at temperatures over 200°C. Only vanadium-catalysed WO₃ exhibits strong Brønsted acidity, as concluded from both DRIFTS and TPD experiments.
- There are at least two different Lewis acid sites (unsaturated cations) in the examined WO₃ powders and ammonia is stable in one of them up to 300°C.
- On pure WO₃, ammonia is apparently reacting with oxygen species belonging to terminal W=O bonds as DRIFTS measurements show. Besides, nitrosil species are also detected, probably coming from adsorbed NO. These features are not found in catalysed WO₃, what may indicate that additives prevent this reaction from happening.
- The previous point is clarified by TPD measurements, that reveals fundamental differences in the desorption of ammonia-oxygen combustion products (nitrogen, nitrous oxide, nitrogen monoxide and water). According to TPD data and assuming the reaction mechanisms explained above, it is proposed that more sites for NH_x species are available when additives are present. Moreover, ammonia reacts with other oxygen species than terminal W=O groups, tentatively oxygen species associated to the additives. As the concentration of NH_x species is high, the reaction of NO with one of

5. Surface species and reactions on WO₃-based powders

this species to form N₂O is enhanced and so NO is less present on the surface, what may account for the DRIFTS data.

- Remarkably, chromium addition leads to nitrogen desorption at low temperatures, reflecting that a high concentration of NH_x reactive species appear when chromium is present.
- Hydrogen sulphide is both undissociatively and dissociatively adsorbed on pure and chromium catalysed WO₃, although only HS species are found over 100°C. The combustion products desorbed are sulphur dioxide and water
- Chromium introduction provides a new adsorption site for SH species, apparently contributing to the dissociation of hydrogen sulphide. Moreover, chromium addition leads to enhance the catalytic combustion of hydrogen sulphide, although more SO₂ is adsorbed.

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