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Mechanism of NH_3 interaction with transition metal-added nanosized WO_3 for gas sensing: In situ electron paramagnetic resonance study

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Abstract

The interaction of ammonia with transition metal (Cr, V, Cu)-added WO_3, base materials for NH_3 gas sensing devices, was investigated by electron paramagnetic resonance. The EPR analysis was carried out on samples obtained as nanosized powders by wet method. It was demonstrated that the addition of transition metal ions promotes the ammonia oxidative dehydrogenation to N_2 and N_2O, due to trapping of NH_3 electrons on Cu(II), V(V) and Cr(V) centres. The higher catalytic efficiency of Cr(V) is relatable to the acceptance of two electrons by each metal ion, instead of one electron as by Cu(II) and V(V) ions. Cr(V) centres are present as chromyl groups, $[Cr{=}O]^{3+}$, which were found in higher amount when the annealing takes place without an effective oxidative dehydration (673 K instead of 973 K). This condition stabilizes the chemisorption of NO on the oxide surface annealed at 673 K. A relevant quantity of NO affects the resistance base line of the electrical response and has to be avoided.

Keywords: Ammonia sensing; Transition metal added WO_3; Electron paramagnetic resonance

1. Introduction

Among the semiconductor metal oxides which vary their electrical resistance properties under reaction with surrounding gases, WO_3 is considered one of the most promising materials for ammonia detection [1–3]. As a consequence, the understanding of the surface reactions at the solid–gas interface and the identification of reactive species were the object of several studies, aimed to improve the WO_3 electrical response.

We recently investigated [4,5] the interaction of ammonia with both pure and transition metal (Cu, V, Cr)-added nanosized WO_3 powders. Transition metals were selected among those successfully employed as promoters of semiconductor oxide-assisted NH_3 oxidation [6,7]. It resulted that the electrical response ($S = R_{air}/R_{NH_3}$) generally increases by metal addition, the sensitization depending on the type of metal with the order $Cr \gg Cu \approx V$ [4,5]. Moreover, the dynamic behaviour towards ammonia was associated to the addition of metals [4,5]; specifically, the trend of resistance decreases after NH_3 contact and of recovering the initial value after NH_3 removal did not show overshooting effects in the resistance of transition metal-added materials, instead observed in pure WO_3 [4,5].

In order to suggest a rationale for the above described behaviour, it was proposed [5] that ammonia molecules chemisorb on acidic Lewis and Broested sites (reactions (1) and (2)). If not simply desorbed, NH_3 undergoes dehydrogenation through interaction with oxygen lattice centres O_0, producing hydroxyl groups. As a consequence the process generates $NH_{3-n}{}^{n-}$ ($n = 1$, 2 and 3) species (reaction (3)) which, interacting with another $NH_{3-n}{}^{n-}$, produces molecular nitrogen (reaction (3A)); alternatively $NH_{3-n}{}^{n-}$ reacts with an oxygen centre to form nitrogen monoxide (reaction (3B)). $NH_{3-n}{}^{n-}$ is also able to interact with NO, this being reduced to N_2O (reaction (3C)):

$$NH_{3(g)} \leftrightarrows M{-}NH_3\ (M = W, Cr, Cu, V) \qquad (1)$$

$$NH_{3(g)} + M{-}OH \leftrightarrows M{-}O^{-}NH_4{}^{+}\ (M = W) \qquad (2)$$

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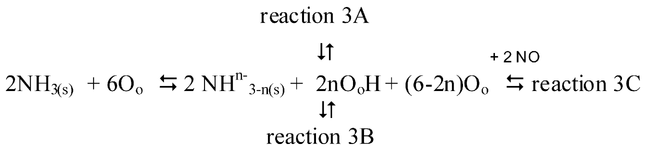


$$\begin{array}{c} \text{reaction 3A} \\ \downarrow\uparrow \\ 2NH_{3(s)} + 6O_o \leftrightarrows 2\,NH^{n-}_{3-n(s)} + 2nO_oH + (6\text{-}2n)O_o \overset{+\,2\,NO}{\leftrightarrows} \text{reaction 3C} \\ \downarrow\uparrow \\ \text{reaction 3B} \end{array} \qquad (3)$$

$$\leftrightarrows N_2 + 6O_0H + 6e^- \leftrightarrows N_2 + 3H_2O + 3O_0 + 6e^- \qquad (3A)$$

$$\leftrightarrows 2NO + 6O_0H + 10e^- \leftrightarrows 2NO + 3H_2O + 3O_0 + 10e^- \qquad (3B)$$

$$\leftrightarrows 2N_2O + 6O_0H + 6e^- \leftrightarrows 2N_2O + 3H_2O + 3O_0 + 6e^- \qquad (3C)$$

Reactions (1), (2), (3A)–(3C) were suggested basing on the results of diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy and of temperature programmed desorption (TPD), which allowed to detect either chemisorbed ammonia species or its combustion products, N_2, NO, N_2O [4,5]. Nevertheless, although the promoting effects of transition metal ions in reactions (3A)–(3C) were well assessed, no explanation is still available at molecular level about the different capability of the metals in assisting NH_3 deprotonation on WO_3 surface.

Considering that all the examined transition metal centres in principle give rise to paramagnetic electronic states which are expected to be modified by NH_3 interaction, an electron paramagnetic resonance (EPR) investigation was performed on Cu, V and Cr-added WO_3, treated with ammonia under conditions reproducing the operative ones in sensor devices.

The results of the spectromagnetic investigation were discussed in relation with the data of the electrical response, in order to find a rationale for the main resistance variations among samples added by different metals.

