Thermal stability of $NO_2^{\cdot}$ and $NO^{\cdot}$ radicals formed in an Al_2O_3 catalyst during its preparation from a nitrate precursor

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During the preparation of alumina as a catalyst support from aluminium nitrates by precipitation with a NH_4OH base, $NO_2^{\cdot}$ radicals have been formed in the catalyst after calcination under air in the solid at different temperatures. These radicals remained stable until a calcination temperature of 800 °C. When the calcined catalyst was degassed under vacuum above 300 °C, the $NO_2^{\cdot}$ was reduced to give $NO^{\cdot}$ and O^- species which were both tightly trapped in the solid. These latter species remained stable until vacuum treatment at 800 °C.

Keywords: alumina, $NO_2^{\cdot}$ radical, $NO^{\cdot}$ radical, O^- species

1. Introduction

NO_x (NO, NO_2) adsorbed on catalyst surfaces was widely used as a probe molecule to study the acidic Lewis sites, i.e., electron acceptor. Such adsorption generally leads to the formation of paramagnetic complex species [1–5]. In fact, the nitroxide acting as a Lewis base coordinates to an electron acceptor through the non-bonding electron pair of the nitroxide oxygen. The unpaired π electron does not participate directly in the dative bond, but serves as a probe of the electronic structure of the complex.

Numerous catalysts are almost prepared from nitrate salts and then calcined under air at different temperatures. Generally, it was always supposed that after calcination, the nitrates are totally decomposed at temperatures less than 500 °C without taking into consideration if any NO_x species resulting from nitrate anions remain adsorbed on the catalyst surfaces.

The high sensitivity of the EPR technique has been often very useful in the identification of the catalytic active sites when these represent a very minor fraction of the surface atoms or ions.

The purpose of this work is to evidence by EPR the thermal stability of $NO_2^{\cdot}$ and $NO^{\cdot}$ radicals adsorbed on an alumina catalyst surface during its preparation.

2. Experimental

Aluminium hydroxide $Al(OH)_3$ was prepared at room temperature by adding a known solution of aluminium nitrate (0.5 M) to an aqueous ammonium hydroxide at pH = 9.5. Thereafter, the precipitate was washed, filtered and dried at 100 °C, before a calcination treatment in a flow of dried air (0.5 °C min^{-1} heating rate and 4 h at calcination temperature, up to 800 °C).

Thermal analysis measurements were performed using a Netzsch STA-409 equipped with a micro-balance, differential thermal analysis (DTA) and a flow gas system. The dried aluminium hydroxide was treated under air. The temperature was raised at a rate of 5 °C min^{-1} from room temperature to the desired temperature.

The electron paramagnetic resonance (EPR) measurements were performed at −196 and 20 °C on an EMX Bruker spectrometer. A cavity operating with a frequency of ∼9.5 GHz (X-band) was used. The magnetic field was modulated at 100 kHz. The g values were determined from precise frequency and magnetic field values.

3. Results and discussion

3.1. Thermal analysis

The thermal decomposition of the dried aluminium hydroxide is illustrated in figure 1. A significant loss of weight was obtained at the beginning of heating to reach a plateau at 600 °C. The total loss is about 33.29%. This value, which is very close to the theoretical loss (34.61%) calculated from $2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$, indicates that the solid was completely dehydrated to give finally Al_2O_3. From these results it is evident to deduce that $Al(OH)_3$ was the only product present in the solid before the thermal treatment. In addition, in figure 1, a DTA curve was obtained when the untreated hydroxide was heated in a dry air flow. An endothermic peak appeared at 263.5 °C. This peak can be unambiguously attributed to the dehydration of $Al(OH)_3$ solid.