2. Experimental

2.1. Preparation of materials

Tungstic acid (10.0 g) was dissolved in 31.0 mL of methanol. After stirring for 15 min at room temperature, 18.0 mL of water were slowly dropped into the tungstic acid–methanol solution (1:25, tungstic acid:water molar ratio), which was refluxed in air at 80 °C under stirring for 24 h. Afterwards it was dried in vacuum and the obtained powder further treated for 5 h at 110 °C in air. WO_3 was obtained by annealing at 673 or 973 K the dried powder for 4 h, under dry flowing air, operating in a quartz apparatus suitable for both gas flow and EPR measurements. copper-, vanadium- and chromium-catalysed WO_3 (Cu or V:WO_3 molar ratios 0.002 and 0.02; Cr:WO_3 molar ratios 0.002, 0.01, 0.02, 0.05) were prepared by adding the stoichiometric amounts of monohydrate copper acetate (dissolved in methanol), ammonium metavanadate (dissolved in aqueous oxalic acid, 10^{-4} M), chromium nitrate nonahydrate (dissolved in methanol) to the tungstic acid–methanol solution and refluxing at 80 °C under stirring for 24 h. Drying and annealing steps were the same as for pure WO_3.

Cu-, V- and Cr-added WO_3 will be hereafter named WO_3:M(*T*%), where M is Cu, V and Cr, *T* is the thermal annealing temperature, % is the M:WO_3 molar ratio percent. As example WO_3:Cu (673, 2%) indicates WO_3 added by Cu in a Cu:WO_3 0.02 molar ratio, annealed in air at 673 K.

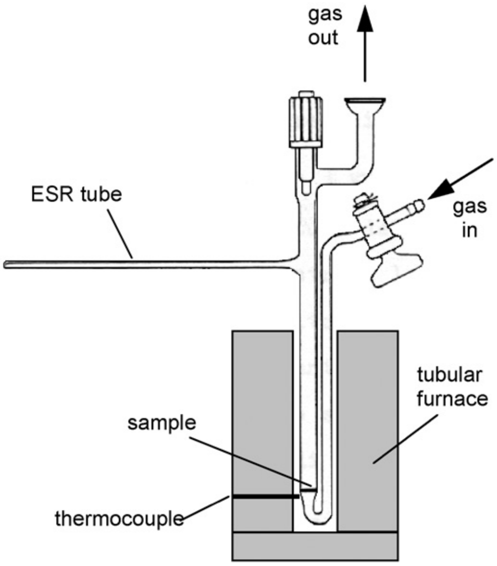
The crystal size of powders was estimated from XRD spectra [4,5] and it ranged between 19 and 26 nm for 673 K annealed samples, between 52 and 64 for the 973 K annealed ones.

2.2. Electron spin resonance measurements

Electron spin resonance measurements were performed on WO_3:M (*T*%) after the following successive treatments:

(i) as prepared WO_3:M (*T*%) samples M = Cr, Cu, V;
(ii) samples treated 10 min at room temperature with flowing NH_3 (500 ppm)/air or NH_3 (500 ppm)/argon;
(iii) samples treated 20 min at 473 K with flowing NH_3 (500 ppm)/air or NH_3 (500 ppm)/argon;
(iv) samples treated 10 min at room temperature with flowing air;
(v) samples treated 20 min at 473 K with flowing air.

The (i)–(v) gas-thermal treatments were performed on weighted amount of sample, in a quartz apparatus suitable for both gas-flow (30 cm^3 min^{-1} for all gases) and EPR measurements (Scheme 1) in order to avoid contact with uncontrolled atmosphere. After each treatment the gas flow was stopped and samples were quenched at room temperature before recording the spectrum. Spectra were recorded at 123 K both under the same treatment atmosphere and under argon atmosphere after evacuation (10^{-1} Torr). In case of different results, both spectra were reported; otherwise it is intended that the atmosphere does not affect the observed paramagnetic species.



Scheme 1. Experimental set up to perform gas treatments and to record EPR spectra.

The X band CW-EPR spectra were recorded at 123 K on a Bruker EMX spectrometer, using 20 mW microwave power and 5 G modulation amplitude. The temperature control was achieved through an Oxford cryostat for X band spectrometer. The g values were measured by standardisation with diphenylpicrylhydrazyl (DPPH). The amounts of paramagnetic centres were calculated by using a calibration curve of the resonance areas of $Cu(NO_3)_2\cdot 1/2H_2O$ in frozen ethylene glycol–water solutions. Spectra were simulated by using the Brucker WINEPR Simfonia program.

3. Results

3.1. Nanosized WO_3

Pure WO_3, annealed at 673 or 973 K in air, showed the resonance lines of vanadium(IV) impurities; no different paramagnetic species were observed under the treatments (i)–(v).

3.2. Cr-added WO_3

The results of our previous EPR investigation [5] on WO_3:Cr (673 or 973, %), annealed in air, are here summarised for the sake of clarity, in order to allow easy comparison with the behaviour of these samples treated by NH_3. EPR spectra of WO_3:Cr (673, 1%) and WO_3:Cr (973, 1%), are reported as examples in Fig. 1a and b.