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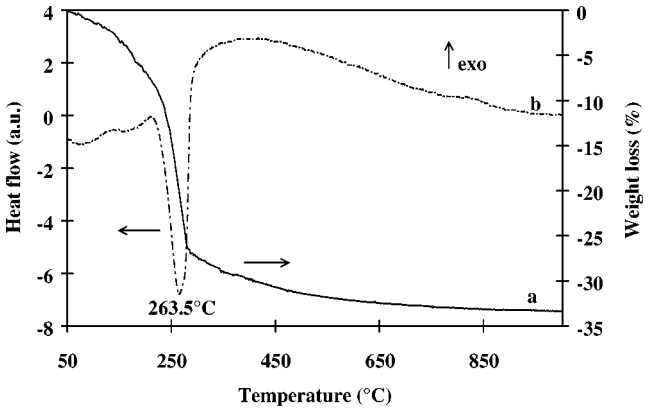


Figure 1. Thermal decomposition of $Al(OH)_3$ sample under air. Heating rate: $5\,^{\circ}C\,min^{-1}$. (a) TG; (b) DTA.

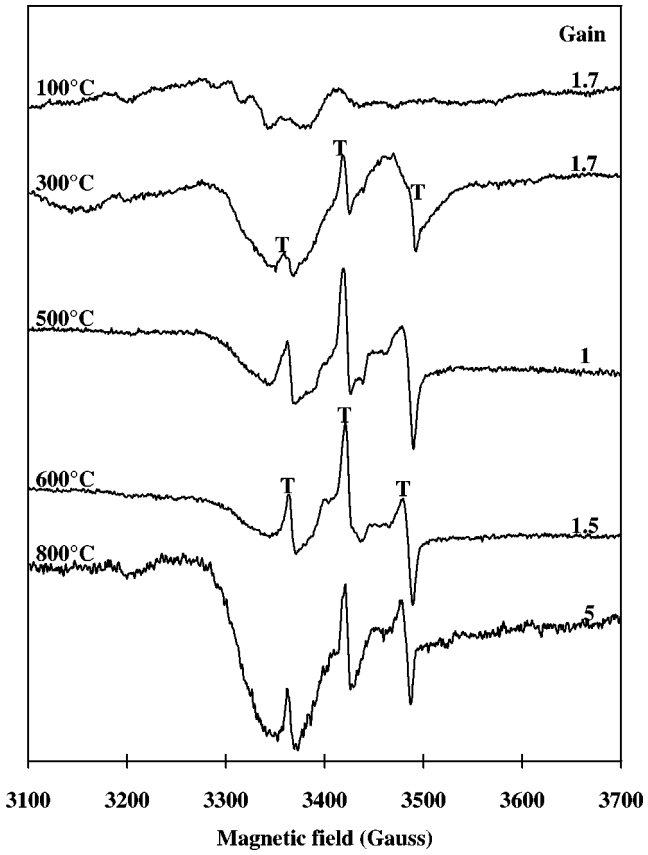


Figure 2. EPR spectra recorded at $-196\,^{\circ}C$ of $Al(OH)_3$ sample calcined under air at different temperatures.

3.2. EPR

3.2.1. $NO_2^{\cdot}$ radical

Figure 2 shows the EPR spectra recorded at $-196\,^{\circ}C$ of the aluminium hydroxide sample calcined under air at different temperatures. The signal obtained after a calcination at $300\,^{\circ}C$ is a triplet denoted by T. When the calcination temperature increases, the intensity of the triplet increases to reach a maximum at $500\,^{\circ}C$, then decreases at higher temperatures and vanishes at above $800\,^{\circ}C$. The spectra were not observed when the samples were recorded