The resonances indicated by δ consist of a broad positive lobe around $g = 3.5–5.0$ and were attributed to Cr(III) centres in strongly distorted octahedral symmetry [8]. The β signal, broad resonances centred at $g = 1.98$, were attributed to Cr_2O_3-like clusters [8]. The γ signal is strongly dependent on the thermal treatment. In fact in samples annealed at 673 K (Fig. 2, line a) a single signals with axial symmetry, $g_\perp = 1.967$, $g_{||} = 1.886$, was observed and this was named species A; in samples annealed at 973 K (Fig. 3, line a) two signals, the above axial one and a new rhombic one with $g_1 = 1.949$, $g_2 = 1.912$, $g_3 = 1.823$ appeared. The rhombic centre was called species B. Both γ signals were attributed to isolated Cr centres with d^1 electronic configuration, formally Cr(V) centres, whose symmetry field is distorted from the cubic one by the presence of the chromyl, $[Cr{=}O]^{3+}$, group [5]. The amount of Cr(V) in chromyl species (A and B) depends on the Cr content and the annealing temperature; the molar ratios Cr(V): total Cr were in the range 0.02–0.08 for samples annealed at 673 K and 0.01–0.08 at 973 K. For a given chromium content, Cr(V) centres are generally less abundant in samples annealed at higher temperature, 973 K, probably due to a reductive dehydration active at this temperature, behaviour observed also in Cu and V-added samples [4,5,9].

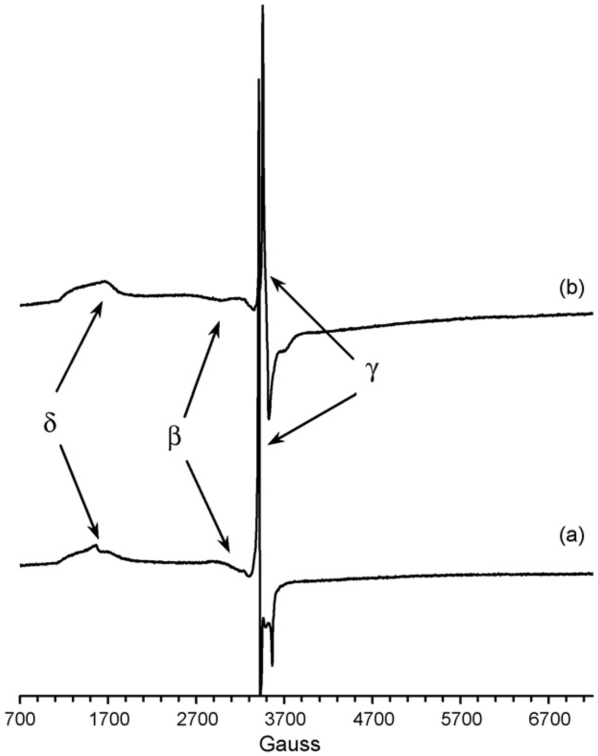


Fig. 1. EPR spectra of Cr:WO_3 samples annealed in air at: (a) 673 K and (b) 973 K. Cr(III) (labelled β and δ) and Cr(V) (labelled γ) species are indicated.

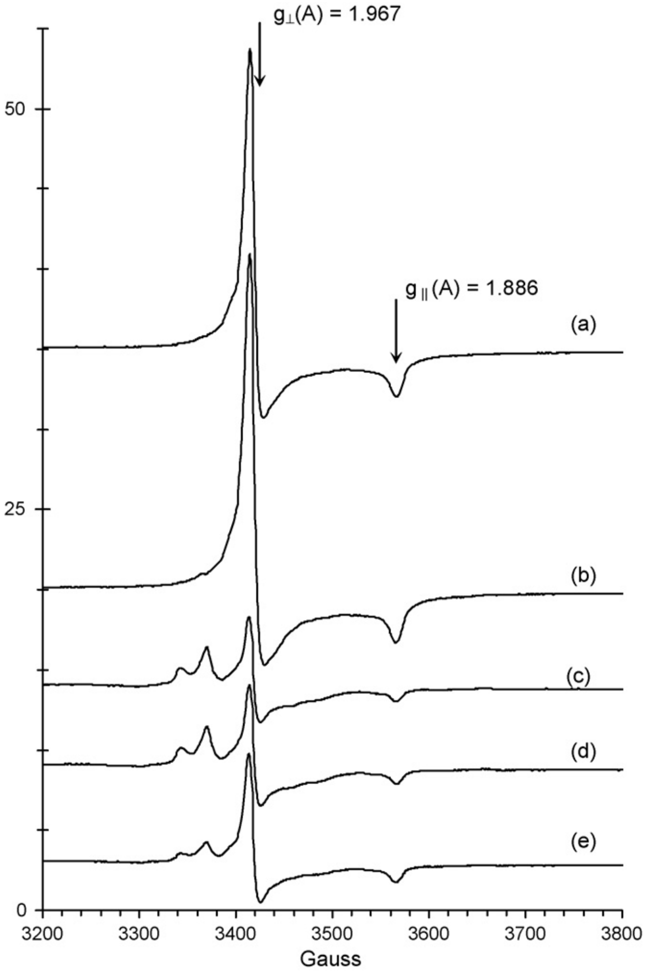


Fig. 2. EPR spectra of Cr:WO_3 (0.01 mol:mol) (a) annealed at 673 K in air and after the following successive treatments (b) NH_3/air at RT; (c) NH_3/air at 473 K; (d) air at RT; (e) air at 473 K.