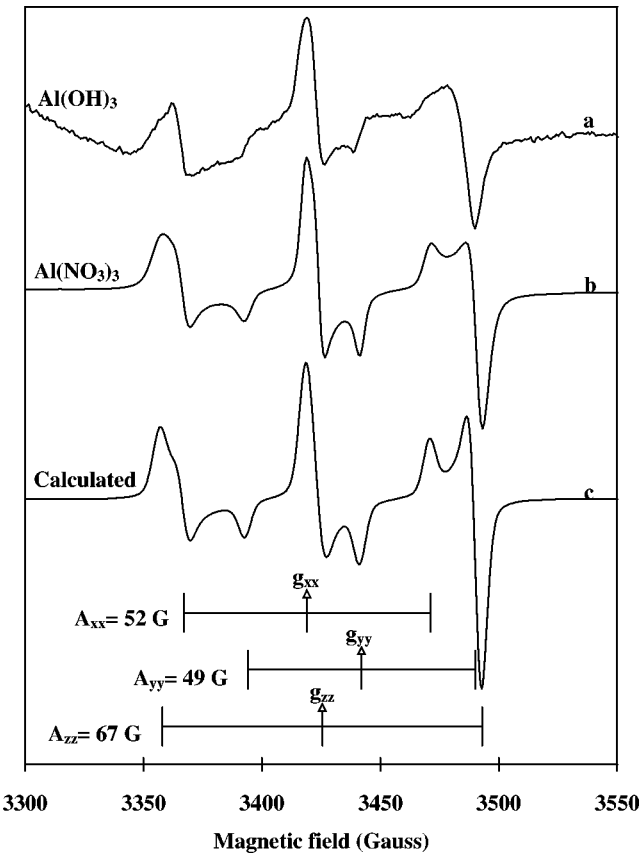


Figure 3. EPR spectra recorded at $-196\,^{\circ}C$ of $Al(OH)_3$ (a) and $Al(NO_3)_3$ (b) samples calcined under air at $500\,^{\circ}C$; (c) calculated EPR spectrum.

at room temperature. This phenomenon is probably due to a rapid motion of the adsorbed species.

The EPR parameter values of the triplet were determined from the calculated spectra. Theoretical signals were calculated using the effective spin Hamiltonian:

$$\mathcal{H} = \beta H_j S_j g_j + A_j S_j I_j,$$

where j is the component along one of the three axes x, y and z, H is the applied magnetic field, S is the total electron spin, A is the hyperfine interaction, I is the nuclear spin of nitrogen ($I_N = 1$), g is the spectroscopic factor and β is the Bohr magneton. A polyoriented sample EPR signal was simulated by generating 9000 random orientations of magnetic field and by summing the corresponding 9000 absorption signals. The final signal was obtained (figure 3) by performing a convolution (Gaussian or Lorentzian line shape) of each transition line, adding all contributions, and calculating the first derivative of the signal; the linewidth for convolution was optimised in order to obtain the best accordance with the observed experimental values. The EPR parameter values of the triplet are given in table 1. Compared to other signals obtained in different matrices [2,6–9], the triplet can be unambiguously attributed to $NO_2^{\cdot}$ radicals. In order to confirm the origin of these radicals, a sample of $Al(NO_3)_3$ which has been calcined under air up to a temperature of $600\,^{\circ}C$ for 4 h, has given at $-196\,^{\circ}C$ a

Table 1
EPR parameter values of the g tensor and hyperfine splitting for $NO_2^{\cdot}$ radicals.

	g factor			Hyperfine structure (G)				Ref.
	g_{xx}	g_{yy}	g_{zz}	b_{xx}	b_{yy}	b_{zz}	A_{iso}	
ZnO	2.007	1.994	2.003	−2.5	−7.5	10	54.6	[7]
MgO	2.005	1.9915	2.002	−3.5	−7.5	10.9	56.5	[8]
Al_2O_3	2.003	1.9895	2.000	−4	−7	11	56	[present work]

well-resolved and large EPR signal very similar to those obtained above in Al_2O_3 (figure 3). Consequently, the precursor of such a radical must be nitrate traces remaining with the aluminium hydroxide after its precipitation with the NH_4OH base. When the $Al(OH)_3$ was calcined above 300 °C, the nitrate remaining in interaction with alumina gave trapped $NO_2^{\cdot}$ radicals.