XPS investigation performed on annealed samples [5 and references therein] presented a main Cr $2p_{3/2}$ peak with binding energy around 577.0 eV, typical of Cr(III); the small metal

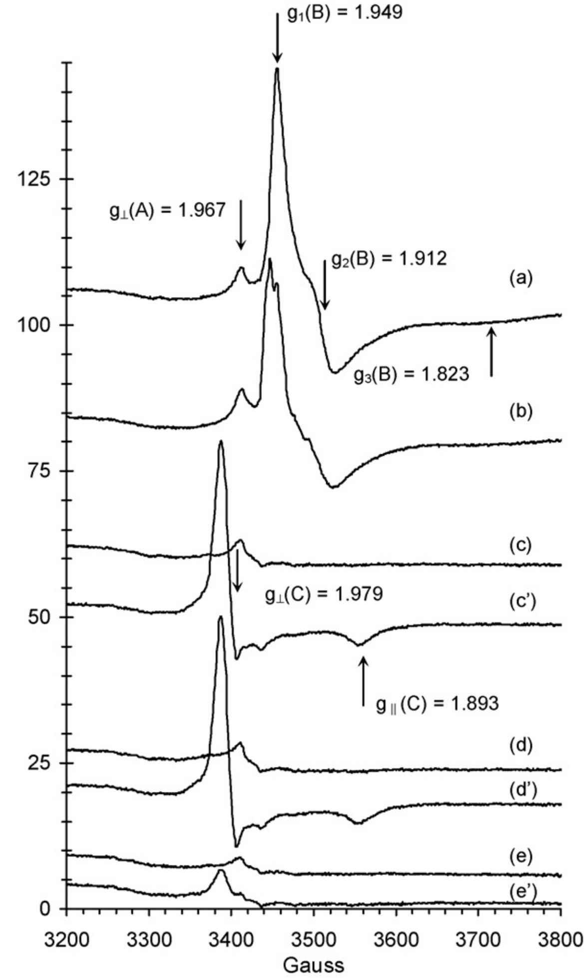


Fig. 3. EPR spectra of Cr:WO$_3$ (0.01 mol:mol) (a) annealed at 973 K in air and after the following successive treatments (b) NH$_3$/air at RT; (c) NH$_3$/air at 473 K; (c′) EPR spectrum recorded in argon atmosphere after treatment (c); (d) air at RT; (d′) EPR spectrum recorded in argon atmosphere after treatment (d); (e) air at 473 K; (e′) EPR spectrum recorded in argon atmosphere after treatment (e).

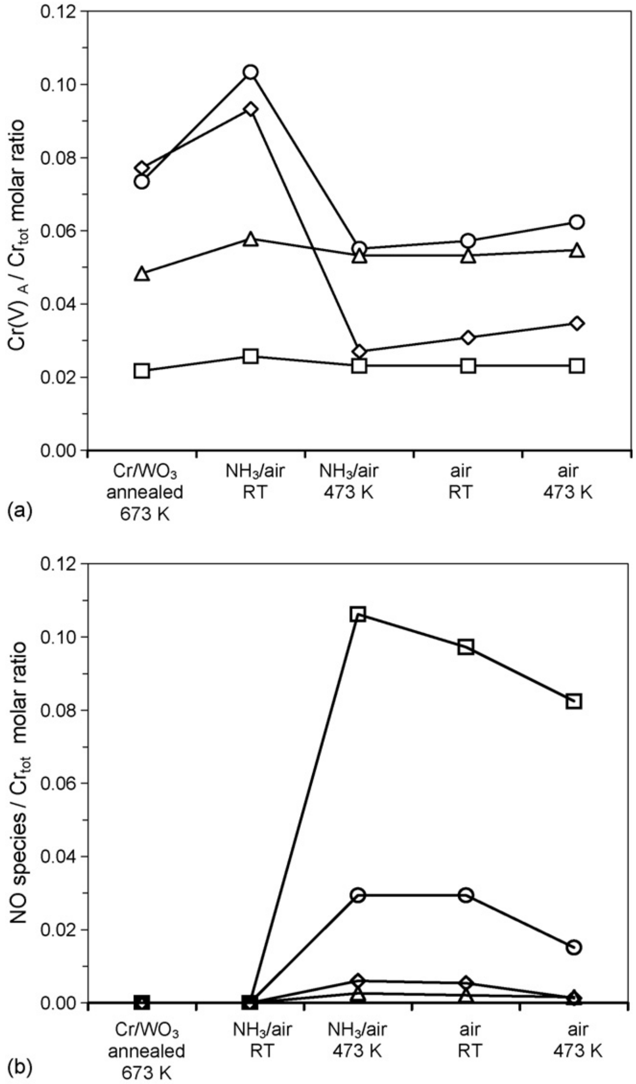


Fig. 4. Trends of: (a) Cr(V)$_A$:Cr$_{tot}$ molar ratio and (b) NO:Cr$_{tot}$ molar ratio vs. gas treatments for the Cr:WO$_3$ samples annealed at 673 K: (□) Cr:WO$_3$, 0.002 mol:mol; (○) 0.01; (◇) 0.02; (△) 0.05.

amount and the band broadness hindered to identify different oxidation states of Cr.

By contacting WO$_3$:Cr (673, 1%) with flowing NH$_3$ (500 ppm)/air or NH$_3$ (500 ppm)/argon, for 10 min at room temperature, no resonance variation was observed (Fig. 2, line b). If the contact was performed at 473 K for 20 min, dramatic changes became evident (Fig. 2, line c). Specifically the [Cr═O]$^{3+}$ resonances underwent strong decrease, likely due to reduction of Cr(V) centres, and new strong signals at lower fields (later attributed to the nitrosyl group NO) became evident. The [Cr═O]$^{3+}$ decrease and the increase of the new resonances depend on the Cr content (Fig. 4a and b), being the new resonances more intense in samples with lower Cr amount. The decrease of the chromyl A species, Cr(V)$_A$, was higher than the increase of NO, except for WO$_3$:Cr (673, 0.2%) where the variation trend is reversed. This suggests that the WO$_3$ surface, when Cr:WO$_3$ $\geq$ 0.01, is not able to chemisorb all the produced NO; thus any quantitative relation between the Cr(V)$_A$ and the EPR-detected NO should be avoided. The sample behaviour did not change even if the treatment was performed by NH$_3$ (500 ppm)/argon instead of NH$_3$ (500 ppm)/air. Thus the formation of the NO species is not depending on the presence of molecular oxygen in the treatment atmosphere.