The hyperfine tensor A of the triplet ($I = 1$) can be decomposed into an isotropic and an anisotropic part as follows:

$$A_{\text{iso}} + B = \begin{pmatrix} A_{xx} & 0 & 0 \\ 0 & A_{yy} & 0 \\ 0 & 0 & A_{zz} \end{pmatrix} = A_{\text{iso}} + \begin{pmatrix} b_{xx} & 0 & 0 \\ 0 & b_{yy} & 0 \\ 0 & 0 & b_{zz} \end{pmatrix},$$

since $A_{xx} = 52$ G, $A_{yy} = 49$ G and $A_{zz} = 67$ G (figure 3), this leads to $A_{\text{iso}} = (A_{xx} + A_{yy} + A_{zz})/3 = 56$ G and $b_{xx} = -4$ G, $b_{yy} = -7$ G and $b_{zz} = 11$ G. In a number of cases, the second term matrix of the anisotropic part is a traceless tensor ($b_{xx} + b_{yy} + b_{zz} = 0$) and has an axial symmetry form ($-b$, $-b$, $2b$). Therefore,

$$A_{\text{iso}} + B = \begin{pmatrix} 52 & 0 & 0 \\ 0 & 49 & 0 \\ 0 & 0 & 67 \end{pmatrix} = 56 + \begin{pmatrix} -4 & 0 & 0 \\ 0 & -7 & 0 \\ 0 & 0 & 11 \end{pmatrix}.$$

Following the approach of Symons et al. [10,11], the experimental tensor B, which has no axial symmetry may be resolved into two tensors, B_1 and B_2, which have axial symmetry forms. Thus,

$$B = B_1 + B_2 = \begin{pmatrix} -\alpha & 0 & 0 \\ 0 & -\alpha & 0 \\ 0 & 0 & 2\alpha \end{pmatrix} + \begin{pmatrix} 2\beta & 0 & 0 \\ 0 & -\beta & 0 \\ 0 & 0 & -\beta \end{pmatrix}.$$

Since $b_{xx} = -4$ G, $b_{yy} = -7$ G and $b_{zz} = 11$ G, these values give $\alpha = 6$ G and $\beta = 1$ G:

$$B = \begin{pmatrix} -4 & 0 & 0 \\ 0 & -7 & 0 \\ 0 & 0 & 11 \end{pmatrix} = \begin{pmatrix} -6 & 0 & 0 \\ 0 & -6 & 0 \\ 0 & 0 & 12 \end{pmatrix} + \begin{pmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}.$$

The molecular orbital of the unpaired electron in NO_2 as well as the ONO angle may be deduced from the hyperfine splitting constant values. The s character of the orbital hosting the unpaired electron is given by

$$a_{\text{s}}^2 = \frac{A_{\text{iso}}}{A_0},$$

where A_{iso} is the experimentally determined isotropic hyperfine splitting and A_0 is the pure s orbital splitting for nitrogen. Since $A_{\text{iso}} = 56$ G in our case and A_0 is equal to 550 G [11] for nitrogen, a_{s}^2 is 0.102.

The p_x and p_z characters are given by the following relations:

$$a_{\text{p}_x}^2 = \frac{2\beta}{B_0} \quad \text{and} \quad a_{\text{p}_z}^2 = \frac{2\alpha}{B_0},$$

respectively, where B_0 is the theoretical value for an electron in a pure nitrogen p orbital ($B_0 = 34.1$ G) [11]. The $a_{\text{p}_x}^2$ and $a_{\text{p}_z}^2$ values found were 0.059 and 0.352, respectively. The fraction of the electron associated with the nitrogen nucleus is given by

$$a_{\text{s}}^2 + a_{\text{p}_x}^2 + a_{\text{p}_z}^2 = 0.513.$$

Using the relations described by Atkins et al. [10], the ONO angle θ can be calculated from the following equation:

$$\cos\frac{\theta}{2} = \frac{1}{\sqrt{\lambda^2 + 2}},$$

where λ is $a_{\text{p}}/a_{\text{s}}$. The ONO angle is equal to 131.9°. This may be compared to that obtained by Lunsford [8] for NO_2 adsorbed on magnesium oxide.