Deconvolution and fitting of the resonance lines after NH$_3$ contact at 473 K, well evident in WO$_3$:Cr (673, 0.2%) owing to the absence of overlapped [Cr═O]$^{3+}$ lines, strongly suggested that the new resonances (Fig. 5) are attributable to NO chemisorbed on WO$_3$ surface and interacting with high charge cations [10–14]. As a matter of fact, referring to the molecular energy level diagram of NO interacting with a metal ion (Fig. 6) [10], the following first order approximated relations between the orbitals and the g tensor values can be obtained:

$$g_{xx} = g_e, \qquad g_{yy} = g_e - 2\left(\frac{\lambda}{\Delta}\right), \qquad g_{zz} = g_e - 2\left(\frac{\lambda}{\delta}\right)$$

The electrostatic field associated with the interacting cation mainly affects the δ value, that is the separation between the π^*

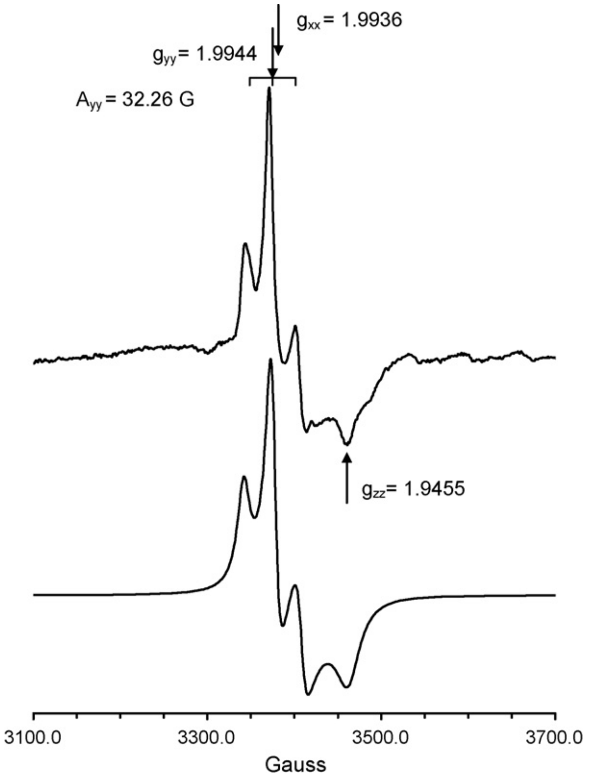


Fig. 5. Experimental (top) and simulated (bottom) EPR spectrum of chemisorbed NO species in Cr:WO_3 sample (Cr:WO_3, 0.002 mol:mol) annealed at 673 K after treatment with NH_3/air at 473 K.

NO orbitals, and consequently modifies the value of g_e–g_{zz}. As a matter of fact, many papers [10–14] about NO interacting with differently charged cations in zeolites demonstrated that the largest shifts from g_e value are observed for g_{zz} value. As an example, the interaction of NO with divalent and trivalent cations causes g_e–g_{zz} values lower than with monovalent ones.

In our case the experimental spectrum was reproduced by $g_{yy} = 1.9944$, $g_{xx} = 1.9936$, $g_{zz} = 1.9455$ being the g_{zz} value typical of the interaction with high charge surface cation. The hyperfine interaction with ^{14}N nucleus ($I = 1$), $A_{yy} = 32.26$ G, was in the range of those reported for NO–zeolite adducts [10]. The absence of detectable hyperfine interaction both with ^{53}Cr and with ^{183}W nuclei indicates that the unpaired electron is mainly located on NO; thus it cannot be suggested whether Cr or W centres fix NO moieties. Considering that the molar ratio between the adsorbed NO species and the total amount of chromium is higher in samples with lower Cr content (Fig. 4b), it seems more probable that NO interacts with W(VI) centres. The shoulders observed at higher field nearby g_{zz} resonance may be due to a triplet species deriving from NO–NO interaction [10] or to V(IV) impurities present in WO_3; however further assessment of these signals is outside the goals of the present paper.

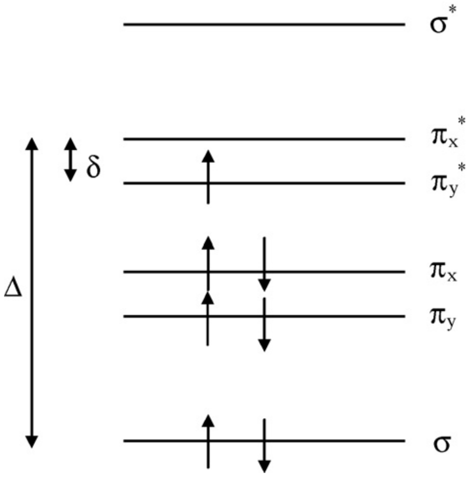


Fig. 6. NO energy level diagram.

Signals of NO chemisorbed on WO_3 in WO_3:Cr (673, %) decrease in intensity (Fig. 4b) by treating samples with air (treatments iv and v), probably because of the formation of NO_2 or chemisorbed diamagnetic NO_x^- ($x = 2$ and 3) species.