3.2.2. $NO^{\cdot}$ radical and O^- species

A fraction of the NO_2 was removed by degassing the solid, already calcined at 600 °C, under vacuum (3×10^{-5} mbar) for 20 h up to 200 °C. In fact, the symmetry of the triplet slightly changed and its intensity drastically decreased (figure 4). When the sample was degassed at higher temperatures (>200 °C), the intensity of the triplet continued to decrease whereas two new signals appeared: the first one with three components ($g_{xx} = 2.0243$, $g_{yy} = 2.0160$ and $g_{zz} = 2.0095$) and denoted by O, whereas the other which is assigned by S is symmetric and centred at $g = 1.97$ (figure 4). The intensity of the S signal reached a maximum after degassing the solid at 600–700 °C whereas the triplet signal disappeared. The S signal is very similar to

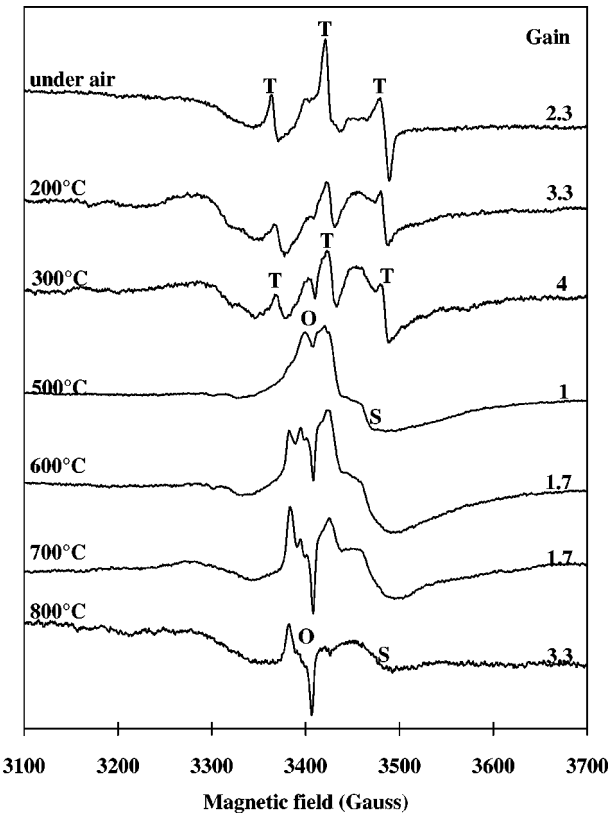


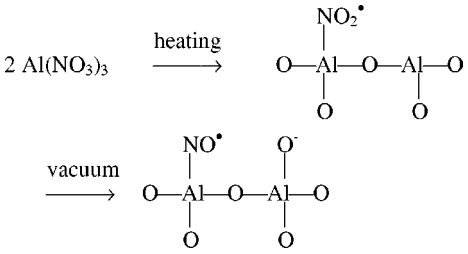
Figure 4. EPR spectra recorded at −196 °C of $Al(OH)_3$ sample previously calcined under air at 600 °C and then degassed under vacuum at different temperatures.

those observed when NO was adsorbed on alumina and attributed to NO^- radicals [12,13]. Indeed, Lunsford [12] has interpreted the origin of this signal that the unpaired electron on NO interacts magnetically with its nitrogen nucleus which has a nuclear spin of 1 and with an aluminium nucleus which has a nuclear spin of $5/2$. This leads to a total of 18 hyperfine lines. In the resulting spectrum there may be an overlap of some of these lines. In our case, these radicals were obtained by simple reduction under vacuum of NO_2^- radicals.

When the sample was degassed at temperatures higher than 700 °C, the intensity of the S signal decreased and disappeared at temperatures above 800 °C, whereas the variation of the O signal three-component intensities versus the degassing temperature leads us to suppose that this signal is effectively the result of two different oxygen species. The intensity of this signal increased with the degassing temperature to reach a maximum at 600 °C and then decreased and, finally, disappeared above 800 °C. Similar signals have been already obtained by numerous authors [14–18] and were attributed to O^- species.

4. Conclusion

In this work, the EPR technique evidenced the formation of NO_2^- radicals when a hydroxide aluminium, already prepared by precipitation from aluminium nitrate and NH_4OH, was calcined under air at high calcination temperatures (300–800 °C). The formation of such unexpected radicals could affect the catalytic properties of solids in the case where they not previously evidenced. The NO_2^- radicals can be reduced to NO^- radicals while the calcined sample is degassed under vacuum from a temperature of 300 °C. During the formation of such radicals, O^- paramagnetic species were formed following the reactions:



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