WO_3:Cr (973, 1%) samples, contacted with NH_3 (500 ppm)/air or NH_3 (500 ppm)/argon, for 10 min at room temperature, displayed fully different behaviour with respect to the corresponding WO_3:Cr (673, 1%) sample (Fig. 3). In fact the γ signals observed in WO_3:Cr (973, 1%) and attributed to $[Cr{=}O]^{3+}$ centres with axial (species A) and rhombic (species B) symmetry (Fig. 3, line a), both decreased in intensity after NH_3 (500 ppm)/air(Ar) contact at room temperature, but the species B almost disappeared after 20 min contact at 473 K with the same gas mixture (Fig. 3, line c). Rhombic $[Cr{=}O]^{3+}$ centres, present in higher amount in WO_3:Cr (973, %) samples, undergo much stronger variation in intensity than the axial ones as it appears from Fig. 7a and b, where the behaviour of samples with different Cr contents is reported. It seems that the rhombic $[Cr{=}O]^{3+}$ centres are particularly reactive towards NH_3, being Cr(V) probably reduced to Cr(III), but the NO stabilisation on the WO_3 surface was not observed.

Interestingly, when the spectra of NH_3 (500 ppm)/air treated samples were recorded under argon atmosphere or the treatments were performed in NH_3 (500 ppm)/argon, a new resonance, attributable to a $[Cr{=}O]^{3+}$ group with axial symmetry, appeared (species C, Fig. 3, line c′ and Fig. 7c). The values of magnetic tensor are $g_{\perp} = 1.979$, $g_{||} = 1.893$, slightly different from those of the species A, observed in WO_3:Cr (973, %) samples before NH_3 treatment. This new $[Cr{=}O]^{3+}$ centre is a surface species, as indicated by the disappearing of the spectra when recorded under air.

Although it seems difficult to definitely assign its coordination properties, it is possible to hypothesise that the $[Cr{=}O]^{3+}$group is coordinated equatorially to four lattice oxides and axially to one NH_3 molecule, according with the consideration that this species occurs only under NH_3 treatment in the presence of the strongly reactive rhombic pentacoordinated B species. Hyperfine interaction between Cr(V) and ^{14}N is not expected, because the unpaired electron of the d^1 $[Cr{=}O]^{3+}$ group is located in the d_{xy} in plane orbital. The formation of C species suggests that $[Cr{=}O]^{3+}$ does not undergo reduction by NH_3 coordination to Cr.

Figs. 2 and 3 (lines d, e, d′, e′) showed that if Cr-added samples are treated with air, after interaction with ammonia

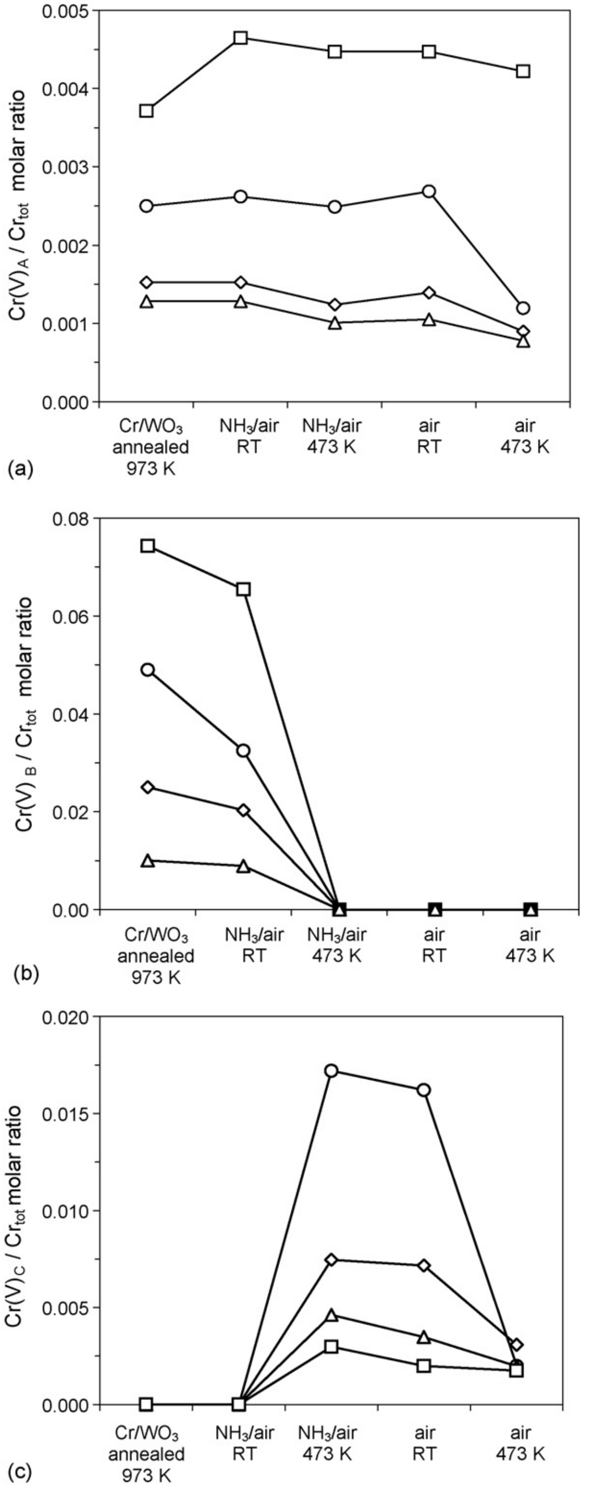


Fig. 7. Trends of: (a) Cr(V)$_A$:Cr$_{tot}$ molar ratio; (b) Cr(V)$_B$:Cr$_{tot}$ molar ratio and (c) Cr(V)$_C$:Cr$_{tot}$ molar ratio vs. gas treatments for the Cr:WO$_3$ samples annealed at 973 K: (□) Cr:WO$_3$, 0.002 mol:mol; (○) 0.01; (◇) 0.02; (△) 0.05.

(treatments iv and v), $[Cr{=}O]^{3+}$ species are not restored. As a matter of fact Cr(V) became stable during the preparation of the Cr-added WO$_3$; once Cr(V) has been reduced by NH$_3$ interaction, the successive re-oxidation of Cr centres probably proceeds until Cr(VI), much more stable state than Cr(V).

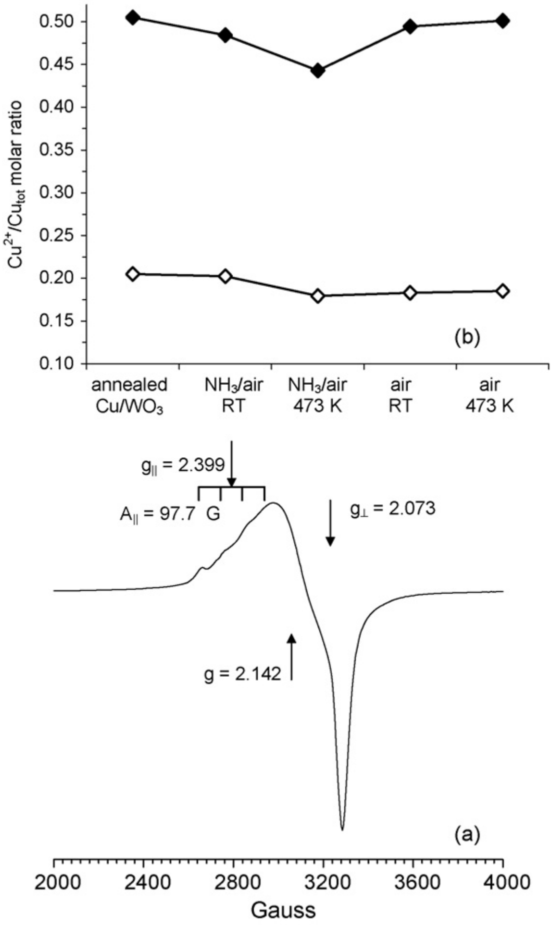


Fig. 8. (a) EPR spectrum of Cu:WO$_3$ (0.02 mol:mol) annealed at 673 K in air; (b) trend of Cu(II):Cu$_{tot}$ molar ratio vs. gas treatments for the Cu:WO$_3$ samples annealed at (◆) 673 K and (◇) 973 K.

3.3. Cu and V-doped WO$_3$

The results of the EPR investigation on WO$_3$:Cu and WO$_3$:V (673 or 973, 2%), annealed in air, were extensively described in a previous paper [4]; they are here summarised in order to allow easier comparison with the behaviour of samples treated by NH$_3$. EPR spectra of WO$_3$:Cu and WO$_3$:V (673 or 973, %) are reported in Figs. 8 and 9.

The spectra of WO$_3$:Cu samples showed the resonance lines of both magnetically isolated, $g_{||} = 2.399$, $g_{\perp} = 2.073$, $A_{||}(Cu) = 97.7$ G, and coupled, $g = 2.142$, Cu(II) centres, the intensity of the coupled species increasing with the annealing temperature [4]. The molar ratios Cu(II): total Cu for WO$_3$:Cu (2%) were ≈0.50 and 0.20 (Fig. 8b) depending on, respectively, the annealing temperature 673 and 973 K.

The spectra of WO$_3$:V samples, annealed at 673 and 973 K, showed resonances attributable to tetracoordinated V(IV) centres [5,15,16], $g_{||} = 1.821$, $g_{\perp} = 1.926$, $A_{||}(V) = 195$ G $A_{\perp}(V) = 53.8$ G. The molar ratios V(IV):total V for WO$_3$:V (2%) were ≈0.03 and 0.005 (Fig. 9b) at, respectively, 673 and 973 K annealing temperature.

XPS spectra of WO$_3$:Cu and WO$_3$:V demonstrated the presence of comparable amount of Cu(II) and Cu(I) and

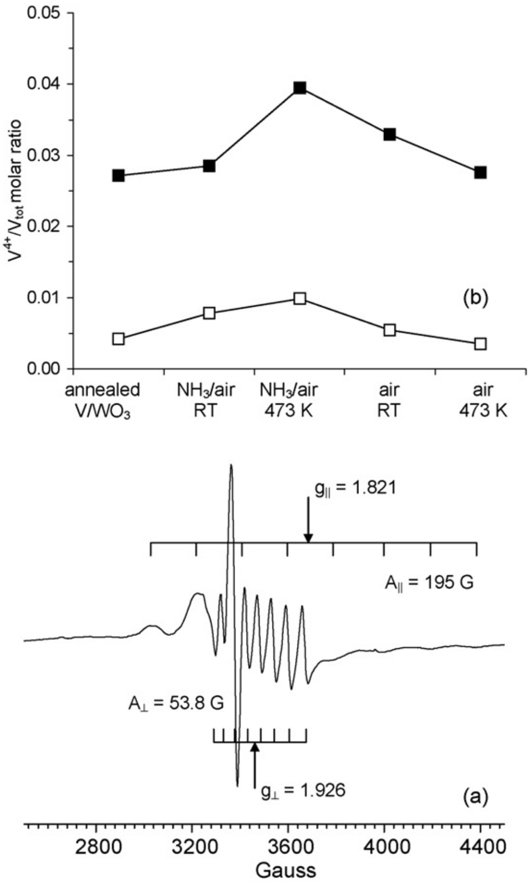


Fig. 9. (a) EPR spectrum of V:WO_3 (0.02 mol:mol) annealed at 673 K in air; (b) trend of V(IV):V_{tot} molar ratio vs. gas treatments for the V:WO_3 samples annealed at (■) 673 K and (□) 973 K.

confirmed that the predominant vanadium oxidation state is V(V) [4].

By contacting WO_3:Cu (673 or 973, %) with flowing NH_3 (500 ppm)/air or NH_3 (500 ppm)/argon at room temperature and, successively, at 473 K, a decrease in intensity of Cu(II) resonances was observed (Fig. 8). Instead WO_3:V (673 or 973, %) revealed an increase in intensity of the resonance lines after the same treatments with NH_3 (Fig. 9). Successive treatments with air restored the initial signal intensity in both cases (Figs. 8 and 9).

The results suggest that NH_3 was able to increase the amount of paramagnetic V(IV) centres, probably reducing some of EPR inactive V(V) centres. Similar reductive process from Cu(II) to Cu(I) is active in Cu-doped samples. No chemisorbed NO species were detected in both samples.

4. Discussion and conclusions

The present discussion is aimed to rationalize the effect of the different added metals in promoting the WO_3 electrical response to the ammonia interaction.

The results of EPR investigation suggest that, under NH_3 gas treatment, EPR active paramagnetic Cu(II) centres partly reduce to diamagnetic Cu(I), diamagnetic V(V) centres partly reduce to V(IV) and $[Cr{=}O]^{3+}$ centres partly reduce to Cr(III), both paramagnetic. Because of the broadness of Cr(III) resonance lines the reduction of chromium can be more easily assessed by the decrease of $[Cr{=}O]^{3+}$ signals than by the increase of Cr(III) signal intensity.

In general the paramagnetic oxidation states V(IV), Cu(II) and $[Cr{=}O]^{3+}$ are not major quantities of the transition metal ions added to WO_3 oxide, the molar ratio with respect to total metal amount varying from 0.005 to 0.03 for V(IV) and from 0.20 to 0.50 for Cu(II). However, their variations, observed under treatments (ii)–(v), are representative of the reductive–oxidative processes induced by NH_3 and O_2. In fact these processes can occur only involving the oxidation states Cu(I), V(V), Cr(III) that were detected by XPS analysis as the predominant ones.

Thinking that NH_3 deprotonation generally proceeds through interaction of H^+ with lattice O_0 (reaction (3)), it may be suggested that, in the presence of Cr(V), Cu(II) or V(V) as interstitial sites of WO_3 lattice, the (3A)–(3C) equilibria undergo right hand shift, being the produced electrons trapped by the transition metal ions.

The resistance decrease, observed in the presence of NH_3 [4,5] is thus based on reaction (3) (in all its pathways A–C) and is promoted by the electron transfer from NH_3 to transition metal centres, not necessarily through coordination of ammonia to Cr. This process both reduces the metal centres and injects electrons to the conduction band.

The values of electrical sensitivity resulted relevant [4] in the case of WO_3:Cu (973, 2%), S = 25, and WO_3:V (973, 2%), S = 15. Unexpectely all Cr-added samples [5] showed higher values with respect to Cu and V-added ones, spanning from S = 68, WO_3:Cr (973, 0.2%), to S = 82, WO_3:Cr (973, 5%). It may be suggested that while the trapped electrons change Cu(II) into Cu(I) and V(V) into V(IV), each ion accepting one electron, chromium undergoes reduction from Cr(V) to Cr(III), accepting a double number of electrons for each ion. It seems that the electrical response depends on the number of electrons accepted by the metal centres in agreement with the conclusions concerning noble metal-doped SnO_2 [17].

Accordingly from TPD measurements [5,18] on WO_3:Cr (973, %), N_2O resulted three to four times higher than in pure WO_3 and it desorbed at very low temperature, below 473 K; on WO_3:Cu(V) (973, %), N_2O is still three to four times higher than in pure WO_3, but it desorbed at temperature above 473 K. This confirms the easier NH_3 oxidation on Cr-added WO_3.

The EPR investigation on WO_3:Cr (673, %) samples revealed that interaction with ammonia leads to the formation of NO, chemisorbed at the surface, and that nitrosyl is specially abundant at low Cr amounts (0.2 and 1%) (Fig. 4). This species, if not activated by the metal catalyst, Cr, Cu or V towards reaction (3C), is able to reduce the oxide surface forming NO_2.

NO and NO_2 may trap electrons from the conduction band giving NO_x^- ($x = 2$ and 3) and inducing a resistance increase opposite to the variation caused by NH_3. In fact the formation of NO_x^- was thought to be responsible for the abnormal dynamic behaviour of the electrical resistance in pure WO_3 [4] treated by NH_3 and agrees with the absence of EPR active NO on WO_3. The formation of chemisorbed NO was not observed in WO_3:Cr (973, %) and WO_3:Cu or V (973 or 673%), where the reaction (3C) is probably able to reduce all the NO molecules to N_2O. Instead in WO_3:Cr (673, %), where a higher amount of $[Cr{=}O]^{3+}$ groups is present, it may be that NH_3 could capture O both from the chromyl group and from the lattice O_0, producing higher amount of NO not eliminated by reaction (3B). Accordingly no coordination of NH_3 to Cr was observed in WO_3:Cr (673, %).

In conclusion the electron paramagnetic resonance study performed on Cr (Cu, V)-added WO_3 undergone NH_3 interaction, suggests that the best electrical sensitization was obtained by the metal which can accept the major number of electrons from ammonia; the electron transfer does not imply the NH_3 coordination to the transition metal.

The changes of metal oxidation state revealed by EPR are not all the possible ones, but constitute the experimental assessment that an electron transfer takes place from ammonia.

The presence of oxygens of M=O groups, emerging from the surface, is undesired, due to their attitude to form nitrosyls anchored to the surface and acting as electronic antagonists to ammonia.

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